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PHYSIOCHEMICAL STUDIES OF CROWN-SOLVENT COMPLEXATIONS

By

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ABSTRACT

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By

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Recent studies by several investigators have shown that in some solvents crown ethers strongly interact with the solvent molecules. Solid adducts of 18-crown-6 with acetonitrile, formamide and nitromethane have been isolated. Obviously, if fairly stable adducts of these complexes can be isolated, these same interactions must also occur in solution. Such interactions could modify the complexing abilities of macrocyclic ligands by altering the conformation of the ligand and/or by varying the thermodynamics of ligand desolvation. Solvent-ligand interactions could, therefore, play a prominent role in the thermodynamics of complexation. It seems that the understanding of the mechanism of macrocyclic complex formation cannot be complete without some quantitative knowledge of solvent-ligand interactions. This investigation is an attempt in this direction.

In this investigation, the complexation of several crown ethers, including 18C6, 15C5, and B15C5, with acetonitrile, nitromethane, etc. has been studied by carbon-13 NMR and IR spectroscopy using benzene, acetone, chloroform and carbon tetrachloride as "inert" background

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solvents. The degree of complexation depends upon the background solvent used. These studies are complicated by interactions of the complexing solvent with the background solvent as well as self-association of the complexing solvent. They are further complicated by crown interactions with the background solvent. This is especially true if either chloroform or acetone are used as the background solvent. In the case of B15C5, the aromatic ring forms a π -complex with benzene.

Solvation studies of the crown ethers show that the conformation of these cyclic ligands is very solvent and temperature dependent. The formation constants of ligand-solvent complexation obtained for linear and cyclic polyether ligands indicate that ligand solvation is not a major contributor to the "macrocyclic effect". The effect of the solvent-ligand interactions on the complexation of metal-ions is also discussed.

To the most important people in my life:

Roger, Matthew, Nathan and

my parents.

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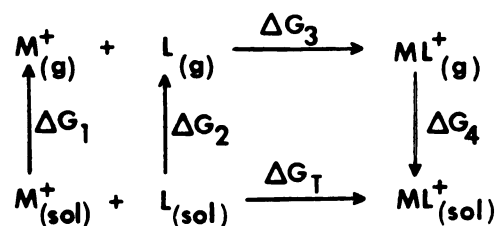
CHAPTER I

INTRODUCTION

INTRODUCTION

The available information in the field of alkali metal ion complexation has grown dramatically since the discovery of crown ethers and later the synthesis of cryptands. Much of the complexation work has been done in nonaqueous solvents. Since crowns and cryptands are neutral ligands, it seems reasonable to assume that they interact with polar organic solvent molecules and that these interactions can have an important effect on the formation of the alkali complexes with these ligands. Yet quantitative data on the ligand-solvent interactions are meager. The purpose of this investigation was, therefore, to study solvent-ligand interactions and to determine what effect they have on metal complexation.

A thermodynamic cycle for the complexation of a metal cation, M^+ , with a ligand, L , is shown below (1):



According to this cycle, the total free energy of complexation, ΔG_T , can be broken down into free energies for the desolvation of the metal ion and ligand, ΔG_1 and ΔG_2 respectively, complexation in the gas phase, ΔG_3 , and solvation of the complex, ΔG_4 . Of these processes,

desolvation of the metal ion has been considered to be the most important. Since most solvents used in the study of metal ion complexation are polar; i.e., they have a dipole moment; they solvate ions by way of an ion-dipole interaction. The energy of an ion-dipole interaction is proportional to r^{-2} , where r is the effective ionic radius of the ion (r is the sum of the radius of the ion and diameter of the solvent molecule). Consequently ΔG_1 has been estimated to be several hundreds of kcal/mole. Because desolvation of the metal ion is considered to be the most important process, it has been studied the most. There are in the literature compilations of free energies of transfer for many salts. Conversely, ΔG_2 , the desolvation of the ligand, has been estimated to lie between -1 and 12 kcal/mole (1). Consequently it is considered to be the least important process and has been studied the least.

This thermodynamic cycle, however, is very simplistic. Other reactions occur in solution and these side reactions can and do affect the overall free energy of complexation, ΔG_T . These other reactions include ionic associations, solvent self-associations, and ligand-solvent complexations. It has been shown that ion pairs, triple ions, and higher ionic aggregates can occur in solution. The extent that the ions associate depend upon the properties of the solvent, in particular its

donicity and its dielectric constant. The effect ionic associations have on crown complexations has been aptly demonstrated by Khazaeli (2), Szczygiel (3), and Strasser (4).

Polar solvents, because of their dipole moments, can self-associate. The extent of self-association depends upon the strength of the dipole moment as well as the extent of distortion each molecule must undergo in order to interact. A well documented example of solvent self-association is the hydrogen bonding that occurs between water molecules. It is reasonable to expect that these solvents can also interact with macrocyclic ligands.

As was already stated, the role solvent-ligand interactions plays in the thermodynamics and kinetics of metal complexation has been largely ignored. The purpose of this investigation was, therefore, to study these solvent-ligand interactions and to determine the extent to which these interactions affect metal complexation. Typically, the ligand solubility in a solvent is rather low. For example, the solubility of 18-crown-6, a cyclic polyether ligand, is approximately 0.2 M in acetonitrile (5). Consequently any change in the physical property of the solvent upon complexation with the ligand will not be observed since the concentration of "free" solvent will be much greater than that of "complexed". Therefore solvent-ligand interactions should be studied in the

presence of an "inert" background solvent. However, no solvent is completely inert; dipole-dipole and dipole-induced dipole interactions as well as dispersion forces occur between solvent molecules and, therefore, the chemistry occurring between the background solvent and complexing solvent and the ligand and background solvent must be understood before the ligand-complexing solvent interaction can be studied.

HISTORICAL PART

1. SOLVENT INTERACTIONS

Intermolecular association in acetonitrile, AN, vapor and liquid has been investigated by a variety of techniques. In the gas phase the molecule has a large dipole moment ($\mu = 3.92$ D) (6), which is mainly caused by the lone-pair orbital centered on the nitrogen atom and directed along the CN axis of the nitrile group. In addition the π -orbitals of the nitrile group are displaced towards the nitrogen atom. Appreciable polar interaction between acetonitrile molecules has been indicated by the large negative heat and entropy of dimerization derived from second virial coefficient measurements (7,8).

In general, nitriles have considerably higher boiling points, viscosities, and heats of vaporization than the corresponding hydrocarbons (9). This difference in properties strongly suggests intermolecular association.

The viscosity data obtained by Saum suggest that in the liquid state the association of mononitriles approaches but does not exceed the dimer level (10), which implies that the interaction is between two CN groups rather than a hydrogen bonding interaction in which, as in alcohols, association would be expected to exceed the dimer stage. Saum (9) also demonstrated that t-butyl cyanide, which has no hydrogens on the α -carbon atom, has nearly the same boiling point elevation compared to the hydrocarbon as do the n-butyl and s-butyl cyanides. This evidence also indicates that association is through the CN group. However there is some controversy as to the structure of the dimer. Dielectric polarization studies (10) show a dipole moment of 2.67 D for the gaseous dimer at 80°C and suggest an antiparallel alignment of the two molecules (Figure 1). The dielectric work done by Dannhauser and Flueckinger (11) as well as the measurements of second virial coefficients by Lambert et al. also support antiparallel dipole pairs. Infrared studies of MeCN, and MeNC, in a solid argon matrix at 20°K were done by Freedman and Nixon (12). From the pattern of dimer absorption in the infrared spectra of both MeCN and MeNC they concluded that the dimer existed as antiparallel dipole pairs. Murray and Schneider (13), however favored a skewed configuration for the dimer as shown in Figure 1. They reasoned that the skewed configuration would minimize

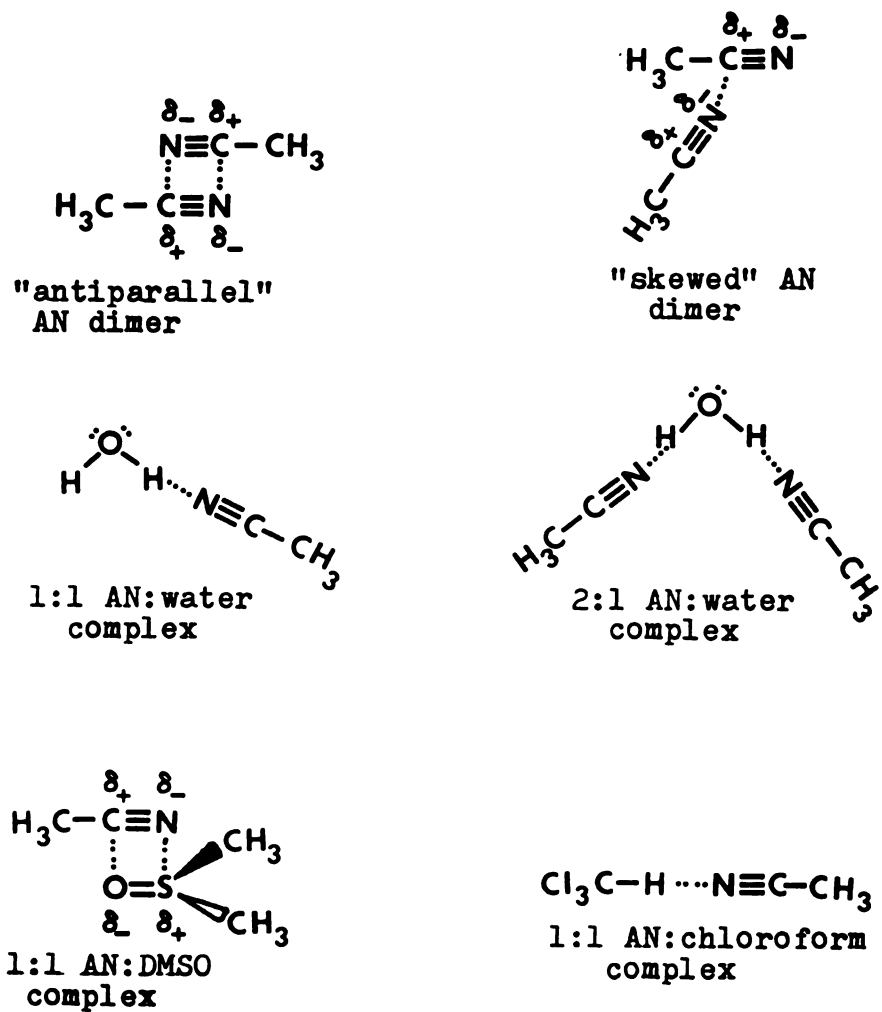
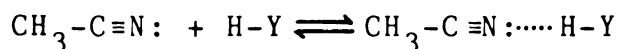


Figure 1. Structures proposed for the dimer and some complexes of acetonitrile.

the mutual repulsions of the high charge densities of the CN group. Such high charge densities should make the antiparallel configuration unfavorable. This assumption has some support from NMR data (14).

The frequency of the CN stretch of nitriles depends upon the phase and, in solution, varies with the solvent (15). Of all the nitriles studied by Thomas et al., the highest frequency for the CN stretch, ν_{CN} , was found in the vapor phase while the lowest frequencies were for the liquids. The solution values of ν_{CN} were found to lie between the two extremes. The decrease in ν_{CN} as the nitrile goes from the gaseous state to the liquid was attributed to the association of the nitriles in the liquid phase brought about by the polar nature of the CN group. The variation in frequency observed for the fundamental vibrations of AN in different phases, solutions, or complexes has been explained in terms of several types of interactions. The CN stretching frequency is lower in the pure liquids than in dilute solutions. It has been argued that in the pure liquid the antiparallel arrangement postulated for the associated molecules causes a decrease in the polarity of the CN bond with a weakening of the bond and a decrease in the vibrational frequency (15). Coordination through the nitrogen lone pair, which has been established for complexes of AN with Lewis acids (e.g. BF_3 and SnCl_4)

leads to substantial increases in both ν_{CN} and ν_{CC} (16). Hydrogen bonding to phenol and trichloroacetic acid also results in higher stretching frequencies for the CN group (17). Recent MO calculations by Purcell (18) indicate that, in general, coordination by the lone pair electrons results in stronger σ -bonding and slightly weakened π -bonding. Intermolecular hydrogen bonding has been shown to occur between AN and HF and AN and HCl (19,20):



The complex formed is linear. In the infrared spectra, a shift to lower frequencies and a broadening of the H-Y stretching band and an increase of the C $\equiv$ N stretching frequency were observed. The increase in ν_{CN} indicated that the complex is formed via the nitrogen lone pair electrons and not via the π -electrons of the triple bond. The observation of a decrease in ν_{CH} and ν_{CD} but little change in ν_{CN} when salts such as LiBr and NaI are dissolved in AN or AN-d₃ has been interpreted in terms of interaction between the methyl groups and the halide anion (21).

It has been shown that AN forms complexes with other solvents. Infrared studies of water and AN in carbon tetrachloride showed a sharp band at 3690 cm⁻¹ attributed to a free O-H stretch and a broad band at 3615 cm⁻¹ attributed to bound O-H (22). Since the symmetric and

asymmetric O-H stretch modes gave two equally broad bands at 3640 and 3545 cm^{-1} , both 1:1 and 2:1 AN-water complexes were postulated. The structures proposed for these complexes are shown in Figure 1. Proton NMR studies of AN and dimethyl sulfoxide, DMSO, indicated complex formation (23). The structure proposed for this complex is also shown in Figure 1. The proton chemical shifts of AN and toluene were found to be highly temperature dependent (24). This temperature dependence was attributed to complex formation between AN and toluene. Abraham (25) proposed that the methyl hydrogens of AN are hydrogen bonded to the benzene ring. Since the same effect was observed for propionitrile, the assumption of hydrogen bonding was questioned (26). The enthalpies of mixing of nitriles in benzene (27) and toluene (28,29) were indicative of complex formation. Goates et al. (30), in constructing phase diagrams, observed an incongruent melting point for the AN-benzene system, revealing a 2:1 benzene:AN complex. However, the freezing point curves for substituted benzenes gave no indication of complexes.

Raman studies of the ν_1 band at low concentrations of AN in carbon tetrachloride indicate that a clustering of AN molecules and that collisional interactions between AN and carbon tetrachloride may be occurring (31). However there is no evidence for formation of complexes between AN and carbon tetrachloride in the solid-liquid phase diagram

(32).

The AN-chloroform system has been studied by proton NMR by Berkeley and Hanna (33) and Lin and Tsay (34). In dilute solutions the chemical shift of the chloroform proton was interpreted in terms of AB association, where A refers to AN and B to chloroform. Equilibrium constants were determined from the proton chemical shift data and these values are tabulated in Table 1. The structure proposed for the 1:1 AN:chloroform complex is shown in Figure 1. Handa and Jones (35) measured the molar excess enthalpies of AN-chloroform at 298°K. They found that the AB associated model was too simple to interpret the molar excess enthalpies as well as vapor pressure data and molar excess volumes obtained by other workers (36,37,38); to explain the thermodynamic data, a model which also included self-association was required. The model used to interpret the molar excess enthalpy data and excess Gibbs energies (39,40), heats of mixing (40,27), and volumes of mixing (39,40) was derived by Lorimer and Jones (41). This model took into account a one step association of AN (corresponding to roughly antiparallel alignment of CN bond dipoles), chain association of AN (corresponding to head-to-tail alignment of AN dipoles) with the same association constant for all steps, chain association of chloroform with the same equilibrium constant for each association step, and 1:1 and 1:2 AN-chloroform complexes

Table 1. Equilibrium Constants for Solvent-Solvent Interactions.

System	Equilibria	Equilibrium Constant	Method	Reference
AN, gas phase	$2A \rightleftharpoons A_2$	$42 \pm 26 \text{ M}^{-1}$	Far IR	162
AN-CCl ₄	$2A \rightleftharpoons A_2$	$0.13 \pm 0.03 \text{ m.f.}^{-1}$	¹³ C NMR	78
AN-CCl ₄	$2A_1 \rightleftharpoons A_2^1$ $A_1 + A_1 \rightleftharpoons A_{1+1}$	$8.35 \pm 0.12 \text{ m.f.}^{-1}$ $2.1 \pm 1.2 \text{ m.f.}^{-1}$	Molar Excess Volumes	41
AN-DMSO in CCl ₄	$AB \rightleftharpoons A+B$	0.85 M	IR	23
AN-DMSO	$A+B \rightleftharpoons AB$	3.8 m.f.^{-1}	¹ H NMR	61
AN-CHCl ₃	$A+B \rightleftharpoons AB$	3.4 m.f.^{-1} 3.2 m.f.^{-1}	¹ H NMR ¹ H NMR	34 33
AN-CHCl ₃ in CCl ₄	$A+B \rightleftharpoons AB$	$1.14 \pm 0.04 \text{ m.f.}^{-1}$	¹ H NMR	60
AN-CHCl ₃	$A_1 + B_1 \rightleftharpoons A_1B_1$	$1.52 \pm 0.074 \text{ m.f.}^{-1}$	Molar Excess Volumes	41

Table 1. Continue.

System	Equilibria	Equilibrium Constant	Method	Reference
AN-C ₆ H ₆	$2A \rightleftharpoons A_2$ $A+B \rightleftharpoons AB$	0.36 m.f.^{-1} $1.30 \text{ m.f.}^{-1} @ X_{AN}=0.0$ $1.77 \text{ m.f.}^{-1} @ X_{AN}=1.0$	¹ H NMR	163
NM-CCl ₄	$2A \rightleftharpoons A_2$	$0.53 \pm 0.11 \text{ m.f.}^{-1}$	¹³ C NMR	78
NM-CCl ₄	$2A \rightleftharpoons A_2$	105.1 M^{-1}	UV-VIS	49
NM-C ₆ H ₆	$A+B \rightleftharpoons AB$	0.029 M^{-1}	UV-VIS	164
NM-n-Heptane	$2A \rightleftharpoons A_2$	104.2 M^{-1}	UV-VIS	49
NM-MeOH	$2A \rightleftharpoons A_2$	501.0 M^{-1}	UV-VIS	49
NM-cyclohexane	$2A \rightleftharpoons A_2$	110 M^{-1}	UV-VIS	47
NM-C ₆ H ₆	$2A \rightleftharpoons A_2$ $A+B \rightleftharpoons AB$	0.71 m.f.^{-1} $1.12 \text{ m.f.}^{-1} @ X_{NM}=0.0$ $1.92 \text{ m.f.}^{-1} @ X_{NM}=1.0$	¹ H NMR	163
CHCl ₃ -cyclohexane	$2A \rightleftharpoons A_2$	$0.16 \pm 0.006 \text{ m.f.}^{-1}$	¹ H NMR	59

Table 1. Continue.

System	Equilibria	Equilibrium Constant	Method	Reference
$\text{CHCl}_3\text{-CCl}_4$	$2\text{A} \rightleftharpoons \text{A}_2$ $\text{A}+\text{B} \rightleftharpoons \text{AB}$	$0.16 \pm 0.006 \text{ m.f.}^{-1}$ $0.10 \pm 0.03 \text{ m.f.}^{-1}$	^1H NMR	59
$\text{CHCl}_3\text{-CCl}_4$	$\text{B}_1 + \text{B}_i \rightleftharpoons \text{B}_{i+1}$	$0.060 \pm 0.026 \text{ m.f.}^{-1}$	Molar Excess Volumes	41
$\text{CHCl}_3\text{-DMSO}$	$\text{A}+\text{B} \rightleftharpoons \text{AB}$	3.2 m.f.^{-1}	^1H NMR	34
$\text{CHCl}_3\text{-DMSO}$	$2\text{A} \rightleftharpoons \text{A}_2$ $\text{A}+\text{B} \rightleftharpoons \text{AB}$ $\text{AB}+\text{A} \rightleftharpoons \text{A}_2\text{B}$	0.017 M^{-1} $0.30 \pm 0.01 \text{ M}^{-1}$ $0.10 \pm 0.01 \text{ M}^{-1}$	^1H NMR	61
$\text{CHCl}_3\text{-C}_6\text{H}_6$	$\text{A}+\text{B} \rightleftharpoons \text{AB}$	0.36 m.f.^{-1}	^1H NMR	34
$\text{CHCl}_3\text{-C}_6\text{H}_6$ in cyclohexane	$\text{A}+\text{B} \rightleftharpoons \text{AB}$	1.58 m.f.^{-1}	^1H NMR	165
$\text{CHCl}_3\text{-toluene}$	$\text{A}+\text{B} \rightleftharpoons \text{AB}$	0.67 m.f.^{-1}	^1H NMR	34
$\text{CHCl}_3\text{-mesitylene}$	$\text{A}+\text{B} \rightleftharpoons \text{AB}$	0.86 m.f.^{-1}	^1H NMR	34

Table 1. Continue.

System	Equilibria	Equilibrium Constant	Method	Reference
$\text{CHCl}_3\text{-Et}_2\text{O}$ in cyclohexane	$\text{A+B} \rightleftharpoons \text{AB}$	$3.76 \pm 0.10 \text{ m.f.}^{-1}$	^1H NMR	60
$\text{CHCl}_3\text{-Et}_2\text{O}$ in CCl_4	$\text{A+B} \rightleftharpoons \text{AB}$	$1.46 \pm 0.04 \text{ m.f.}^{-1}$	^1H NMR	60
$\text{CHCl}_3\text{-(isopropyl)}_2\text{O}$ in CCl_4	$\text{A+B} \rightleftharpoons \text{AB}$	$2.06 \pm 0.08 \text{ m.f.}^{-1}$	^1H NMR	60
DMF-CCl_4	$2\text{A} \rightleftharpoons \text{A}_2$	0.60 M^{-1} $0.20 \pm 0.04 \text{ m.f.}^{-1}$	^1H NMR ^{13}C NMR	70 78
DMF-cyclohexane	$2\text{A} \rightleftharpoons \text{A}_2$	$0.495 \text{ M}^{-1}; 4.762 \text{ m.f.}^{-1}$	^1H NMR	167
$\text{DMF-C}_6\text{H}_6$ in cyclohexane	$\text{A+B} \rightleftharpoons \text{AB}$	0.96 m.f.^{-1} with αCH_3 1.19 m.f.^{-1} with βCH_3	^1H NMR	165
AC-CCl_4	$2\text{A} \rightleftharpoons \text{A}_2$	0.51 m.f.^{-1}	^{13}C NMR	78
$\text{AC-C}_6\text{H}_6$	$2\text{A} \rightleftharpoons \text{A}_2$ $\text{A+B} \rightleftharpoons \text{AB}$	0.40 m.f.^{-1} $1.32 @ \text{X}_{\text{AC}}=0.0$ $1.85 @ \text{X}_{\text{AC}}=1.0$	^1H NMR	163
$\text{AC-C}_6\text{H}_6$ in CCl_4	$\text{A+B} \rightleftharpoons \text{AB}$	0.066 M^{-1}	^1H NMR	166

Table 1. Continue.

System	Equilibria	Equilibrium Constant	Method	Reference
CHCl_3 -Py in CCl_4	$\text{A} + \text{B} \rightleftharpoons \text{AB}$	$1.90 \pm 0.04 \text{ m.f.}^{-1}$	^1H NMR	60
CHCl_3 -Py	$\text{A} + \text{B} \rightleftharpoons \text{AB}$	0.69 m.f.^{-1}	^1H NMR	33
CHCl_3 - N-methylpyrrolidine	$\text{A} + \text{B} \rightleftharpoons \text{AB}$	2.2 m.f.^{-1}	^1H NMR	33
CHCl_3 - ethylideneisopropylamine	$\text{A} + \text{B} \rightleftharpoons \text{AB}$	5.2 m.f.^{-1}	^1H NMR	33
CHCl_3 -AC	$\text{A} + \text{B} \rightleftharpoons \text{AB}$	0.13 M^{-1}	^1H NMR	61
CHCl_3 -AC in CCl_4	$\text{A} + \text{B} \rightleftharpoons \text{AB}$	$2.07 \pm 0.05 \text{ m.f.}^{-1}$	^1H NMR	60
CHCl_3 -Ethylene Carbonate	$\text{A} + \text{B} \rightleftharpoons \text{AB}$ $\text{AB} + \text{A} \rightleftharpoons \text{A}_2\text{B}$	0.06 M^{-1} 0.04 M^{-1}	^1H NMR	61
CHCl_3 -PC	$\text{A} + \text{B} \rightleftharpoons \text{AB}$ $\text{AB} + \text{A} \rightleftharpoons \text{A}_2\text{B}$	0.08 M^{-1} 0.06 M^{-1}	^1H NMR	61
CHCl_3 -Et ₃ N in cyclohexane	$\text{A} + \text{B} \rightleftharpoons \text{AB}$	$4.70 \pm 0.12 \text{ m.f.}^{-1}$	^1H NMR	60

Table 1. Continue.

System	Equilibria	Equilibrium Constant	Method	Reference
AC-DMSO in CCl_4	$\text{AB} \rightleftharpoons \text{A+B}$	2.7 M	IR	61
AC-acetic acid	$\text{A+B} \rightleftharpoons \text{AB}$	0.23 M^{-1}	^{13}C NMR	62
$\text{CCl}_4\text{-C}_6\text{H}_6$	$\text{A+B} \rightleftharpoons \text{AB}$	$0.86 \text{ m.f.}^{-1} @ \text{X}_{\text{CCl}_4} = 0.0$ $0.85 \text{ m.f.}^{-1} @ \text{X}_{\text{CCl}_4} = 1.0$	^1H NMR	163
$\text{CCl}_4\text{-C}_6\text{H}_6$ in n-hexane	$\text{A+B} \rightleftharpoons \text{AB}$	$0.009 \pm 0.004 \text{ M}^{-1}$	UV-VIS	110
DMSO- C_6H_6	$2\text{A} \rightleftharpoons \text{A}_2$ $\text{A+B} \rightleftharpoons \text{AB}$	0.55 m.f.^{-1} $1.43 \text{ m.f.}^{-1} @ \text{X}_{\text{DMSO}} = 0.0$ $2.22 \text{ m.f.}^{-1} @ \text{X}_{\text{DMSO}} = 1.0$	^1H NMR	163
Cyclohexane- C_6H_6	$\text{A+B} \rightleftharpoons \text{AB}$	$0.86 \text{ m.f.}^{-1} @ \text{X}_{\text{C}_6\text{H}_{12}} = 0.0$ $0.86 \text{ m.f.}^{-1} @ \text{X}_{\text{C}_6\text{H}_{12}} = 1.0$	^1H NMR	163

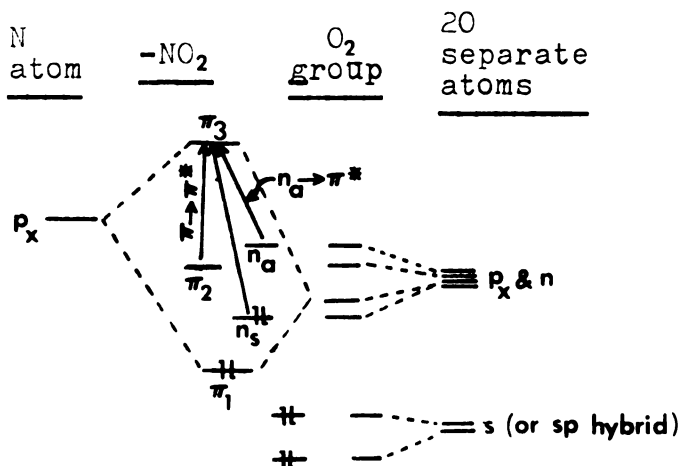
with $K_1=K_2$.

Quantitative data for the dimerization of AN as well as the complexation between AN and other solvents are rather sparse. Table 1 tabulates some of the equilibrium constants obtained for these systems as well as the method by which they were determined.

Nitromethane, NM, has also been studied extensively both in liquid and in gaseous phases. It has also been studied in solutions. The techniques used in these studies include calorimetry, cryoscopy, vapor pressure measurements, electrochemistry, X-ray and electron diffraction, magnetic susceptibility, dielectric polarization, ultrasound, microwave, IR, Raman, and UV absorption studies (42-47). From these studies, researchers have concluded that NM is associated in the pure liquid and in dilute solution with inert solvents. This is not surprising since, just as AN, NM has a large dipole moment ($\mu = 3.46 \pm 0.02$ D) (48). De Maine and coworkers (47,49) determined the dimerization constant for NM in methanol, n-heptane, and carbon tetrachloride from UV data. These dimerization constants are tabulated in Table 1. Infrared studies of the 3040 cm^{-1} vibration band of NM in solutions of NM in carbon tetrachloride were done by de Maine et al. (50,51). They found that the molar absorptivity of the 3040 cm^{-1} band increased with decreasing concentration of NM, suggesting that a specific

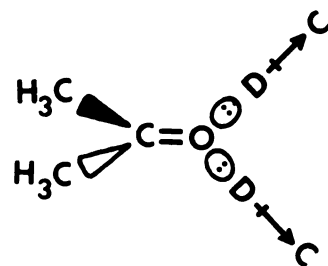
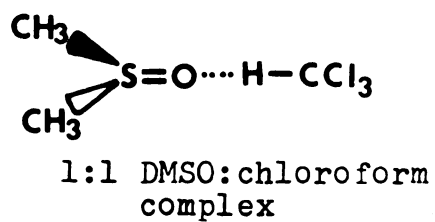
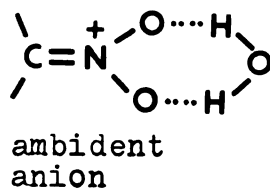
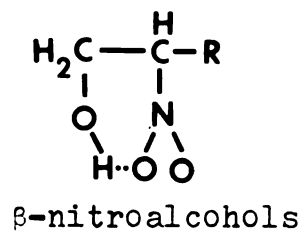
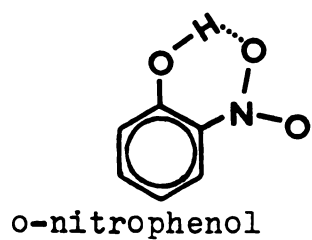
interaction between two NM molecules was occurring in solution.

Nitromethane has two absorption bands in the UV - one at 270 nm ($\log \epsilon$ 1.3) and another at 210 nm ($\log \epsilon$ 4.2) (52). The energy level diagram for nitromethane is shown below:



The 270 nm band does not show fine structure even in nonpolar solvents but is shifted to lower wavelengths with the increasing polarity (or proton-donating ability) of the solvent. This behavior is typical for an $n \rightarrow \pi^*$ transition. Consequently the 270 nm band has been attributed to the $n_a \rightarrow \pi_3^*$ transition. Nagakura (53) was able to show that the 210 nm absorption was due to the $\pi_2 \rightarrow \pi_3^*$ transition. Balasubramanian and Rao (54) have studied the effects of nonpolar, polar, and proton-donating solvents on the $n \rightarrow \pi^*$ transition of NM. The shifts of the absorption maximum in polar and nonpolar solvents have been related to the electrostatic interaction between the solute and solvent molecules. In

solvents which can donate protons, however, the solvent shifts are mainly determined by hydrogen bonding between the solute and solvent molecules. Schleyer and coworkers (55) reviewed the literature on the hydrogen bonding of the nitro group up to 1964. In general, the hydrogen bonding of the nitro group is weak except in the case of o-nitrophenol and its analogs. For o-nitrophenol, intramolecular hydrogen bonding occurs between the nitro and the hydroxyl group as shown in Figure 2. That the increase in the strength of hydrogen bonding results from resonance stabilization and because the hydrogen bonding is intramolecular was demonstrated from IR studies which showed that the $\Delta\nu_{\text{OH}}$ of o-nitrophenol is $\sim 400 \text{ cm}^{-1}$ whereas for nitrobenzene and phenol $\Delta\nu_{\text{OH}}$ is 80 cm^{-1} . Ungnade et al. (56,57) showed that β -nitroalcohols are nearly monomeric in chloroform and partially associated in carbon tetrachloride. They attributed this behavior to intramolecular hydrogen-bonding as shown in Figure 2. It has been shown that, in both the gas phase and in solution, nitroalkanes are among the strongest CH-acids (58). Their negative charge is significantly localised on the oxygen atoms. The charge delocalisation on the oxygen atoms in the nitro group is dependent on the solvent. Hydroxyl containing solvents solvate predominantly the oxygen site of the ambident anion by forming hydrogen bonds as shown in Figure 2. As was the case with AN,



2:1 acetone:chloroform-d
complex

Figure 2. Structures proposed for some complexes of nitromethane and chloroform.

formation constants for NM-solvent interactions are sparse. Table 1 tabulates some formation constants as well as the method by which they were determined.

As was discussed earlier, chloroform, CHCl_3 , is not an inert solvent. Chloroform has been shown to be an associated liquid by Jumper et al. (59) and it forms complexes with other solvents. The complexation and self-association capabilities of chloroform result from the acidity of its proton. The presence of a carbon-halogen linkage is associated with a powerful electron-withdrawal from the carbon atom. Hence it increases the acidity of any hydrogen atoms linked to the same carbon atom. This effect is inappreciable in compounds such as methyl chloride, but in the case of polyhalogenated compounds it can have the effect of rendering the residual atoms sufficiently acidic to make them potential proton donors in hydrogen bond formation. A pK_a of 15 ± 1 for chloroform has been measured by polarography (methane has a pK_a of 57 ± 8 and HCN one of 12 ± 1) (58). Jumper, Emerson, and Howard (59) measured the self-association constant of chloroform in carbon tetrachloride and cyclohexane by using proton NMR. In their model they assumed that chloroform associates to form only dimers. The dimerization constant for chloroform is tabulated in Table 1. Furthermore, their chemical shift data indicated that chloroform associates

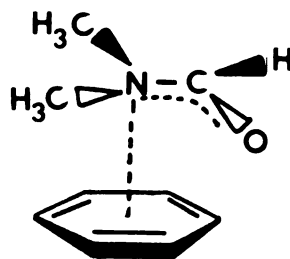
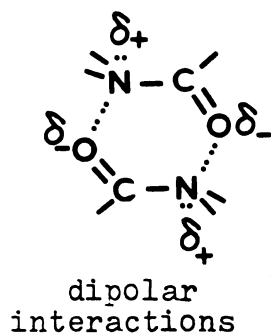
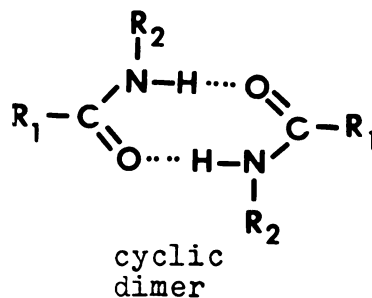
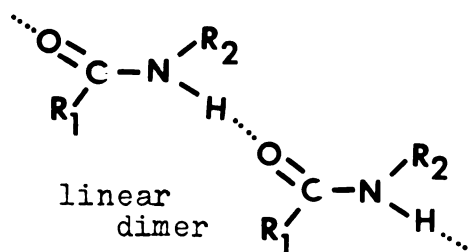
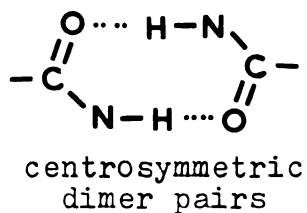
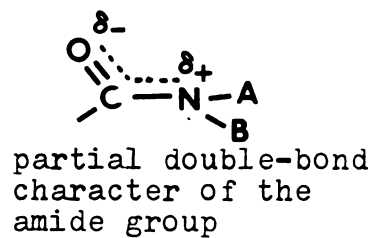
with carbon tetrachloride. The same workers also used proton NMR to study complexation between chloroform and various organic bases (60). In their study they used either carbon tetrachloride or cyclohexane as the background solvent and they corrected for the self-association of chloroform and for interactions with the background solvent. The results of their study are tabulated in Table 1.

A proton NMR study of hydrogen bonding between chloroform and DMSO, ethylene and propylene carbonate was done by McClellan et al. (61). Unlike Jumper, Howard, and Emerson who used ternary systems (60), McClellan and his coworkers only studied binary systems. The chemical shift data of chloroform indicated that besides formation of a 1:1 complex, dimerization of chloroform and formation of a 2:1 chloroform-solvent complex were also occurring. From their studies, Lin and Tsay (34) proposed a structure, shown in Figure 2, for the chloroform complex with DMSO. Infrared studies of acetone and deuterated chloroform indicated the formation of a 2:1 chloroform-d-acetone complex (62). The structure for this 2:1 complex is shown in Figure 2. Other workers have studied the hydrogen bonding of chloroform with benzene, toluene, pyridine, etc. The association constants obtained by these workers and the references are tabulated in Table 1.

Amides are relatively weak bases, and the elucidation

of their protonation behavior and related phenomena, such as hydrogen bonding and Lewis acid complexation, has aroused a great deal of attention. As shown in Figure 3 the amide group has partial double-bond character (63). The gas-phase values of amide dipole moments are remarkably constant from molecule to molecule (64). At 110°C, N-methylformamide has a dipole moment of 3.82 D; N,N-dimethylformamide, 3.80 D; acetamide, 3.75 D; N-methylacetamide, 3.71 D; N,N-dimethylacetamide, 3.80 D; and N-methylpropionamide, 3.59 D. Gaseous formamide has a dipole moment of 3.7 D (65). From these values, it seems that the amide group itself can be assigned a moment of 3.75 D. On treatment with a strong acid the lone pairs of electrons on the oxygen and nitrogen atoms of the amide function may be utilized by direct bonding to a proton to form a cation or they may hydrogen bond to a weak acid. An amide molecule may function in the dual role of proton donor and acceptor resulting in dimerization or oligomerization. X-ray structure analysis of amides which have no alkyl groups on the nitrogen show that the amide exists as centrosymmetric dimer pairs as shown in Figure 3 (66).

NMR and IR studies have shown that amides self-associate. Amides which have protons on their nitrogen atom can hydrogen-bond either linearly or cyclicly as shown in Figure 3 (67,68). For cyclic dimer



1:1 DMF:C₆H₆ complex

Figure 3. Structures proposed for the dimers and the benzene complex with amides.

formation, the cis conformation of the N-H and carbonyl groups about the C-N bond is required which, in turn, requires very bulky N-substituents (69). In N,N-dialkylamides, hydrogen-bonded self-association is not possible (except, perhaps that involving the formyl protons in formamides for which there is no conclusive evidence). Neuman and coworkers (70) have observed small chemical shift changes of the NCH_3 protons of N,N-dimethylformamide, N,N-dimethylacetamide, and N,N-dimethylthioacetamide upon dilution in carbon tetrachloride. This result was explained in terms of dipole-dipole association to form dimers. Woodbrey and Rogers (71) observed an increase in the energy barrier to rotation about the C-N bond of N,N-disubstituted amides with increasing concentration. Their results indicate association through dipolar interactions as shown in Figure 3. Dimerization constants have been determined for N,N-dimethylformamide, DMF, in carbon tetrachloride, benzene, and cyclohexane. The values are tabulated in Table 1.

Because of the partial double bond character of the C-N bond, rotation about the C-N bond is slow. As a result, the environments of the groups on the nitrogen atom are not averaged and can usually be observed separately by NMR. Many workers have used variable temperature NMR to measure the barrier to rotation about

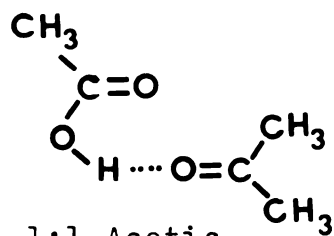
the C-N bond (72,73). It was found that polar solvents preferentially stabilize the ground state and thus increase the barrier height. Likewise, in nonpolar solvents dipole-dipole association stabilizes the ground state and increases the barrier at higher concentrations.

Chloroform is known to hydrogen bond to amides (74). It has been found that the relative proton shieldings of alkyl groups in N,N-dialkylamides are highly dependent upon the solvent and in fact may be reversed in aromatic solvents (75). Hatton and Richards (75) have proposed the structure shown in Figure 3 for the amide-benzene complex. Complexation constants have been determined for DMF and various other solvents. Some of these complexation constants are tabulated in Table 1.

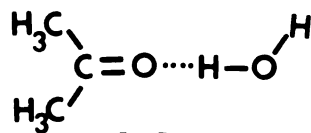
Carbonyl compounds, such as acetone, can either accept or donate electrons and protons (76). The oxygen atom of a carbonyl group carries four nonbonding electrons in its outer valence shell in addition to the electrons of the carbon-oxygen double bond. As a consequence of the above, and also as a consequence of the greater electronegativity of oxygen relative to carbon, the oxygen atom is electron-rich compared to the carbon atom. This is manifested by a permanent dipole moment (acetone has a dipole moment of 2.8 D (62)). Consequently the carbonyl group acts as a basic center. For a given carbonyl compound, the extent to which a proton can be accepted

depends upon the strength of the acid that is used. Acetone has a pK_a of 19 and is almost completely protonated by concentrated sulfuric acid and is half protonated by 82% sulfuric acid (76). Millen et al. (62) showed by gas phase IR studies that acetone forms a hydrogen-bonded complex with hydrogen fluoride. They found that the addition of acetone shifted the ν_{H-F} band by 490 cm^{-1} from 3470 cm^{-1} . They also observed additional bands at 3280 and 3700 cm^{-1} which they attributed to the complex. Carbon-13 NMR studies showed that acetone hydrogen bonds with acetic acid (62). The structure proposed for the 1:1 complex is shown in Figure 4. The formation constant for the complexation of acetone and acetic acid is tabulated in Table 1. Acetone acts as an n donor for water and forms the 1:1 complex shown in Figure 4. As was discussed earlier, acetone also complexes chloroform and there is IR evidence for a 2:1 chloroform-acetone complex. Infrared data also indicate that acetone forms a hydrogen-bonded complex with t-butanol (77).

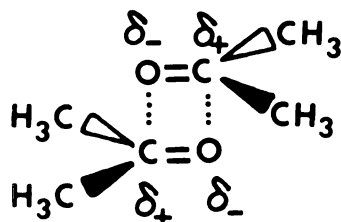
The carbonyl group can accept electrons. This is attested by the numerous reactions in which atoms or groups are added across the carbon-oxygen double bond. Carbonyl compounds containing a hydrogen atom attached to the carbonyl group may function as proton acids as well as Lewis acids. Although acetone with a pK_a of 19 is weakly



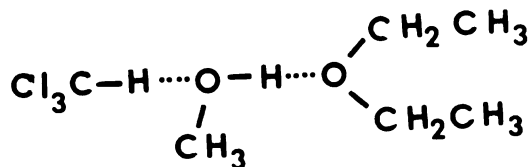
1:1 Acetic
Acid:Acetone
Complex



1:1 Acetone:
Water Complex



Acetone Dimer



1:1:1 Chloroform:Methanol:Diethyl Ether
Complex

Figure 4. Proposed structures for the dimer and solvent complexes of acetone. Also the proposed structure for the $\text{CHCl}_3\text{-MeOH-Et}_2\text{O}$ ternary complex.

acidic, it does have the capability of dissociating a hydrogen. This is indicated by the base-induced deuterium-hydrogen exchange; i.e., CH_3COCH_3 treated with D_2O and NaOD gives CD_3COCD_3 (76).

Acetone has been shown to self-associate. Dimerization constant has been determined using both proton and carbon-13 NMR. Table 1 tabulate this dimerization constant. Saito et al. (78), from their carbon-13 NMR data proposed that the dimer consisted of antiparallel dipoles shown in Figure 4. Acetone also forms a complex with benzene. Table 1 tabulates the association constants obtained for acetone-solvent interactions.

Methanol is a highly associated solvent in both the vapor and the liquid phase. Infrared studies of methanol in the vapor phase show the presence of monomer, dimer, and tetramer (79,80). Table 2 tabulates the thermodynamics for the formation of dimers, ΔH_2 and ΔS_2 , and tetramers, ΔH_4 and ΔS_4 , in the gas phase. However, the association of alcohols is further complicated by the coexistence of cyclic and linear hydrogen bonded species (62). The self-association of alcohols can be generalized schematically as in Figure 5. Obviously, the analysis of such systems requires the determination of many equilibrium constants. The self-association of alcohols has been studied by IR, proton NMR, calorimetry, and

Table 2. Thermodynamics for the Formation of Dimers and Tetramers of Methanol in the Gas Phase.

	$-\Delta H_2$ (kcal/mol)	$-\Delta S_2$ (e.u.)	$-\Delta H_4$ (kcal/mol)	$-\Delta S_4$ (e.u.)	Reference
Methanol	3.22	16.5	24.2	81.3	79
	4.0	11.0	22.1	94	172
	4.1	17.5			171
	3.5		18.4		173, 174
					31
Methanol-d (CH ₃ OD)	5		14		174

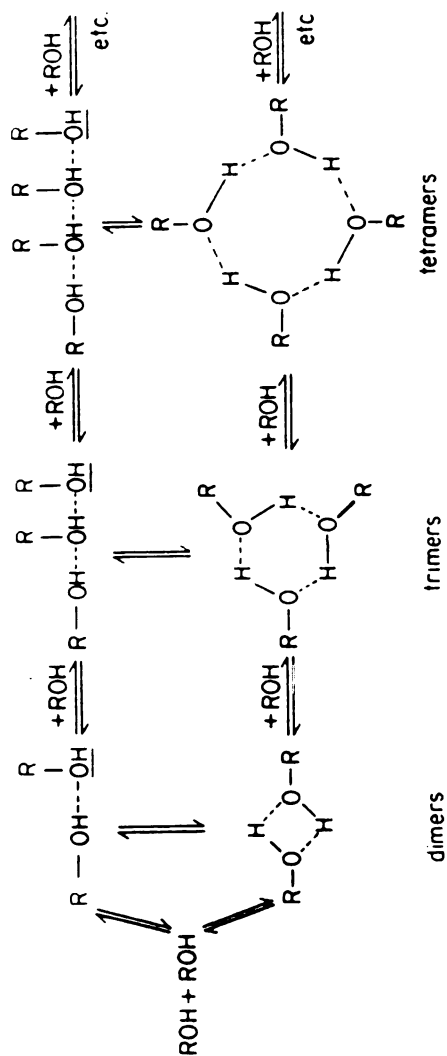


Figure 5. Possible equilibria in the self-association of phenols and alcohols. (The terminal OH groups are underlined.)

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measurements of vapor pressures and viscosities (81-101).

At 20°K the OH stretching region of methanol shows five bands (90). Becker et al. have attributed these to monomer at 3660 cm^{-1} , cyclic dimer at 3490 cm^{-1} , cyclic trimer at 2445 cm^{-1} , cyclic tetramer at 3290 cm^{-1} , and higher linear polymers at 3250 cm^{-1} . It is widely believed that the dimers of methanol and ethanol are probably cyclic (85,89); however, for higher alcohols the linear dimer becomes predominant (89). Fletcher and Heller (62), however, concluded from the IR studies that (1) the tetramer is the predominant polymer for unhindered alcohols and (2) the dimer is linear and absorbs at $\sim 3500\text{ cm}^{-1}$. Although cyclic trimers are supposed to exist for methanol (82,90,94), other studies suggest that cyclic tetramers are more likely (79,84,95). Obviously, for the pure solvent there is considerable disagreement as to the species existing in solution. Interpretations get more complicated when the self-association of the alcohol is studied in solution in nonpolar solvents by IR. The method is based on the principle that if an OH group undergoes hydrogen-bonding, a shift to lower frequency occurs. In general, $\nu_{(\text{monomer})} > \nu_{(\text{dimer})} > \nu_{(\text{trimer})} > \nu_{(\text{tetramer})}$ for the association of a particular alcohol (90,91,101). In an IR study of ethanol in carbon tetrachloride, the ethanol was assumed to exist as a monomer, linear dimer and trimer, and cyclic tetramer

(62). This interpretation yielded $K_{\text{dimer}} = 0.95 \text{ l mole}^{-1}$, $K_{\text{trimer}} = 95 \text{ l}^2 \text{ mole}^{-2}$, and $K_{\text{tetramer}} = 650 \text{ l}^3 \text{ mole}^{-3}$. In this same study, the dielectric polarization of ethanol was measured and found to increase up to weight fraction of 0.001 and then to decrease with further increase in ethanol concentration. This evidence was judged to indicate increased dipole moments in the order monomer < dimer < trimer, due to open or linear form, and decreased dipole moment in the tetramer, due to the latter's cyclic form.

Bellamy and Pace (86) studied solutions of methanol in carbon tetrachloride by IR. They found that the O-H stretch consisted of four bands. The band at 3642 cm^{-1} was assigned to the monomer, 3542 cm^{-1} to the dimer, and 3346 cm^{-1} to the polymer. A band at 3637 cm^{-1} was said to be due to the OH group acting as acceptor, but not donor. From their IR data, Bellamy and Pace favored an open dimer for methanol. This conflicts with the conclusion of van Thiel et al. (90) who conducted an IR study of the $\nu_{\text{O-H}}$ band of methanol multimers isolated in a solid nitrogen matrix.

It is not unexpected that alcohols form hydrogen-bonded complexes with a wide variety of Lewis bases. Gordy and Stanford (102) found that the $\nu_{\text{O-D}}$ band of CH_3OD was very solvent dependent and that the shift of the $\nu_{\text{O-D}}$ band from pure CH_3OD varied linearly with the log

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of the basicity constants of the solvent. They interpreted this behavior as resulting from the interaction of CH_3OD with the unshared electrons on an atom of the solvent since solvents containing O and N atoms shifted the OD band the most. Inskeep and coworkers (103) measured, by IR, a dissociation energy of 4.7 ± 0.7 kcal/mole for the methanol-diethyl ether complex in the gas phase. From IR data for methanol and diethyl ether in chloroform, Bellamy, Morgan, and Pace (87) proposed the existence of a ternary complex shown in Figure 4. Becker (77) obtained thermodynamic data for the complexation of methanol with several acceptors. These data are tabulated in Table 3. Gordon (104) discussed correlations between K_{assoc} and IR frequency shifts, $\Delta\nu$, for hydrogen-bond complex formation, $\text{p}K_{\text{a}}$ for hydrogen-bond donors and $\text{p}K_{\text{b}}$ for hydrogen-bond acceptors. In his correlations, Gordon found that the association constants for the complexes of CH_3OD hydrogen-bonded with the π -systems of substituted benzenes increase with increasing proton basicity of the benzenes. Evidence for the complexation of methanol by benzene was demonstrated by Bayliss and Cant (105). In methanol, water, and carbon tetrachloride solutions, new bands are observed which have been attributed to charge-transfer complexes.

It has been shown that carbon tetrachloride and benzene form a fairly strong complex (106-108). Goates et

Table 3. Thermodynamic Data for the Complexation of Methanol With Several Acceptors^a.

Donor	Acceptor	-ΔG (kcal/mol)	-ΔH (kcal/mol)	-ΔS (e.u.)
Methanol	Acetone	0.35	2.52	7.3
	Dioxane	0.24	2.80	8.6
	Dimethylformamide	1.01	3.72	9.1
	Pyridine	0.65	3.88	10.8

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^aReference 77.

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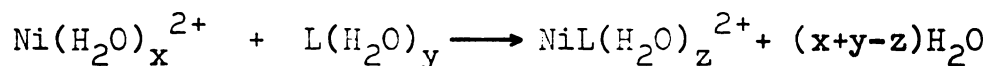
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a1. (109) in constructing a phase diagram for the carbon tetrachloride-benzene system isolated a 1:1 compound at 239°K. In n-hexane, Anderson and Prausnitz (110,111) measured an association constant of 0.009 ± 0.004 l/mole for the complexation between carbon tetrachloride and benzene by UV-VIS (the charge transfer complex absorbs at 225 nm).

2. SOLVATION OF CROWNS AND CRYPTANDS

It has been shown that in solutions the metal ion complexes of macrocyclic ligands tend to be more stable than complexes of analogous noncyclic ligands. Equilibrium and calorimetric studies of Ni^{2+} complexes done by Margerum and Hinz (112,113) showed that the greater stability of the macrocyclic complex was due to a more favorable change in ΔH^0 which overcomes a less favorable change in ΔS^0 . They explained their observations in terms of ligand solvation. For the reaction shown below, the primary solvation (y) of the ligand is variable:



Therefore, ΔH^0 for the reaction increases as the enthalpy of solvation of L increases and ΔS^0 increases as y increases due to the additional water molecules released in the reaction. For a macrocyclic ligand, ΔH^0 is more negative than for a noncyclic ligand because the macrocycle is less solvated by water due to steric

hindrance. It then follows that ΔS^0 must be less positive because fewer water molecules are released from the ligand. There is, however, another contribution to the ΔS^0 of reaction which is due to the conformational entropy. One would expect a greater loss in the conformational entropy in the reaction of the open-chain ligand to form its complex than in the reaction of the macrocyclic ligand to form its complex. In conclusion, Margerum and Hinz said that the increased stability was due to a "macrocyclic effect" and that the primary contributors to this phenomenon were the conformation and solvation of the free ligand.

Others have also studied the macrocyclic effect and there is some controversy as to the thermodynamic origin of the macrocyclic effect. Margerum and co-workers (113-115) found the enthalpy term to predominate in the observed macrocyclic effect when the formation of Ni(II) complexes of cyclam and those of 2,3,2-tet, shown in Figure 6, are compared. Dei and Gori (116) reached a similar conclusion using the Cu(II) complexes of the these two ligands. Izatt et al. (117) measured the thermodynamic parameters for Na^+ , K^+ , and Ba^{2+} complexation with pentaglyme and 18-crown-6, the structures of the ligands are shown in Figure 6, in methanol and methanol/water mixtures. The results of their studies are tabulated in Table 4. From their

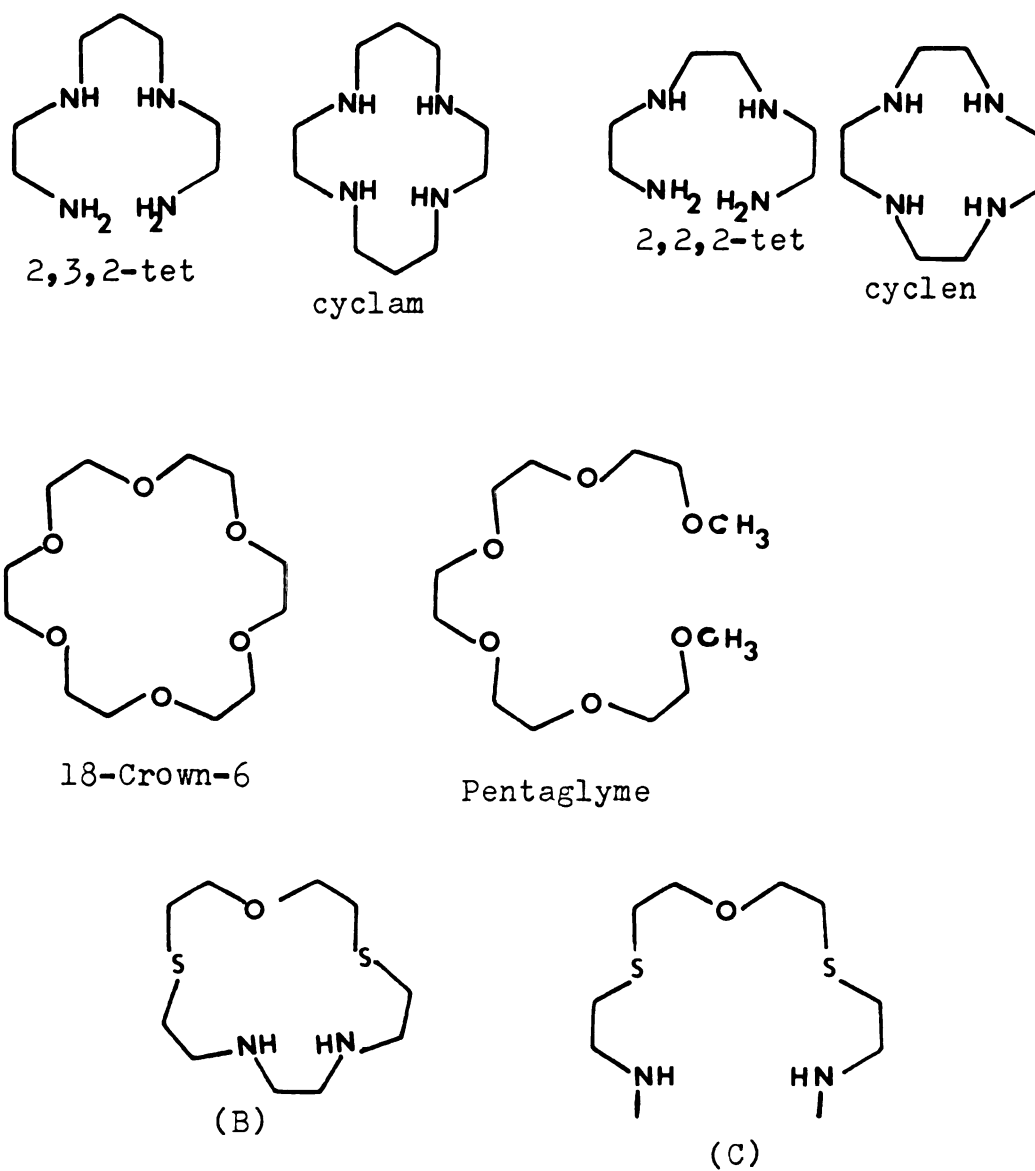


Figure 6. Structures of some linear and cyclic ligands.

Table 4. Thermodynamic Data for the Complexation of Linear and Cyclic Ligands.

Cation	Solvent	Ligand	log K (at 25°C)	ΔH (kcal/mol)	$T\Delta S$ (kcal/mol)
Na^+ ^a	90% MeOH/H ₂ O	18C6	3.66±0.02	-6.64±0.07	-1.65
	99% MeOH/H ₂ O	18C6	4.33±0.02	-8.11±0.05	-2.20
	MeOH	18C6	4.36±0.02	-8.36±0.37	-2.41
		PG	1.44±0.05	-4.02±0.28	-2.06
K^+ ^a	90% MeOH/H ₂ O	18C6	5.35±0.25	-11.77±0.05	-4.47
		PG	1.95±0.01	-7.00±0.08	-4.34
	99% MeOH/H ₂ O	18C6	6.05±0.05	-13.21±0.07	-4.96
		PG	2.27±0.02	-8.15±0.12	-5.05
	MeOH	18C6	6.06±0.03	-13.41±0.06	-5.14
		PG	2.1	-8.70	-5.8
Ba^{2+} ^a	90% MeOH/H ₂ O	18C6	6.56±0.09	-10.33±0.11	-1.38
		PG	2.33±0.03	-7.10±0.16	-3.92
	99% MeOH/H ₂ O	18C6	7.03±0.06	-10.38±0.15	-0.79
		PG	2.51±0.01	-5.65±0.05	-2.23
	MeOH	18C6	7.04±0.08	-10.41±0.06	-0.80
		PG	2.3	-5.55	-2.4

Table 4. Continue.

Cation	Solvent	Ligand	log K (at 25°C)	ΔH (kcal/mol)	$T\Delta S$ (kcal/mol)
Ni^{2+} ^b	H_2O	cyclam	22.2	-31	2.1
		2,3,2-tet	15.8	-19.4	-0.6
Zn^{2+} ^c	H_2O	cyclen	16.2 $\pm$ 0.2	-7.9 $\pm$ 0.4	14.0 $\pm$ 0.6
		2,2,2-tet	12.1	-8.9	7.45
Cu^{2+} ^c	H_2O	cyclen	24.8	-18.3	5.8
		2,2,2-tet	20.2	-21.6	5.8
Cd^{2+} ^d	H_2O	cyclen	14.3 $\pm$ 0.2	-8.2 $\pm$ 0.5	11.3 $\pm$ 0.6
		2,2,2-tet	10.4	-9.2	5.7
Pb^{2+} ^d	H_2O	cyclen	15.9 $\pm$ 0.2	-6.6 $\pm$ 0.5	15.2 $\pm$ 0.6
		2,2,2-tet	10.3 $\pm$ 0.3	-8.3 $\pm$ 0.5	6.0 $\pm$ 0.3
Hg^{2+} ^d	H_2O	cyclen	25.5	-23.6	11.3
		2,2,2-tet	24.5	-30.2	3.3

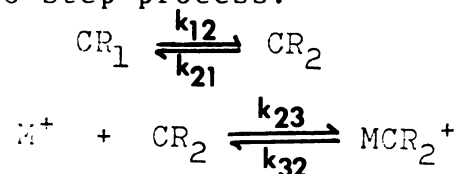
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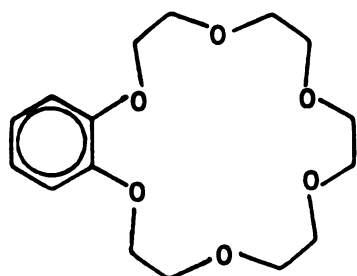
Cation	Solvent	Ligand	$\log K$ (at 25°C)	ΔH (kcal/mol)	$T\Delta S$ (kcal/mol)
Cu^{2+} ^e	H_2O	(B)	13.26 ± 0.02	-12.54 ± 0.27	5.52 ± 0.30
		(C)	9.15 ± 0.04	-9.56 ± 0.75	2.71 ± 0.80
Pb^{2+} ^e	H_2O	(B)	6.78 ± 0.02	-9.52	-0.29
		(C)	7.49 ± 0.04	-9.54	0.67

^aReference 117.^bReference 112.^cReference 121.^dReference 123.^eReference 125.

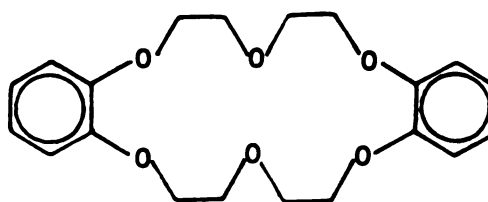
results they concluded that the macrocyclic effect was enthalpic in origin. Both Paoletti and co-workers (118-120) and Kodama and Kimura (121-123) found that the entropy term was primarily responsible for the macrocyclic effect using Cu(II) complexes of cyclen and 2,2,2-tet (shown in Figure 7). Paoletti and co-workers (124) later concluded that the relative magnitude of the enthalpy contribution is critically dependent on the match between cation and ligand cavity sizes for transition metals. In a study of Cu(II) complexes of ligands containing S, N, and O donor atoms, Arnaud-Neu et al (125). concluded that the macrocyclic effect has both enthalpy and entropy contributions.

Besides their importance in the macrocyclic effect, the solvation and conformation of the free ligand may also be involved in the kinetics of complexation. Eyring et al. (126-128) used ultrasonic absorption methods to study the kinetics of complexation of 18-crown-6 with Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Tl^+ , Ag^+ , NH_4^+ , and Ca^{2+} in water. According to these authors, the basic reaction scheme for the complexation which best fit their experimental data is the following two-step process:

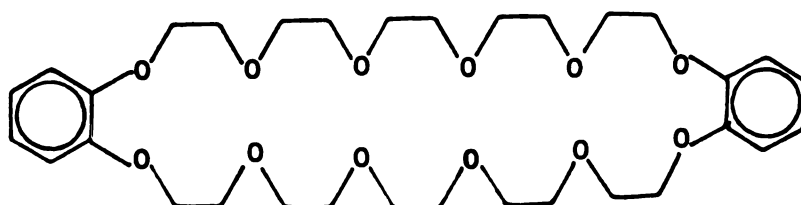




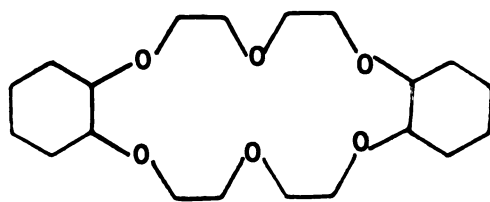
Benzo-18-Crown-6
B18C6



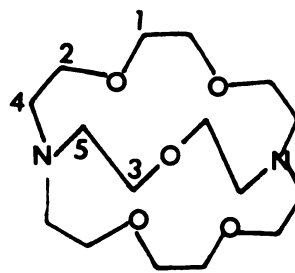
Dibenzo-18-Crown-6
DB18C6



Dibenzo-30-Crown-10
DB30C10



Dicyclohexyl-18-Crown-6
DC18C6



Cryptand 221
C221



nonpolar conformation of
DB18C6



polar conformation
of DB18C6

1,3'-Xylyl-
18-Crown-5

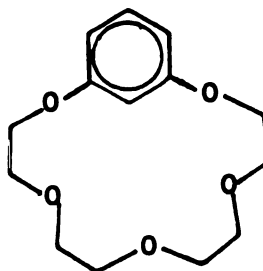


Figure 7. Structures of some crowns and cryptands.

where CR_1 and CR_2 denote two different conformations of the free polyether, M^+ is a metal ion, and MCR_2^+ is the complexed ion. The conformation CR_1 is unreactive. The above mechanism, therefore, involves a fast ligand conformational change followed by a stepwise substitution of the coordinated solvent molecules of the ligand.

Proton and carbon-13 NMR studies of 18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6, and dibenzo-30-crown-10 (the structures of which are shown in Figure 7) in their complexed and uncomplexed states in various solvents were done by Live and Chan (129). These studies show that macrocyclic polyethers exist in solution in at least two, and more probably, three conformations. These three conformations are an unreactive species; an open configuration, which is the predominant species in the absence of cations; and a closed configuration, which is stabilized by a monovalent cation. The NMR data indicate that in the absence of complexing cations these macrocycles undergo a rapid "syn" to "anti" gauche rotamer conversion with an interconversion rate faster than 10^{-3} sec^{-1} . A rapid rotamer interconversion of the ether linkages in the uncomplexed crown ethers is observed with a slowing of the rate in $CDCl_3$. Benzo substituents in the ring do not affect these structural observations. Eyring et al. (130) have studied the dynamics of conformational change of 18-crown-6 in water. The equilibrium constant

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for the conformational transition $CR_1 \xrightleftharpoons[k_{21}]{k_{12}} CR_2$ was determined to be $K = (2 \pm 2) \times 10^{-2}$ with rate constants, at 25°C, of $k_{21} = (1.0 \pm 0.3) \times 10^7 \text{ sec}^{-1}$ and $k_{12} = (6.2 \pm 0.2) \times 10^8 \text{ sec}^{-1}$. The activation parameters are $\Delta H_{21}^\ddagger = 10.2 \pm 1.0 \text{ kcal/mol}$, $\Delta S_{21}^\ddagger = 7.7 \pm 0.2 \text{ cal/(mol} \cdot \text{deg)}$, $\Delta H_{12}^\ddagger = 7.4 \pm 1.0 \text{ kcal/mol}$ and $\Delta S_{12}^\ddagger = 7.7 \pm 0.2 \text{ cal/(mol} \cdot \text{deg)}$, while the thermodynamic enthalpy and entropy were found to be $-2.6 \pm 1.0 \text{ kcal/mol}$ and $0 \pm 0.2 \text{ cal/(mol deg)}$, respectively.

The relaxation of 18-crown-6 has also been measured in several other solvents and the kinetic data are summarized in Table 5. With the exception of water, the rate constants at 25°C have been calculated assuming $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are independent of the temperature. As Table 5 indicates, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are strongly solvent dependent. However, at 25°C, with the exception of ethanol, k_{21} is always $\approx 10^7 \text{ sec}^{-1}$ and, with the exception of water, k_{12} is always $\approx 2 \times 10^9 \text{ sec}^{-1}$. In the two exceptional cases the rate constants differ from the others by less than one order of magnitude. Chen and Petrucci (131) showed that in methanol solutions one molecule of the solvent is eliminated during the isomerization process. In their explanation they said that the open form of the crown is "solvated" or "complexed" by the methanol and releases one molecule during the conformational change.

Solvation studies of crowns and cryptands have been

Table 5. Kinetic Parameters for Relaxation of 18C6 in Various Solvents.

Solvent	k_{21} (sec ⁻¹)	k_{12} (sec ⁻¹)	$\Delta H_{21}^\ddagger$ (kcal/mol)	$\Delta S_{21}^\ddagger$ (e.u.)	$\Delta H_{12}^\ddagger$ (kcal/mol)	$\Delta S_{12}^\ddagger$ (e.u.)	Ref. No.
H ₂ O (25°C)	1.0×10^7	6.2×10^8	10.2	7.7	7.4	7.7	130
DMF (25°C)	9.9×10^6	3.3×10^9					169
(-10°C)	3.6×10^6	5.5×10^8	3.8	-13.8	7.5	10.2	169
MeOH (25°C)	9.0×10^6	2.1×10^9					168
(-20°C)	$\sim 3.0 \times 10^6$	3.1×10^8	3.2	-16.0	5.8	3.54	168
EtOH (25°C)	2.9×10^6	1.9×10^9					170
(-15°C)	1.9×10^6	4.8×10^8	1.1	-25.3	4.8	0	170
Dioxane (-20°C)		$\sim 2.0 \times 10^8$					131

rather sparse despite the evidence that the solvation and conformation of the ligand is important in the thermodynamics and kinetics of metal complexation. Kryukov et al. (132) showed that the proton chemical shifts of the ethylene protons of dibenzo-18-crown-6, DB18C6, were strongly solvent dependent. They found that with increasing dipole moment or dielectric constant of the solvent, the chemical shifts of the ethylene protons decreased. This was taken as evidence that the solvent stabilized one of the possible conformers of DB18C6. Figure 7 shows the nonpolar and polar conformations of DB18C6 proposed by Ting-Po I and Grunwald (133) from permittivity measurements. The results obtained by Kryukov et al. indicate that the more polar solvent stabilizes the conformer with a larger dipole moment; i.e., the boat conformer. Similar results were obtained by Live and Chan (129) in their proton and carbon-13 NMR studies of DB18C6.

Abraham et al. (134,135) showed, by direct calorimetric measurements, that the enthalpy of transfer of cryptand 222 from water to methanol is +13.9 kcal/mol while for 18-crown-6, 18C6, it is +13.6 kcal/mol. These enthalpies of transfers are very large and are indicative of major enthalpic effects associated with the ligand/water and ligand/methanol interactions.

Dale et al. (136-138) have studied the conformation

of free and complexed crown ethers by both NMR and IR. In one study, Dale and Kristiansen (136) obtained IR spectra of solid and molten 18C6 and 24C8 as well as their KBr complexes. From X-ray analysis of the 18C6 complex with KSCN (139), it has been shown that the crown adopts a D_{3d} ring conformation. It was concluded that the vibrational bands of 18C6 observed in the IR spectrum of the KBr·18C6 complex were, therefore, characteristic of D_{3d} symmetry. In the D_{3d} conformation, the $-O-CH_2CH_2-O-$ monomer units are arranged in the anti,gauche,anti conformation and only two bands are visible in the CH_2 -rocking region at 800-1000 cm^{-1} . In the absence of a central cation, five bands are visible in the region instead of two, suggesting that three types of monomer units are present. In the liquid state the IR bands of 18C6 become very broad because of the admixture of additional conformers. Similar conclusions were reached for 24C8 except that the 24C8·KBr complex has D_{2d} symmetry. The carbon-13 NMR studies by Dale et al. (137,138), showed that the carbon-13 chemical shift of the crown is solvent and temperature dependent. The authors also found that with the addition of cation, the carbon-13 resonance of the crown shifted upfield, and concluded that the degree of the upfield chemical shift observed on complexation depended primarily on the type of conformational changes that are needed to form the complex.

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Differences in crown solvation can be seen in the UV spectra of DB18C6 (140). A UV spectrum of 0.000255 M DB18C6 in cyclohexane (cell path 1 cm) showed three bands at 274 nm (ϵ 4400), 278 nm (ϵ 4700) and 283 nm (ϵ 3600). However, in methanol, 0.000183 M DB18C6 (cell path 1 cm) only one band at 274 nm (ϵ 5200) was observed.

Schmidt et al. (141) found that the carbon-13 and proton NMR spectra of cryptand 221, C221, are strongly influenced by the solvent and by temperature. Figure 7 shows the structure of C221. From this structure it can be seen that C221 has five distinct carbon atoms. It was found that the carbon-13 spectra of C221 in different solvents can be separated into two classes which these workers designated by "A" and "B". The A spectra, at room temperature or below, were found to be very similar to that of the $K^+ \cdot C221$ complex. In the class A solvents there is a separation of the carbon-13 resonances of carbons 4 and 5 which increases as the temperature is lowered. By contrast the B spectra resemble that of the $Na^+ \cdot C221$ complex in which the signals of carbons 4 and 5 are superimposed at all temperatures. From these results, Schmidt et al. concluded that the A spectra were indicative of a specific solvent-ligand interaction where a part of the solvent molecule (e.g., OH, NH, or CH_3) penetrates into the cavity of the ligand, forms hydrogen bonds with some (or all) heteroatoms of the latter, and

forces it into an "open face" configuration similar to the one observed for the $K^+ \cdot C221$ complex.

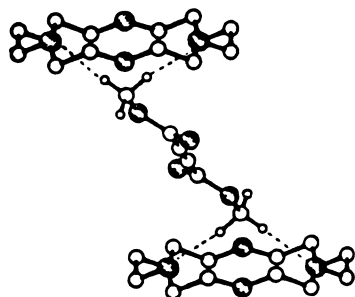
3. SOLVENT-CROWN COMPLEXATION

Crystalline complexes of 18C6 with a variety of neutral organic guests are known (142-144). The complexation of macrocyclic ligands with neutral CH-acidic compounds is of particular interest to industrial chemists. There are patents for the purification of 18C6 using nitromethane (145) and organic nitriles such as $NC(CH_2)_8CN$ (146). Others have proposed to use crown ethers to "fix" volatile, highly toxic chemical reagents such as dimethyl sulfate, methyl tosylate, acetic anhydride, dimethyl nitrosamine, etc. (142). These chemical reagents are important alkylation and acylation reagents for synthesis. They are also very carcinogenic and, due to their volatility, difficult to manipulate. However, the adducts formed with crown ethers are nonvolatile and much more stable and safer to manipulate than the uncomplexed carcinogens. The complexation of crown ethers with neutral organic guests has been studied by X-ray crystallography (147-149), Raman spectroscopy (150,151), and proton NMR spectroscopy (147,151,152-154).

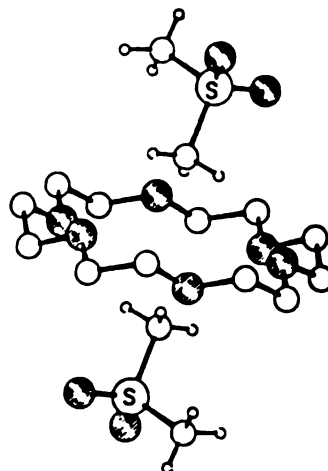
The first crystal structure analysis reported in the literature was that of the 18C6 adduct with dimethyl acetylenedicarboxylate (149). The overall stoichiometric

ratio between host and guest in this complex is 1:1; however, the centrosymmetric bifunctional guest species extends between and interacts simultaneously with two 18C6 rings. Figure 8 shows the crystal structure for the dimethyl acetylenedicarboxylate 18-crown-6 complex. Malonitrile (148) and dimethylsulphone (155) form complexes with 18C6 in a 1:2 crown:guest stoichiometry. The crystal structures for these complexes are also shown in Figure 8. For dimethylsulfone it can be seen that all three methyl hydrogens are involved in the C-H.....O interactions with alternate O-atoms of the crown. In the dimethylsulfone, malonitrile, and dimethyl acetylenedicarboxylate complexes, the 18C6 has D_{3d} symmetry.

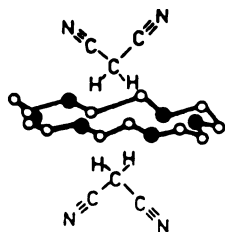
Crystal structures of 18C6 complexes with nitromethane (147) and formamide (156) have been determined and are shown in Figure 8. The intermolecular arrangement and interaction pattern of the 1:2 18C6 complex with nitromethane is similar to that observed for the complex with dimethylsulfone. As Figure 8 shows, formamide complexes 18C6 through the NH_2 group. The crystal structure of a binaphthol crown ether complex with water has been described (157). The water molecule is too small to fit the whole macrocyclic cavity. Coordination occurs through three H.....O hydrogen bonds and one interior-directed CH_2 group. The pyridino crown ether



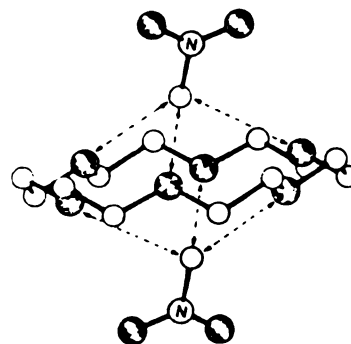
Dimethylacetylene-
dicarboxylate
adduct



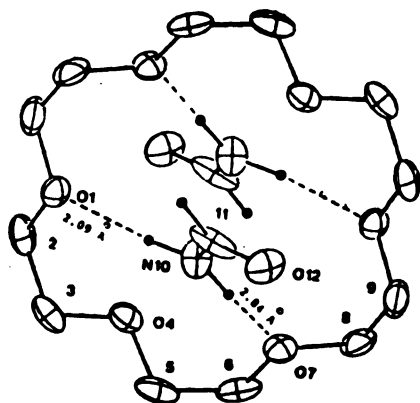
Dimethyl sulfone
adduct



Malononitrile
adduct



Nitromethane
adduct

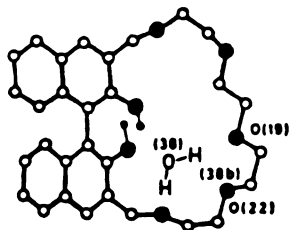


Formamide adduct

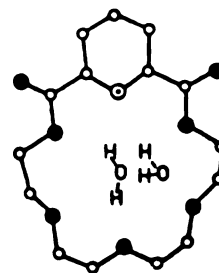
Figure 8. X-ray crystal structures of some guest-18C6 adducts.

forms a 1:2 complex with water (158). In this complex the two water molecules are hydrogen bonded to each other and with two crown ether oxygen atoms, but not to the pyridine nitrogen. The crystal structures for these complexes are shown in Figure 9. An X-ray crystal structure has been determined for the carbon disulfide complex with a cavitand (159). This crystal structure is shown in Figure 10. Figure 11 shows the X-ray crystal structure for the inclusion complex of chloroform and a 30-membered hexalactam host (160). A crystal structure of the malonitrile complex of azacoronand was obtained by von Deuten *et al.* (161) and is shown in Figure 9. Von Deuten *et al.* unsuccessfully attempted to prepare the malonitrile complex with diaza-18-crown-6, DA18C6. They said that the inability to prepare the malonitrile complex with DA18C6 was due to the intramolecular hydrogen bonding of DA18C6.

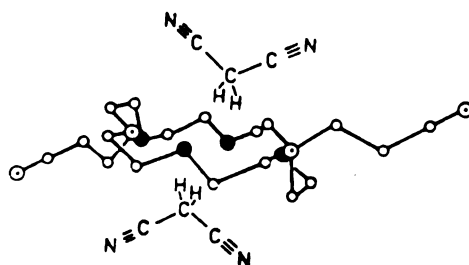
McLachlan (150) has obtained Raman spectra of the crystalline complexes of 18C6 with acetonitrile, acetonitrile- d_3 , nitromethane, and acetic anhydride. In each of these complexes, the vibrational modes of the crown ether indicate that the crown has D_{3d} symmetry. Gold and Rice (151) obtained Raman spectra of the solid complex of acetonitrile with 18C6. They found that the CN stretching frequency of acetonitrile in the solid crystalline complex appears at 2243 cm^{-1} , a shift of 10 cm^{-1} from the CN stretching frequency in pure liquid



$\text{H}_2\text{O} \cdot \text{binaphthol}$
complex



$\text{H}_2\text{O} \cdot \text{pyridino}$
complex



azacoronand·malononitrile
complex

Figure 9. X-ray crystal structures of some crown-guest adducts.

STRUCTURES:

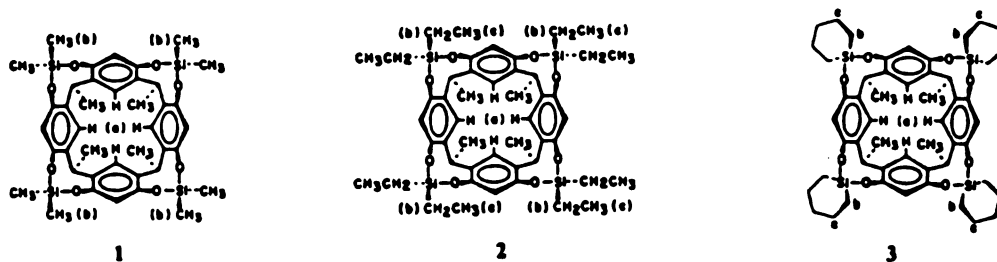
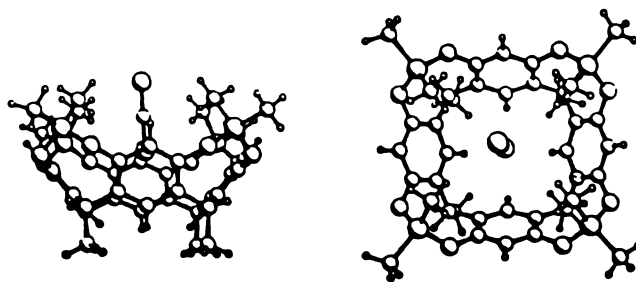
CS₂:Cavitand Complex:

Figure 10. Structures of cavitands and the x-ray structure of the CS₂ complex.

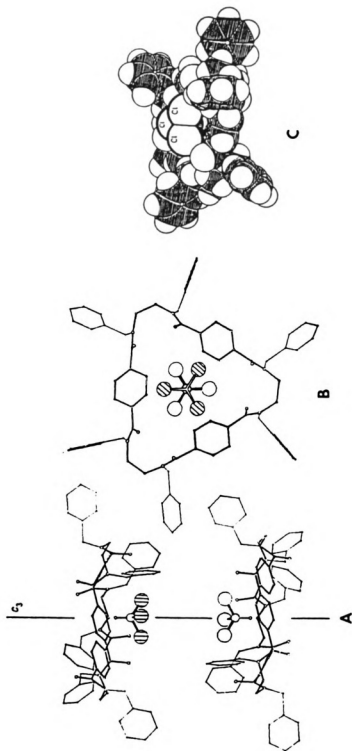


Figure 11. X-ray structure of the hexalactam CHCl_3 inclusion compound: (A) view across the central plane of the macrocyclic ring and (B) view down the trigonal axis perpendicular to the central plane. Space-filling illustration of the key-lock-like arrangement of the CHCl_3 guest in the niche of the host (C).

acetonitrile ($\nu_{\text{CN}}=2255 \text{ cm}^{-1}$). Assuming that complexation between acetonitrile and 18C6 occurs through the methyl group (as was shown in the crystal structure of the nitromethane complex with 18C6), Gold and Rice (151) postulated that the shift of ν_{CN} to lower frequencies was due to a weakening of the CN bond by the increased electron density acquired by inductive effects through the methyl protons.

Knochel et al. (152) have studied the complexation of crown ethers with acetonitrile, nitromethane, and dinitriles by proton NMR and IR. Table 6 summarizes the results obtained for the dinitriles and shows that upon complexation, significant changes are observed in the proton chemical shift of the dinitrile proton(s), the C-H stretching frequency of the dinitrile, and dipole moment of the dinitrile.

Quantitative data on the ligand-solvent interactions are quite sparse. Association constants of 18C6 with nitromethane, acetonitrile, and malononitrile in deuterobenzene solutions were measured by proton NMR by de Boer et al. (147). They also measured the association constant of the nitromethane complexation of 1',3'-xylyl-18-crown-5 (the structure is shown in Figure 7). The association constants they obtained are tabulated in Table 7. Gold and Rice (151) determined the association of 18C6 and acetonitrile in carbon

Table 6. Properties of the Guest Both Free and in the 18-Crown-6 Adduct.^a

GUEST	STOICHIOMETRY OF ADDUCT	MELTING POINT (°C)	¹ H NMR (ppm in CDCl ₃)		IR (cm ⁻¹)		DIPOLE MOMENT (D)	
			FREE	ADDUCT	FREE	ADDUCT	FREE	ADDUCT
NC-CH ₂ -CN	1:2	137-138	3.51	4.00	2970	2950	3.56	5.65
NC-CHBr-CN	1:2	58	4.95	5.42	2975	2945	-----	-----
NC-(CH ₂) ₂ -CN	1:2	88	2.70	2.85	2980	2965	3.91	5.34
NC-(CH ₂) ₃ -CN	1:1	54	-----	-----	2950	2940	3.99	5.29
NC-(CH ₂) ₄ -CN	1:1	56	-----	-----	-----	-----	3.89	4.80

^aReference 152.

Table 7. Association Constants for Several Ligand-Guest Complexations.

Guest	Host	Background Solvent	Temp. (°K)	$K_{1:1}$ ($l\ mol^{-1}$)	$K_{1:2}$ ($l\ mol^{-1}$)	Reference Number
Malononitrile	18C6	C_6D_6	300	150 ± 15	11 ± 2.8	147
Acetonitrile	18C6	C_6D_6	300	0.48 ± 0.05		147
Nitromethane	18C6	C_6D_6	300	1.2 ± 0.12	2.5 ± 0.6	147
Acetonitrile	18C6	CCl_4	298	2.1 ± 0.1		151
Dimethyl Sulfate	18C6	C_6D_6	301	$0.6 \pm ?$		154
Dimethyl Carbonate	18C6	C_6D_6	298	$0.8 \pm ?$		154
Dimethyl Oxalate	18C6	CCl_4/C_6D_6 ($\frac{4}{3}$ v/v)	301	$0.6 \pm ?$		154
Nitromethane	1',3'-xylyl-18C5	C_6D_6	300	$0.61 \pm ?$		147
Carbon Disulfide	Cavitand 1	$CDCl_3$	250	$0.82 \pm ?$		159
Carbon Disulfide	Cavitand 2	$CDCl_3$	250	$8.1 \pm ?$		159

Table 7. Continue.

Guest	Host	Background Solvent	Temp. (°K)	$K_{1:1}$ (1 mol^{-1})	$K_{1:2}$ (1 mol^{-1})	Reference Number
Carbon Disulfide	Cavitand 3	CDCl_3	250	$13.2 \pm ?$		159
Water	1'3'-xylyl- 15C4	CDCl_3	295	8.0 ± 0.8		153
Water	1'3'-xylyl- 18C5	CDCl_3	295	14.0 ± 1.4		153
Water	1'3'-xylyl- 21C6	CDCl_3	295	14.0 ± 1.4		153
Water	1'3'-xylyl- 24C7	CDCl_3	295	20.0 ± 2.0		153
Water	1',3'-xylyl- 27C8	CDCl_3	295	23.0 ± 2.3		153
Water	1'3'-xylyl- 30C9	CDCl_3	295	47.0 ± 4.7		153
Chloroform	dicyclohexyl- 18C6	CCl_4	295	$0.6 \pm ?$		175

tetrachloride by proton NMR. Proton NMR was also used to evaluate the association constants of the complexation of 18C6 with dimethyl sulfate, dimethyl carbonate, and dimethyl oxalate (154). Cram et al. (159) obtained association constants for the carbon disulfide complexation with cavitands 1-3 (structures shown in Figure 10) by proton NMR of the ligand. De Jong et al. (153) determined the association constants for the complexation of water with several crown ethers by proton NMR. Shchori and Jagur-Grodzinski (175) used proton NMR to determine the formation constant for the complexation of chloroform with dicyclohexyl-18-crown-6 (structure shown in Figure 7). The association constants for these studies are tabulated in Table 7.

CHAPTER II

EXPERIMENTAL PART

A. MATERIAL PURIFICATION

1. REAGENTS. Silver nitrate (Fisher) was recrystallized from concentrated nitric acid (Fisher) and dried under vacuum for three days at room temperature. Sodium thiocyanate (Mallinckrodt) and potassium thiocyanate (MCB) were recrystallized from methanol and dried under vacuum at 70°C for three days. Lithium perchlorate (K&K Laboratories) and sodium tetraphenylborate (Aldrich, Gold Label) were dried under vacuum for three days at room temperature.

The following compounds were used as received: malononitrile (Aldrich), o-dimethoxybenzene (Aldrich), hexachlorobenzene (Aldrich), p-dichlorobenzene (MCB), 1,3,5-trichlorobenzene (Aldrich), m-dinitrobenzene (Eastman), hexamethylbenzene (Aldrich), nitrobenzene (MCB), benzonitrile (Eastman), 10% aqueous solution of tetramethylammonium hydroxide (MCB), and concentrated hydrochloric acid (EM).

2. LIGANDS. The macrocyclic polyether 18-crown-6 (18C6, Aldrich) was purified by the usual technique of converting it to the crystalline acetonitrile complex, filtering the solution and driving off acetonitrile under vacuum (5). The dried 18C6 melts at 36-37°C [lit. m.p. 36.5-38.0°C (5), 39.5-40.5°C (176), 39-40°C (140)]. Dibenzo-18-crown-6 (DB18C6, Parish) was recrystallized

twice from benzene and dried under vacuum for three days. The dried DB18C6 had a melting point of 164-166°C [lit. m.p. 164°C (140)]. Diaza-18-crown-6 (DA18C6 or [22], MCB); dithia-18-crown-6 (DT18C6, Parish), 21-crown-7 (21C7, Parish); and cryptands C221 and C211 (MCB) were simply dried under vacuum at room temperature for at least three days. Cryptand C222 (MCB) was recrystallized from n-hexane and dried under vacuum for three days at room temperature. Benzo-15-crown-5 (B15C5, Parish) was recrystallized from n-heptane and dried under vacuum for three days. The melting point of the dried B15C5 was 79-80°C [lit. m.p. 79-79.5°C (140)]. Tetraglyme (TG, Aldrich) and 15-crown-5 (15C5, Aldrich) were fractionally distilled under reduced pressure and dried under vacuum for three days. Pentaglyme (PG) was synthesized by N. Okoroafor following the procedure of Izatt et al. (117). It was dried under vacuum for three days prior to use. The purity of the ligands was checked using proton and carbon-13 NMR spectroscopy. Table 8 lists the common and IUPAC names for these ligands as well as some pertinent physical properties.

3. SOLVENTS. Carbon tetrachloride (Mallinckrodt) and chloroform (Fisher) were refluxed over phosphorous pentoxide for three days and then fractionally distilled. Acetonitrile (AN, Baker) and dimethyl formamide (DMF, Baker) were refluxed over calcium hydride for one week and

Table 8. Pertinent Physical Properties of Some Ligands.

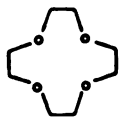
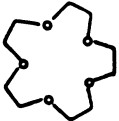
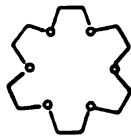
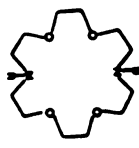
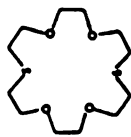
Ligand	IUPAC Name	Structure	^a Cavity Diameter (Å)	M.W. (g/mol)
12-Crown-4 (12C4)	1,4,7,10-Tetraoxacyclododecane		1.2-1.5	176.28
15-Crown-5 (15C5)	1,4,7,10,13-Pentaoxacyclopentadecane		1.7-2.2	220.27
18-Crown-6 (18C6)	1,4,7,10,13,16-Hexaoxacyclooctadecane		2.6-3.2	264.26
Diaza-18- Crown-6 (DA18C6)	1,7,10,16-Tetraoxa-4,13- diazacyclooctadecane		2.6-3.2	262.35
Dithia- 18-Crown-6 (DT18C6)	1,7,10,16-Tetraoxa-4,13- dithiacyclooctadecane		2.6-3.2	296.44

Table 8. Continue.

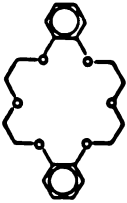
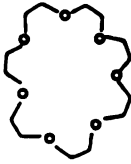
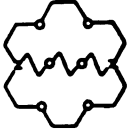
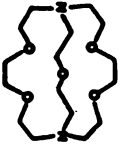
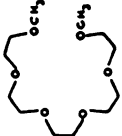
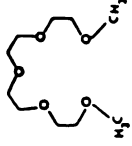
Ligand	IUPAC Name	Structure	Cavity Diameter ^a (Å)	M.W. (g/mol)
Dibenzo-18-Crown-6 (DB18C6)	Dibenzo[b,k][1,4,7,10,13,16]hexaoxacyclooctadecin		2.6-3.2	360.41
Benzo-15-Crown-5 (B15C5)	1,4,7,10,13-Benzopentaoxa-cyclopentadecin		1.7-2.2	268.3 ⁶⁷
21-Crown-7	1,4,7,10,13,16,19-Heptaoxa-cycloheeneicosane		3.4-4.3	376.50
Cryptand 222 (C222)	4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane		2.8	376.50
Cryptand 221 (C221)	4,7,13,16,21-Pentaoxa-1,10-diazabicyclo[8.8.5]tricosane		2.2	332.44

Table 8. Continue.

Ligand	IUPAC Name	Structure	Cavity ^a Diameter (Å)	M.W. (g/mol)
Cryptand 211 (C211)	4,7,13,18-Tetraoxa-1,10-diazabicyclo[8.5.5]eicosane		1.6	288.39
Pentaglyme (PG)	2,5,8,11,14,17-Hexaoxaoctadecane		---	266.27 8
Tetraglyme (TG)	2,5,8,11,14-Pentaoxapentadecane		---	222.27

^aCavity difference is due to the Corey-Pauling-Kolton (CPK) models and the Fischer-Hirschfelder-Taylor (FHT) models used.

then fractionally distilled. Acetone (AC, Mallinckrodt) was purified in the same way, but with Drierite as the drying agent. Nitromethane (NM, Aldrich, Gold Label) was refluxed over calcium hydride under reduced pressure for two days and then fractionally distilled under reduced pressure. Since there is some decomposition of nitroalkanes above 90°C, care was taken to keep the pot temperature under 90°C (177). Likewise dimethylsulfoxide (DMSO, Mallinckrodt) was refluxed over calcium hydride under reduced pressure for two days and fractionally distilled under reduced pressure. Benzene (C_6H_6 , Fisher) was purified by several extractions with concentrated sulfuric acid to remove thiophene. It was then washed with water to remove sulfuric acid, refluxed over calcium hydride for three days and then fractionally distilled. Propylene carbonate (PC, Aldrich) was refluxed over barium oxide under reduced pressure for at least one day and fractionally distilled. Tetrahydrofuran (THF, Mallinckrodt) was refluxed over a mixture of potassium metal and benzophenone for one day and fractionally distilled. Methanol (Baker) was refluxed over magnesium turnings and iodine for three days after which time the solvent was fractionally distilled. Pyridine (PY, Fisher) was refluxed over barium oxide for two days and then fractionally distilled. In all distillations, only the middle sixty percent of the solvent fractions were

collected. All solvents, except NM, were stored over freshly activated 3 Å molecular sieves in brown bottles in a dry box under nitrogen atmosphere. Nitromethane was not stored over molecular sieves but it was kept in a brown bottle in a dry box under nitrogen atmosphere. It was found that nitromethane stored over molecular sieves turns yellow in color within a day.

The water content of all solvents, except NM, was determined by gas chromatography utilizing either one of the methods described in the next section. In all cases the water content was below 50 ppm. The water content of NM had to be checked by proton NMR since NM decomposes in the GC. Since no resonance due to water was detected in the proton NMR spectrum, the water content of NM was judged to be below 100 ppm (a water peak is observed in CCl₄ saturated with water. The concentration of water in this solution is 100 ppm (177)). Important solvent properties are listed in Table 9.

The following deuterated solvents (Aldrich, Gold Label) were used as received in the solvation and complexation studies of the macrocyclic ligands: acetonitrile-d₃, nitromethane-d₃, benzene-d₆, acetone-d₆, methanol-d₄, acetic acid-d₄, chloroform-d, dimethylformamide-d₇, tetrahydrofuran-d₈, 1,4-dioxane-d₈, dimethylsulphoxide-d₆, and pyridine-d₅. Deuterated water (KOR Isotopes) was also used as received. Acetone-d₆

Table 9. Important Solvent Properties.

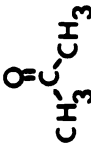
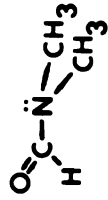
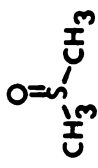
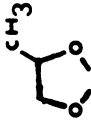
SOLVENT	STRUCTURE	DIELECTRIC CONSTANT (ϵ)	DIPOLE MOMENT (μ)	GUTMANN DONOR NUMBER (D.N.)
Acetic acid		6.18	1.74 ^b	-----
Acetone		20.7	2.88	17.0
Acetonitrile	$\text{CH}_3\text{C}\equiv\text{N}$	37.5	3.96	14.1
Benzene		2.27	0.00	-----
Carbon Tetrachloride	CCl_4	2.24	0.00	-----
Chloroform	CHCl_3	4.81	1.15	-----
N,N-Dimethylformamide		36.7	3.86	26.6
Dimethylsulfoxide		46.68	3.90	29.8

Table 9. Continue.

SOLVENT	STRUCTURE	DIELECTRIC CONSTANT (ϵ)	DIPOLE MOMENT (μ)	GUTMANN DONOR NUMBER (D.N.)
1,4-Dioxane		2.25	0.45	-----
Methanol	$\text{H}_3\text{C}-\text{OH}$	32.7	1.70	25.7 ^a
Nitromethane	CH_3NO_2	35.9	3.44	2.7
Propylene carbonate		65.0	5.20	15.1
Pyridine		12.4	2.23	33.1
Tetrahydrofuran		7.6	1.63	20.0
Water		78.5	1.87	18.0
				(33.0) ^a

^apredicted by ^{23}Na NMR.^bGas phase.

(Stohler Isotope Chemicals, SIC) and chloroform-d (Cambridge Isotope Laboratories) were used as received as external lock and reference in the proton and carbon-13 NMR studies.

**B. WATER DETERMINATION IN NONAQUEOUS
SOLVENTS BY GAS CHROMATOGRAPHY**

Water determinations were made using gas chromatography and the method of standard addition. In these determinations a Varian 920 Gas Chromatograph and a Sargent Welch Model SRG recorder was used. The Varian 920 GC has a thermal conductivity detector. Helium was used as the carrier gas instead of nitrogen because higher filament currents for the detector can be used when helium is the carrier gas (current limits are 150 mA with nitrogen as the carrier gas and 300 mA with helium). Consequently lower concentrations of water can be determined when helium is the carrier gas. A 5 foot x 1/4 inch copper column packed with 80/100 mesh Porapak QS was used to achieve separations. Porapak is the registered trademark for a porous polymer composed of ethylvinylbenzene cross-linked with divinylbenzene to form a uniform structure of a distinct pore size (178). Porapak QS is moderately polar and is stable to 250°C. At temperatures greater than 250°C the packing material begins to decompose. Porapak QS is useful for water

determinations due to the rapid elution of water and other highly polar molecules with little or no tailing.

A technique of standard addition was developed to determine the amount of water present in a nonaqueous solvent. In this method a "10000+x" ppm water stock solution is prepared by taking a 50 μ l aliquot of water and diluting to 5 ml with the solvent of interest. The "x" refers to the water already present in the nonaqueous solvent. This stock solution is then used to prepare spiked samples of 100, 200, and 300 ppm water. This is done by pipetting 50, 100, and 150 μ l aliquots of the stock solution into separate 5 ml volumetric flasks and diluting to volume with the solvent of interest. These samples, as well as an unspiked sample of solvent, are transferred into vials equipped with septa to avoid absorption of atmospheric water. It should be noted that these samples are prepared in glove bags under dry nitrogen.

In doing the analysis, the chromatographic parameters; i.e., column, detector, and injector temperatures and flow rate; must first be optimized to maximize separation. Once this is done 5 μ l aliquots of each sample are injected into the GC. Multiple injections are done to test reproducibility. This is followed by plotting peak height versus ppm water spiked. The plot should be linear and extrapolation to the x-intercept will

give the amount of water present in the solvent.

This method can be used for most solvents except for nitromethane, carbon tetrachloride, benzene and chloroform. In the case of nitromethane, a gas chromatographic method cannot be used since nitroalkanes decompose in the injector port. One of the products of decomposition has the same retention time as water which leads one to suspect that at high temperatures nitromethane decomposes to form water. In the case of carbon tetrachloride, benzene and chloroform, the solubility of water is not sufficient to prepare the "10000+x" ppm stock solution. However, gas chromatography can still be used to determine the amount of water in these solvents by comparing the peak height of the water in these solvents to the peak height of the water in another solvent which had previously been analyzed using the method of standard addition.

Recently an alternative GC method has been developed to determine the amount of water present in these solvents. The standard addition method presents a problem since it requires using 20 ml of solvent for the analysis and also it is tedious and time consuming. In this alternative method, the height of the water peak obtained for the solvent of interest is compared to the water peak obtained for carbon tetrachloride saturated with water. At 24°C, carbon tetrachloride contains 100 ppm water

(177). The amount of water present in the solvent of interest can be calculated using the following relationship:

$$\text{ppm}_{\text{H}_2\text{O}} = \frac{100 I_{\text{solvent}}}{I_{\text{CCl}_4}} \quad [1]$$

where I_{solvent} and I_{CCl_4} refer to the height of the water peak obtained in the solvent of interest and in carbon tetrachloride, respectively.

C. SAMPLE PREPARATION

The mixed solvent solutions were prepared by adding the desired volume of a given solvent A (with either a 10-100 μl or a 100-1000 μl Eppendorf digital micropipette with a continuously adjustable volume) to a weighed 2 ml flask, reweighing, diluting to volume with solvent B and weighing again. From weights, the number of moles of each solvent and resultant mole fraction are calculated.

The solutions for the ligand solvation studies were prepared by weighing out the desired amount of ligand into 2 ml volumetric flasks, diluting to volume with the solvent of interest and weighing again. A similar technique was used to prepare samples for the solvent-ligand complexation studies in an "inert" background solvent. In these studies, the desired amounts

of ligand were weighed out into 2 ml volumetric flasks. Into each of these samples the desired volume of complexing solvent was added with a 10-100 μ l Eppendorf digital micropipette and the samples were weighed. The samples were diluted to volume with the background solvent and weighed again.

Due to the hygroscopic nature of the nonaqueous solvents and of the reagents, all nonaqueous solutions were prepared in a glove bag under dry nitrogen atmosphere.

For DA18C6 samples requiring pH adjustment, all pH measurements were made with the Markson ElectroMark Analyzer ($\text{pH} \pm 0.01$). All readings were taken in pH units. An Orion combination pH electrode, gell-filled (model #91-05) was used. Prior to each run, the electrode was conditioned by soaking it in deuterated water overnight. After conditioning, the electrode and pH meter were calibrated using Fisher pH 4.00, 7.00, and 10.00 aqueous buffers. The pH of the solution of DA18C6 in deuterated water was adjusted by the addition of concentrated hydrochloric acid or 10% aqueous solution of tetramethylammonium hydroxide with a 10-100 μ l Eppendorf micropipette. Because small amounts of the acid and base were added to the sample during pH adjustment and because the concentration of ligand was relatively large to begin with, no corrections were made to compensate for any

changes in volume. At the desired pH, approximately 1 ml of sample was transferred to a 5 mm NMR tube and sealed.

D. NMR MEASUREMENTS

1. INSTRUMENTS. Proton NMR measurements were obtained on a Bruker WM-250 spectrometer operating at a field strength of 58.7 kG and a frequency of 250 MHz in the pulsed Fourier transform mode. Carbon-13 NMR measurements were also obtained on the Bruker WM-250 spectrometer operating at a field strength of 58.7 kG and a frequency of 62.9 MHz. An Aspect 2000 computer was used to carry out data manipulation.

2. REFERENCES AND CORRECTIONS. For the ^{13}C studies of mixed solvents, $\text{MeCN-C}_6\text{H}_6$, MeCN-CHCl_3 , $\text{DMF-C}_6\text{H}_6$, and $\text{MeNO}_2\text{-C}_6\text{H}_6$, acetone- d_6 was used as the lock and the methyl carbon resonance of acetone- d_6 was used as the external reference. Chloroform- d was used as both the lock and external reference for the $\text{MeCN-(Me)}_2\text{CO}$ and $(\text{Me})_2\text{CO-C}_6\text{H}_6$ systems. Sample solutions were placed in a 10 mm o.d. NMR tube and lock solvent was then placed in a 5 mm o.d. NMR tube which was then coaxially inserted into the sample tube with the aide of teflon spacers. A sealed coaxial insert of 0.28 mole fraction tetramethylsilane (TMS, Aldrich) in acetone- d_6 was used as the lock and external reference for the ^{13}C and ^1H studies of MeCN-CCl_4 , MeOH-CCl_4 and $\text{MeOH-C}_6\text{H}_6$ and MeCN-CHCl_3 systems.

In the proton NMR ligand solvation studies for DB18C6, B15C5 and tetraglyme, solutions of the ligand were prepared in the deuterated solvent of interest. This solution was then sealed in a 5 mm o.d. NMR tube. The proton resonances of the ligand were referenced to the internal residual resonance of the deuterated solvent. These resonances were then corrected to TMS. Table 10 tabulates the proton chemical shifts of the residual resonance of pertinent deuterated solvents relative to TMS. The carbon-13 NMR ligand solvation studies were done using the external referencing technique described previously.

In these studies, downfield chemical shifts are taken to be positive. Whenever an external reference was used, the chemical shifts were corrected for differences in bulk magnetic susceptibility between sample and reference according to the equations of Martin et al. (179). For a Fourier transform experiment utilizing a superconducting magnet, such as the WM-250:

$$\delta_{\text{CORR}} = \delta_{\text{OBS}} + \frac{4\pi}{3} (\chi_{\text{REF}} - \chi_{\text{SAMP}}) \quad [2]$$

where χ_{REF} and χ_{SAMP} are the unitless volumetric susceptibilities of the reference and sample, respectively, and δ_{CORR} and δ_{OBS} are the corrected and observed chemical shifts, respectively. In the mixed solvent studies the volumetric susceptibility of the

Table 10. Residual Absorption of Deuterated Solvents Relative to TMS.

SOLVENT	FORMULA	RESIDUAL ^1H NMR ABSORPTION (ppm from TMS)
Acetic acid- d_4	CD_3COOD	2.06, 12.0 ^a
Acetone- d_6	CD_3COCd_3	2.07
Acetonitrile- d_3	CD_3CN	1.96
Benzene- d_6	C_6D_6	7.24
Chloroform- d	CDCl_3	7.25
Deuterium oxide	D_2O	4.61
Dimethylformamide- d_7	$\text{DCON}(\text{CD}_3)_2$	2.79, 2.94, 7.90
Dimethylsulfoxide- d_6	CD_3SOCD_3	2.50
p-Dioxane- d_8	$\text{C}_4\text{D}_8\text{O}_2$	3.56
Methanol- d_4	CD_3OD	3.34, 4.1 ^a
Nitromethane- d_3	CD_3NO_2	4.29
Pyridine- d_5	$\text{C}_5\text{D}_5\text{N}$	7.0-7.8, 8.57
Tetrahydrofuran- d_8	$\text{C}_4\text{D}_8\text{O}$	1.6-2.0, 3.5-3.8

^aThese positions may vary considerably depending on temperature and solute.

solutions were calculated as follows (180):

$$x_{AB}^{CALC} = \left(\frac{V_A}{V_A + V_B} \right) x_A + \left(\frac{V_B}{V_A + V_B} \right) x_B \quad [3]$$

where x_{AB}^{CALC} , x_A and x_B are the volumetric susceptibilities of the solutions, solvent A and solvent B, respectively, and V_A and V_B are the volumes of solvent A and solvent B, respectively. These correction factors are on the order of 0.5 ppm.

3. DATA ACQUISITION AND SIGNAL PROCESSING. Table 11 shows some of the relevant physical properties relating to the ^{13}C and ^1H nuclei. From this table it can be seen that the major limitation to the ^{13}C NMR experiment is the low natural abundance of the ^{13}C isotope. There are, however, several methods by which one can obtain a reasonable signal, S, to noise, N, ratio. For example, large concentrations of complexing solvent and ligand can be used. Typically complexing solvent concentrations of 0.5 M were used in the crown-solvent complexation studies. Sensitivity enhancement was also achieved by signal averaging and exponential line broadening of the free induction decay, FID (181). Since the S/N ratio is proportional to $(n)^{\frac{1}{2}}$, where n is the number of transients scanned, the S/N ratio can be improved by increasing the number of scans. Exponential line broadening is the result of multiplying each point of the FID by a decaying

Table 11. Nuclear Properties Relating to ^{13}C and ^1H .

	^{13}C	^1H
Relative abundance (%)	1.11	99.98
Spin I (in multiples of $\hbar$)	1/2	1/2
Magnetic moment μ (in multiples of the nuclear magneton)	0.70216	2.7927
Larmor frequency ν_0 (at 23.4 kG)	25.2 MHz	100 MHz
Relative sensitivity for equal number of nuclei	1/64	1
Relative sensitivity at natural abundance	1/5800	1

exponential, $\exp(-t/a)$ whose positive time constant, a , matches the apparent FID $T_2^\bullet$. This convolution process introduces line broadening of $(-\pi a)^{-1}$ and the time constant of the exponential is generally entered in as a broadening factor (in Hz). For carbons bonded to protons, sensitivity enhancement of the ^{13}C NMR signal can be achieved by noise decoupling at the ^1H frequency. The carbon-13 nucleus (182) has a nuclear Overhauser effect, NOE, of approximately 3. By decoupling the protons, the signals of most carbons experience an additional threefold enhancement due to the NOE.

To increase digital resolution the zero filling technique was employed (181). In general, one collects an N-point FID and then adds 2-4 N zeroes to the end of the FID before Fourier transformation. This allows an increase in the point to point resolution without distorting the lineshape. Resolution enhancement can also be achieved by Gaussian multiplication; i.e., the FID is multiplied by a weighting binomial exponential function, $\exp(-at-bt^2)$ (181). Such a function improves resolution by artificially narrowing the lines. However, a good signal-to-noise ratio is necessary since Gaussian multiplication generally decreases the signal intensity.

4. EVALUATION OF EQUILIBRIA CONSTANTS. In the systems under investigation, multiple equilibria occur. For a system in fast exchange, the carbon-13 observed

chemical shift, δ_{OBS} , is a population weighted average of the chemical shifts of the individual species, δ_i , occurring in solution:

$$\delta_{\text{OBS}} = \sum_i \delta_i x_i \quad [4]$$

where x_i is the fraction of the i^{th} species. These fractions depend upon the values of the equilibria constants and on analytical concentrations. An expression for the observed chemical shift can, therefore, be derived so as to include the equilibria constants. Then the equilibria constants are adjusted using a weighted, nonlinear least squares program KINFIT (183) until the difference between the experimental and calculated chemical shifts is minimized. The equations and subroutines used are discussed in more detail in Appendix I.

E. IR MEASUREMENTS

Infrared measurements for the AN-CCl₄ study were carried out on a Beckman IR-12 grating Spectrophotometer. The spectra were obtained at a nominal resolution of either 2 or 4 cm⁻¹. A standard demountable Barnes liquid cell with potassium bromide salt plates and a 0.5 mm path length was used. In these studies the 4000-2000 cm⁻¹ spectral region was covered.

For the solvent-ligand complexation studies, infrared

measurements were made on either a Digilab 15 FT-IR Spectrometer with a Data General computer or a Bomem DA3 Series Laboratory Interferometer Spectrometer System with an RSX operating system and PDP-11 computer. Both instruments have interferometers and utilize a global source and a detector cooled by liquid nitrogen. Both instruments are capable of signal averaging and background subtraction. The spectra were obtained at a resolution of 1 cm^{-1} . Standard demountable cells (Barnes Engineering Co.) were used with either Irtran-II or calcium fluoride salt plates since crown ethers attack potassium bromide windows. The path length used was 0.5 mm for the Irtran-II windows and 0.2 mm for the calcium fluoride windows. The spectral region studied was $4000\text{--}800 \text{ cm}^{-1}$ for the Irtran-II and $4000\text{--}900 \text{ cm}^{-1}$ for the calcium fluoride. In the solvent-ligand complexation studies, the background solvent was subtracted out.

In the studies of the complexation of acetonitrile- d_3 with 18C6 in CCl_4 and CHCl_3 solution, it was found that the CN-stretching vibration, ν_2 , is a composite band. The deconvolution of overlapping bands was carried out by assuming that the lineshape of the bands can be described by a Lorentzian-Gaussian product (184):

$$I = I_0 \left\{ \exp[-(\nu - \nu_0)^2 / 2\sigma^2] \right\} \left\{ 1 + (\nu - \nu_0)^2 / \sigma^2 \right\}^{-1} \quad [5]$$

where I is an intensity (in absorbance units) at frequency

ν ; ν_0 is the position of the line center with maximum intensity I_0 ; and σ is the variance ($\sigma = 1.46 \Delta\nu_{\frac{1}{2}}$ where $\Delta\nu_{\frac{1}{2}}$ is the band halfwidth). The Gaussian portion of equation [5] takes into account Doppler broadening (185) of the natural linewidth. Doppler broadening is caused by the fact that a chemical species is observed while moving rapidly toward or away from the observer. The Lorentzian portion of equation [5] takes into account collisional broadening of the natural linewidth. Collisional broadening is caused by collision of the absorbing species with a foreign species (Lorentz broadening) or with the same type of absorbing species (Holtsmark broadening). In the solution phase, collisional broadening outweighs Doppler broadening. After deconvolution the areas under the bands were evaluated using Simpson's rule. The subroutine used is discussed in more detail in Appendix II.

F. VISCOSITY MEASUREMENTS

Figure 12 shows the viscometer arrangement used to measure the viscosity of 18C6 solutions. Ten milliliter solutions of 18C6 in water, acetonitrile and carbon tetrachloride at various concentrations were prepared and their viscosities measured using the Canon-Fenske viscometers. The size 25 and 75 viscometers were used (size 25 is good for the 0.5 to 2.0 centistoke range

whereas size 75 is good for the 1.6 to 8.0 centistoke range). For these experiments the water bath was equilibrated at $26.00 \pm 0.02^{\circ}\text{C}$. The viscometer was mounted vertically in the constant-temperature bath so that both fiducial marks were visible and below the water level. The solution was transferred into the viscometer and was allowed to equilibrate for 20 minutes. In measuring the viscosity of the solution, the solution was drawn up to a point well above the upper fiducial mark by suction through a tygon tube. The suction was released and the flow time between the upper and lower marks was measured with a stopwatch.

For a given volume of liquid, we have the following relationship (186):

$$\eta/\rho = Bt - \frac{V}{8\pi Lt} \quad [6]$$

where η is the viscosity of the solution; ρ is the density of the solution; t is the time required for the upper meniscus to fall from the upper to the lower fiducial mark, a to b (refer to Figure 12), B is an apparatus constant which must be determined through calibration with a liquid of known viscosity, L is the length of the tube, and V is the total volume. The second term in equation [6], $V/(8\pi Lt)$, corrects for the kinetic energy. Since it is usually less than 1% of Bt , it was neglected in this

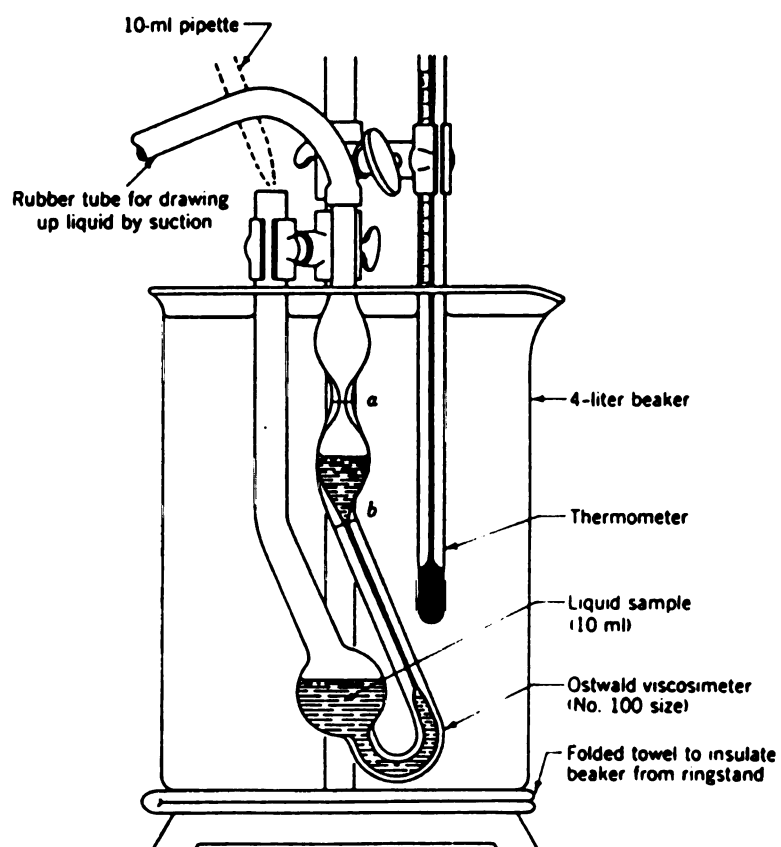


Figure 12. Viscosimeter arrangement used.

work. Therefore, equation [6] simplifies to:

$$\eta / \rho = Bt \quad [7]$$

It was also assumed that,

$$\rho_{\text{soln}} \approx \rho_{\text{solvent}} \quad [8]$$

This assumption is valid for low concentrations. The apparatus constant, B, was determined for each solvent.

CHAPTER III

SPECTROSCOPIC STUDIES
OF SOLVENT MIXTURES

A. INTRODUCTION

Previous solution studies of the complexation of crown ethers by neutral molecules were carried out in an "inert" background solvent. However, solvents are never completely "inert". Dipole-dipole interactions, as well as London, or dispersion forces can occur in solution. The extent of such interactions depends upon the background solvent used. Prior to studying the complexation of the crown ethers, spectroscopic techniques were used to study the mixed solvent systems.

B. RESULTS AND DISCUSSION

1. ACETONITRILE IN CARBON TETRACHLORIDE. Figure 13 shows a plot of the carbon-13 chemical shifts, δ , of MeCN and CCl_4 as a function of mole fraction of acetonitrile, X_{AN} . It can be seen that the concentration dependence of the ^{13}C resonance of the methyl group of MeCN in CCl_4 solutions parallels that of the carbon atom of CCl_4 and may indicate an interaction between the two species. The behavior of the nitrile carbon is quite different and suggests self-association of acetonitrile. This is to be expected since the dipole moment of MeCN is centered on the nitrile group. Closer inspection of the ^{13}C chemical shift behavior of the methyl carbon of MeCN and the carbon of CCl_4 shows that the curve for the methyl carbon bends toward the concentration axis at $X \approx 0.8$ whereas the CCl_4

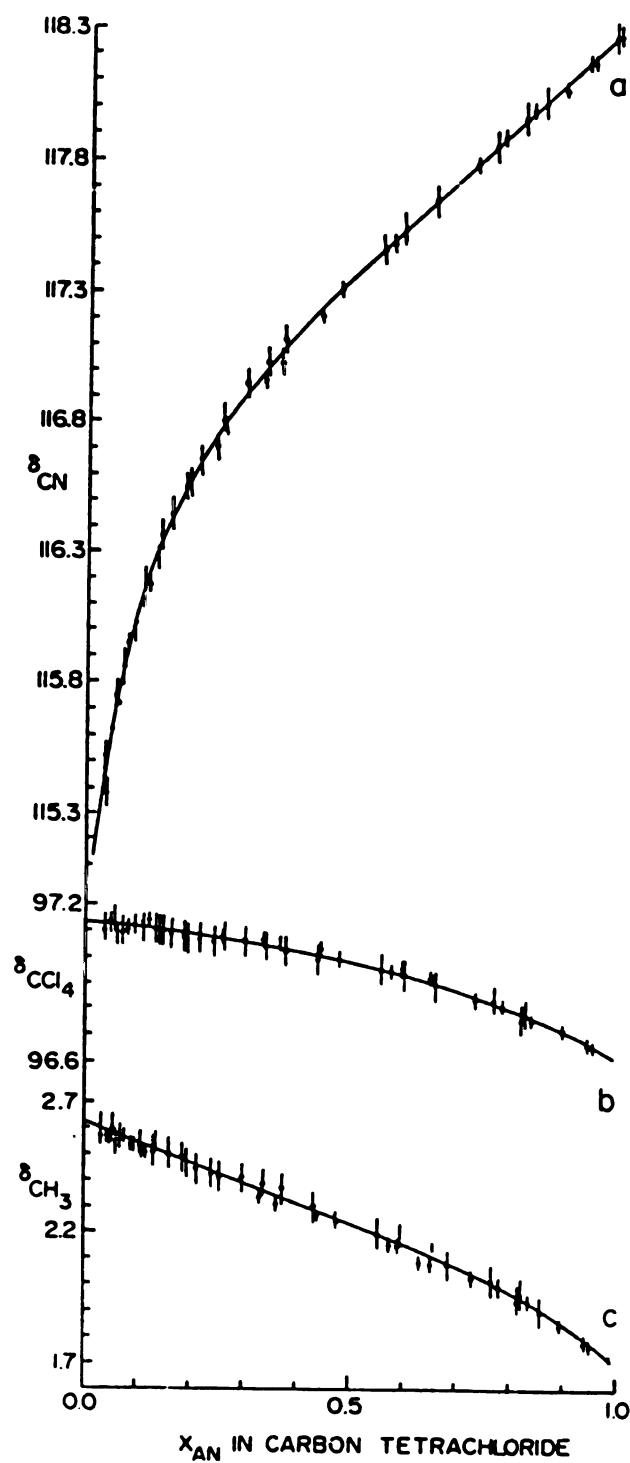


Figure 13. Plots of the carbon-13 chemical shifts of acetonitrile and carbon tetrachloride as a function of mole fraction of AN.

curve bends at $X \approx 0.5$. This suggests that the ^{13}C resonance of the methyl carbon is influenced by both the self-association of MeCN and the interaction with CCl_4 .

The chemical shift behavior of the carbons of acetonitrile and the carbon of CCl_4 must be explained by the same set of equilibria. The chemical shift data were analyzed by using the KINFIT program and multiple data sets. Various models were used to analyze the ^{13}C chemical shift data of acetonitrile: (1) dimerization of acetonitrile only, (2) dimerization of acetonitrile and formation of a 1:1 MeCN- CCl_4 complex and (3) dimerization of acetonitrile, formation of a 1:1 MeCN- CCl_4 complex and formation of a 2:1 MeCN- CCl_4 complex. The equations and subroutines used are shown and discussed in Appendix I. Figures 14-16 show graphical plots obtained from KINFIT for the three models attempted. From these plots it can be seen that the third model gives the best agreement with the observed chemical shift behavior of acetonitrile. In this model, the nitrile carbon of the S_2 and S_2C species, (where S refers to MeCN and C to CCl_4), are assumed to be equal as are the chemical shifts of the S and SC species. This is not an unreasonable assumption since the nitrile carbon is separated by three bonds from the site of interaction between the methyl group and carbon tetrachloride. It was further assumed that the chemical shift of the nitrile group at infinite dilution is equal

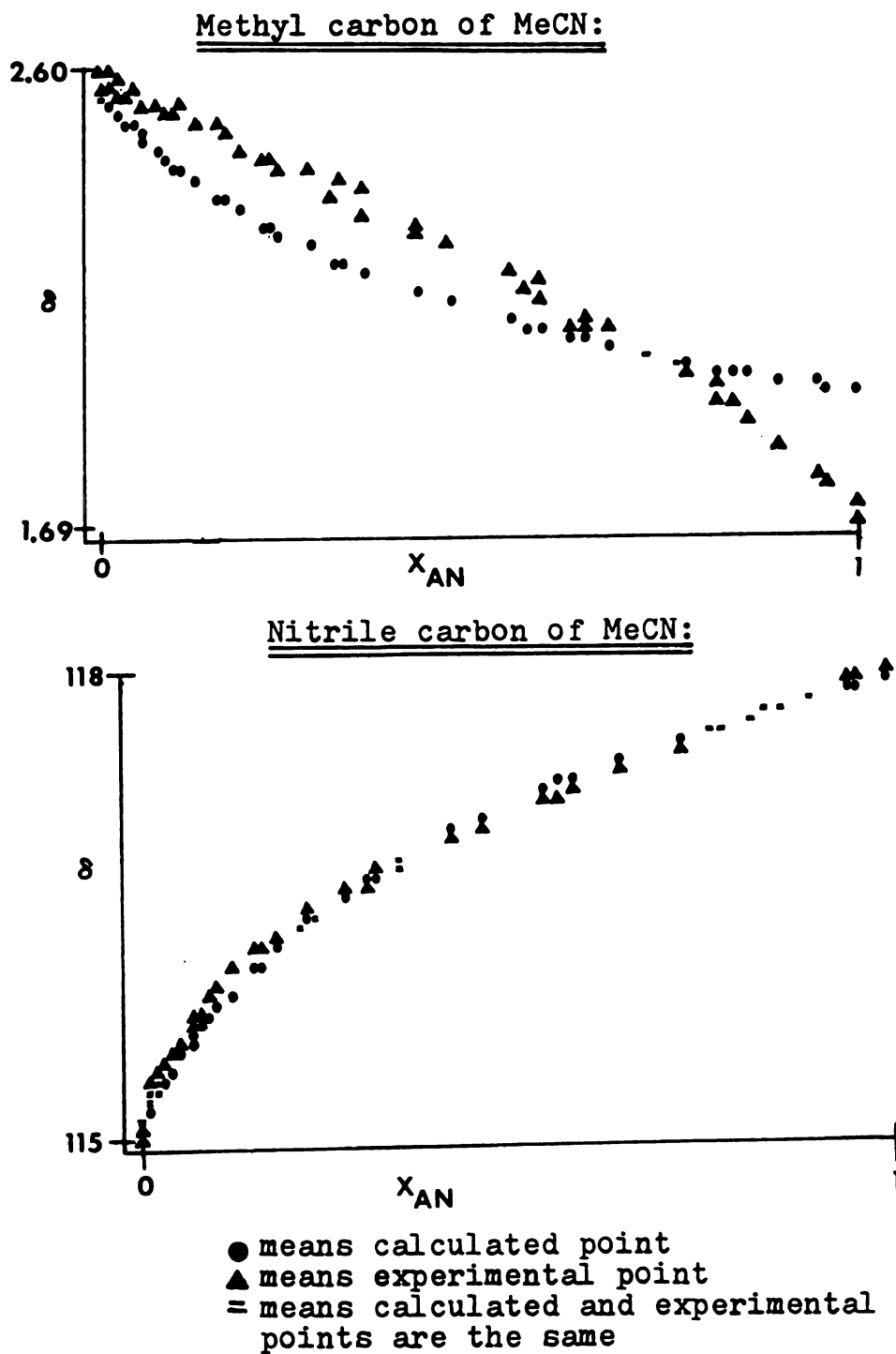
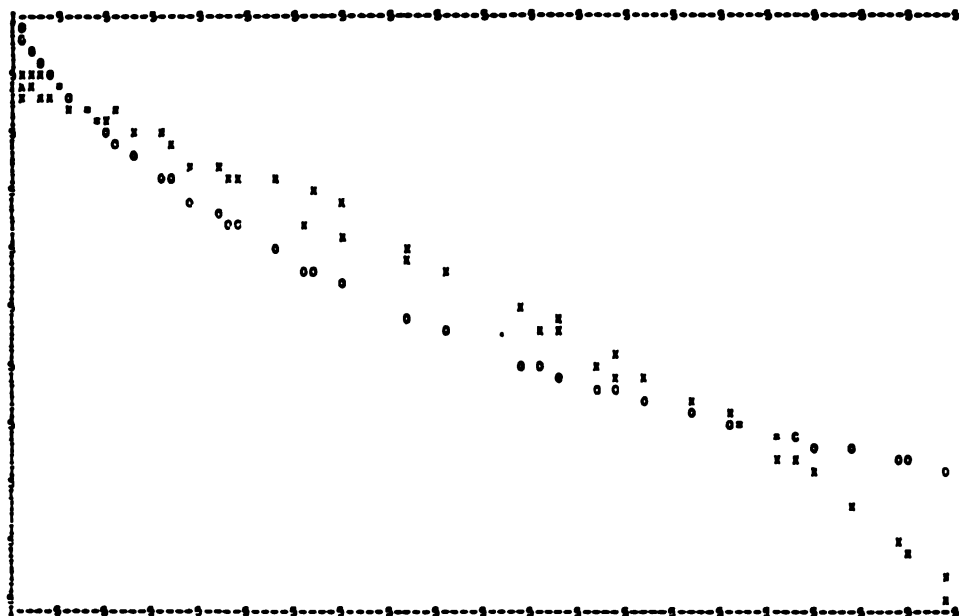


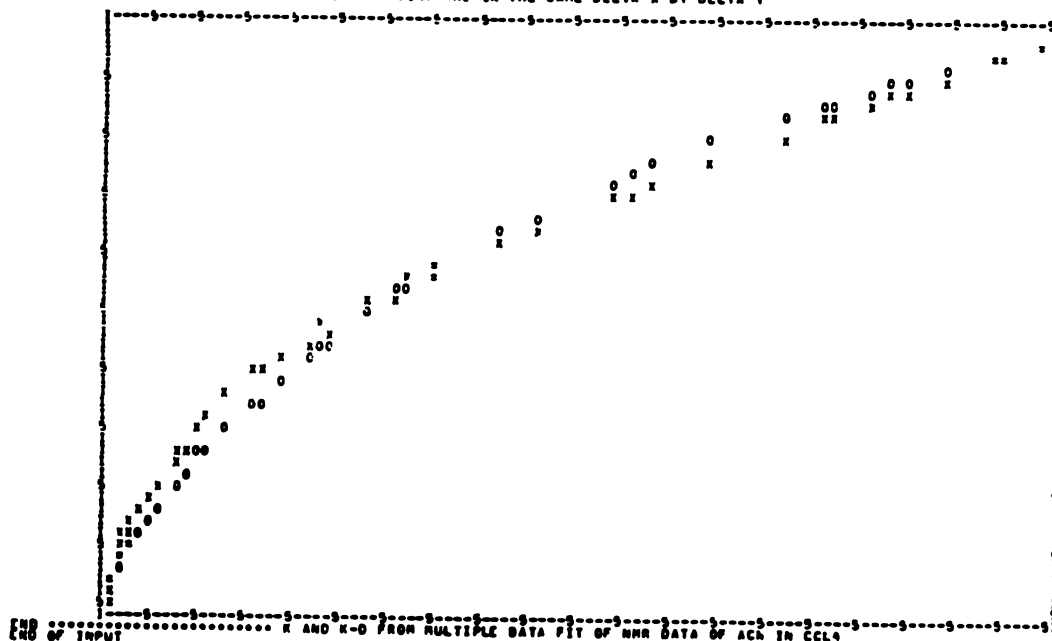
Figure 14. KINFIT outputs obtained from a multiple data fit of the MeCN-CCl₄ system. Model included dimerization of acetonitrile.

Methyl carbon of MeCN:

DATA SET NUMBER 1
 ACROSS IS 111.11 ON RESID. VALUE AT THE LEFT = .220E-01, VALUE AT THE RIGHT = .180E-01, INCREMENT = .077E-02
 VERTICAL IS 111.11 ON RESID. VALUE AT THE TOP = .067E-01, VALUE AT THE BOTTOM = .160E-01, INCREMENT = .083E-01
 * MEANS AN EXPERIMENTAL POINT, * MEANS A CALCULATED POINT (ONLY * IS USED WHEN RESID IS PLOTTED)
 * MEANS AN EXPERIMENTAL AND CALCULATED POINT ARE IN THE SAME DELTA X BY DELTA Y

Nitrile carbon of MeCN:

DATA SET NUMBER 2
 ACROSS IS 111.11 ON RESID. VALUE AT THE LEFT = .130E-01, VALUE AT THE RIGHT = .180E-01, INCREMENT = .077E-02
 VERTICAL IS 111.11 ON RESID. VALUE AT THE TOP = .110E-01, VALUE AT THE BOTTOM = .160E-01, INCREMENT = .083E-01
 * MEANS AN EXPERIMENTAL POINT, * MEANS A CALCULATED POINT (ONLY * IS USED WHEN RESID IS PLOTTED)
 * MEANS AN EXPERIMENTAL AND CALCULATED POINT ARE IN THE SAME DELTA X BY DELTA Y

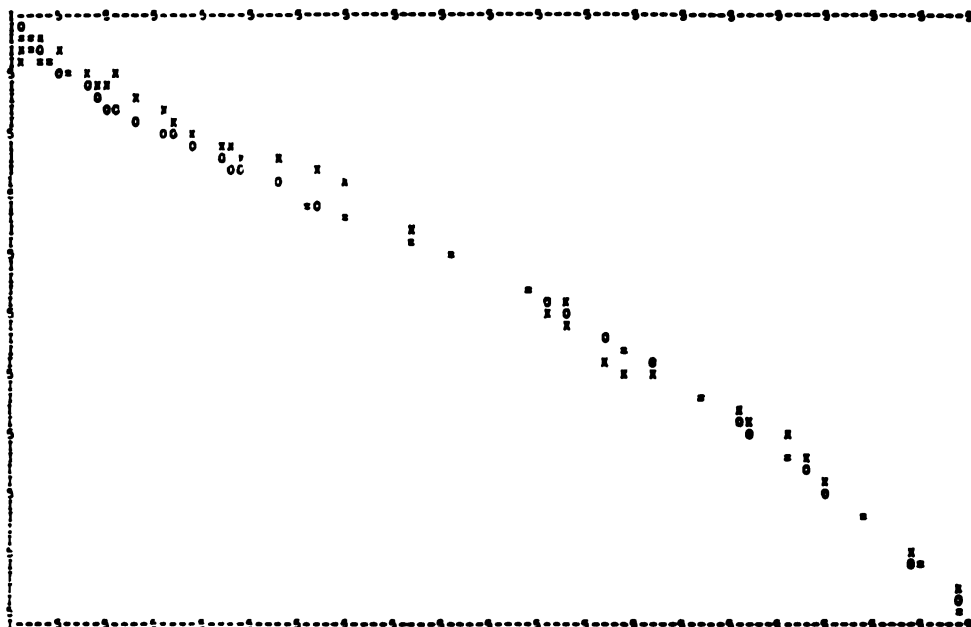


END OF INPUT K AND K-O FROM MULTIPLE DATA FIT OF MNR DATA OF ACK IN CCL4

Figure 15. KINFIT outputs obtained from a multiple data fit of the MeCN-CCl₄ system. Model included formation of S₂ and SC.

Methyl carbon of MeCN:

ACROSS IS 141.11 OR RESID. VALUE AT THE LEFT = .324E-01, VALUE AT THE RIGHT = .150E-01, INCREMENT = .977E-02
 VERTICAL IS 112.11 OR RESID. VALUE AT THE TOP = .268E-01, VALUE AT THE BOTTOM = .164E-01, INCREMENT = .104E-01
 X MEANS AN EXPERIMENTAL POINT, O MEANS A CALCULATED POINT (ONLY X IS USED WHEN RESID IS PLOTTED)
 * MEANS AN EXPERIMENTAL AND CALCULATED POINT ARE IN THE SAME DELTA X / DELTA Y

Nitrile carbon of MeCN:

DATA SET NUMBER 2
 ACROSS IS 141.11 OR RESID. VALUE AT THE LEFT = .324E-01, VALUE AT THE RIGHT = .150E-01, INCREMENT = .977E-02
 VERTICAL IS 112.11 OR RESID. VALUE AT THE TOP = .268E-01, VALUE AT THE BOTTOM = .164E-01, INCREMENT = .104E-01
 X MEANS AN EXPERIMENTAL POINT, O MEANS A CALCULATED POINT (ONLY X IS USED WHEN RESID IS PLOTTED)
 * MEANS AN EXPERIMENTAL AND CALCULATED POINT ARE IN THE SAME DELTA X / DELTA Y

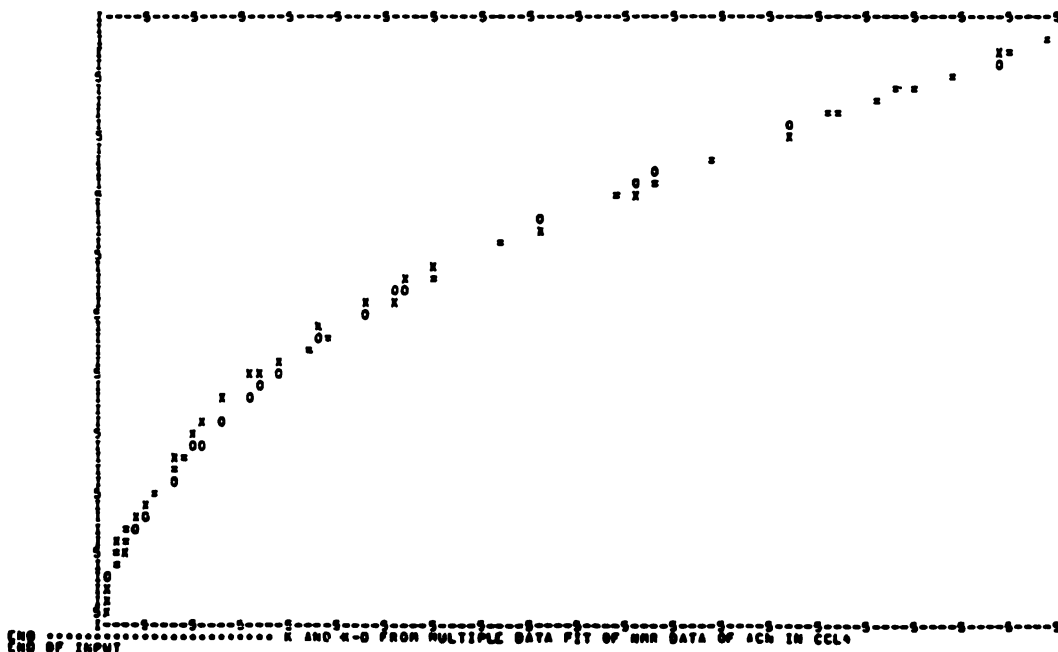


Figure 16. KINFIT outputs obtained from a multiple data fit of the MeCN-CCl₄ system. Model included formation of S₂, SC and S₂C.

to the chemical shift of the S and SC species. The chemical shifts of the methyl carbon were considered to be different for each of the species occurring in solution and the chemical shift at infinite dilution is equal to the chemical shift of the SC species. The equilibrium constants obtained for the third model were used to computer analyze the carbon-13 chemical shift data of CCl_4 . The chemical shifts of the carbon of CCl_4 were also considered to be different for each of the species occurring in solution. The fit is shown in Figure 17. This model also adequately describes the carbon-13 chemical shift behavior of CCl_4 .

The equilibrium constants, in both molarity and mole fraction units, obtained from the computer analysis, are tabulated in Table 12. The uncertainties for these equilibria constants are fairly large since seven unknown parameters were obtained simultaneously. However, these results indicate that the self association of acetonitrile is the dominant reaction. These results are in agreement with vapor pressure data for the MeCN-CCl_4 system which forms a low-boiling azeotrope (39) at 45.00°C (boiling points of CCl_4 and MeCN are 76.65°C and 81.57°C , respectively). The formation of low boiling azeotropes results when the cohesive forces between unlike components are smaller than those within the pure liquids (191). Therefore, in the MeCN-CCl_4 system, the MeCN-MeCN

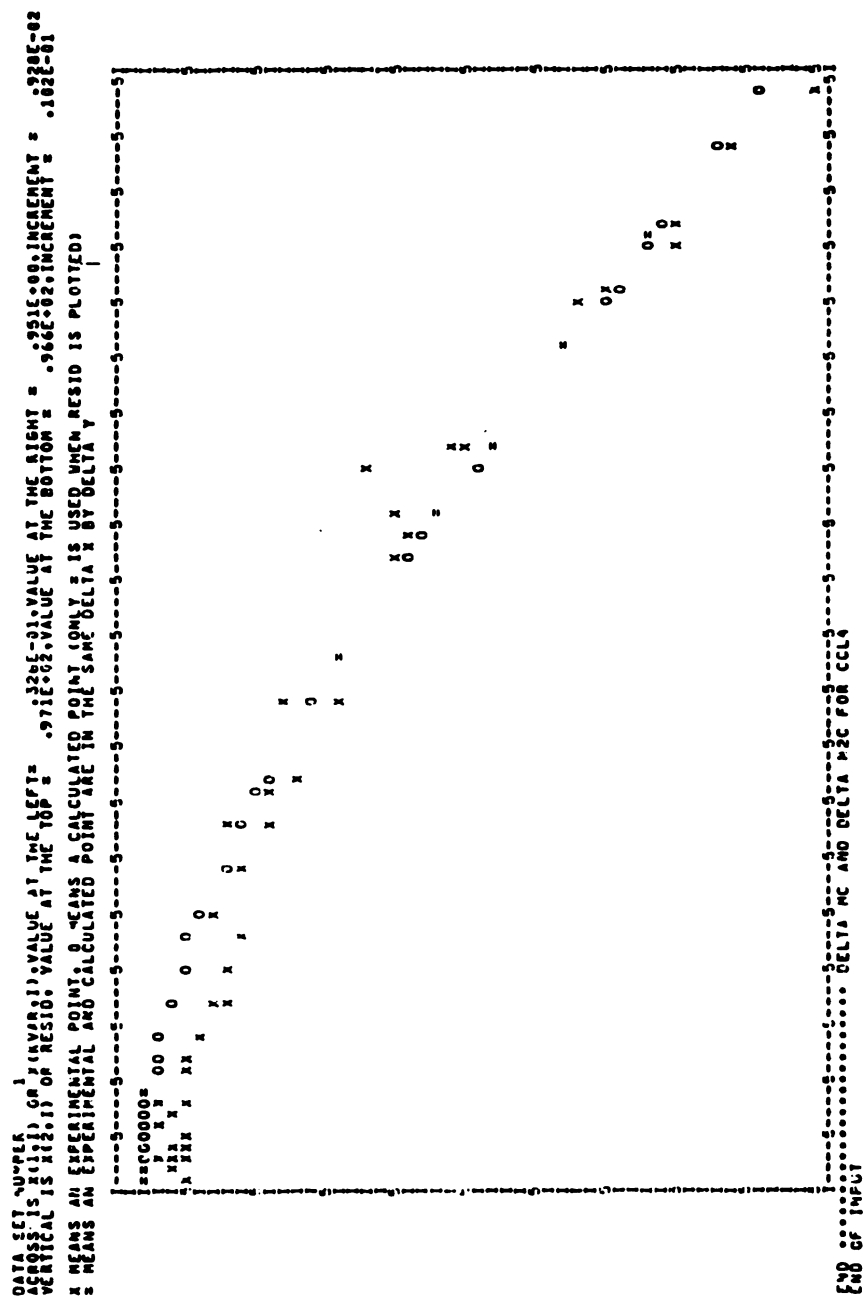


Figure 17. KINFIT output obtained for the computer analysis of the carbon of CCl_4 . Model included formation of S_2 , SC and S_2C .

Table 12. Equilibrium Constants for Solvent-Solvent Interactions.

SOLVENT SYSTEM	EQUILIBRIA	EQUILIBRIUM CONSTANTS (l mol ⁻¹)	EQUILIBRIUM CONSTANTS (m.f. ⁻¹)	¹³ C CHEMICAL SHIFT (ppm.)
MeCN-CCl ₄	$2S \xrightleftharpoons{K_{S_2}} S_2$	$K_{S_2} = 0.56 \pm 0.27$	$K_{S_2} = 5.7 \pm 2.7$	$\delta_S^{CH_3} = 2.75 \pm 0.07$
	$S + C \xrightleftharpoons{K_{SC}} SC$	$K_{SC} = 0.28 \pm 0.07$	$K_{SC} = 2.8 \pm 0.7$	$\delta_{SC}^{CH_3} = 2.63$
	$SC + S \xrightleftharpoons{K_{S_2C}} S_2C$	$K_{S_2C} = 0.56 \pm 0.22$	$K_{S_2C} = 5.7 \pm 2.2$	$\delta_{S_2}^{CH_3} = 1.3 \pm 0.1$
	$S_2 + C \xrightleftharpoons{K_{S_2C}} S_2C$	$K_{S_2C} = 0.28 \pm 0.06$	$K_{S_2C} = 2.8 \pm 0.6$	$\delta_{S_2C}^{CH_3} = 2.2 \pm 0.1$
				$\delta_S^{CN} = \delta_{SC} = 115.23$
				$\delta_{S_2}^{CN} = \delta_{S_2C} = 119.2 \pm 0.3$
				$\delta_C^{CCl_4} = 97.14$
				$\delta_{SC}^{CCl_4} = 97.24 \pm 0.06$
				$\delta_{S_2C}^{CCl_4} = 95.79 \pm 0.06$

^aChemical shifts are reported relative to TMS in acetone-d₆.

Table 12. Continued.

SOLVENT SYSTEM	EQUILIBRIA	EQUILIBRIUM CONSTANTS (l mol ⁻¹)	EQUILIBRIUM CONSTANTS (m.f. ⁻¹)	¹³ C CHEMICAL SHIFT (ppm.)
MeCN-C ₆ H ₆	$2S \xrightleftharpoons{K_{S_2}} S_2$	$K_{S_2} = 0.0224 \pm 0.0007$	$K_{S_2} = 0.263 \pm 0.008$	^b $\delta_{S_2}^{CH_3} = -29.54$ $\delta_{S_2}^{CH_3} = -24.1 \pm 0.1$ $\delta_{S_2}^{CN} = 86.20$ $\delta_{S_2}^{CN} = 94.1 \pm 0.3$
MeNO ₂ -C ₆ H ₆	$2S \xrightleftharpoons{K_{S_2}} S_2$	$K_{S_2} = 0.0205 \pm 0.0008$	$K_{S_2} = 0.232 \pm 0.009$	^b $\delta_{S_2} = 31.49$ $\delta_{S_2} = 37.7 \pm 0.2$
AC-C ₆ H ₆	$2S \xrightleftharpoons{K_{S_2}} S_2$	$K_{S_2} = 0.038 \pm 0.002$	$K_{S_2} = 0.43 \pm 0.02$	^c $\delta_{S_2}^{CO} = 125.73$ $\delta_{S_2}^{CO} = 131.2 \pm 0.1$

^bChemical shifts are reported relative to the methyl carbon of acetone-d₆.^cChemical shifts are reported relative to chloroform-d.

Table 12. Continued.

SOLVENT SYSTEM	EQUILIBRIA	EQUILIBRIUM CONSTANTS (l mol ⁻¹)	EQUILIBRIUM CONSTANTS (m.f. ⁻¹)	¹³ C CHEMICAL SHIFT (ppm.)
MeCN-CHCl ₃	$2S \xrightleftharpoons[K_{S_2}]{K_{S_2}} S_2$	$K_{S_2} = 1.7 \pm 0.5$	$K_{S_2} = 21 \pm 6$	$\delta_S = 2.98 \pm 0.05$ ^a
	$S + C \rightleftharpoons SC$	$K_{SC} = 0.71 \pm 0.02$	$K_{SC} = 8.8 \pm 0.2$	$\delta_{SC} = 2.80$
	$S_2 + C \xrightleftharpoons[K_{S_2C}]{K_{S_2C}'} S_2C$	$K_{S_2C}' = 0.0064 \pm 0.0056$	$K_{S_2C}' = 0.08 \pm 0.07$	$\delta_{S_2C} = 35 \pm 25$
	$SC + S \xrightleftharpoons[K_{S_2C}]{K_{S_2C}''} S_2C$	$K_{S_2C}'' = 0.015 \pm 0.014$	$K_{S_2C}'' = 0.19 \pm 0.18$	$\delta_{S_2C} = 1.44 \pm 0.04$
	$2C \xrightleftharpoons[K_{C_2}]{K_{C_2}} C_2$	$K_{C_2} = 0.13 \pm 0.04$	$K_{C_2} = 1.6 \pm 0.5$	$\delta_{CN} = 117.73 \pm 0.08$
				$\delta_S = 117.20$
				$\delta_{SC} = 118.0 \pm 0.2$
				$\delta_{S_2} = 125 \pm 8$
				$\delta_{S_2C} = 82.4 \pm 0.7$
				$\delta_{CHCl_3} = 79.11$
				$\delta_{SC} = -16 \pm 64$
				$\delta_{S_2C} = 75.0 \pm 0.4$

Table 12. Continued.

SOLVENT SYSTEM	EQUILIBRIA	EQUILIBRIUM CONSTANTS (l mol ⁻¹)	EQUILIBRIUM CONSTANTS (m.f. ⁻¹)	¹³ C CHEMICAL SHIFT (ppm.)
DMF-C ₆ H ₆	$2S \xrightleftharpoons{K_{S_2}} S_2$	$K_{S_2} = 0.036 \pm 0.002$	$K_{S_2} = 0.41 \pm 0.02$	$\alpha\text{CH}_3 = 1.02^b$ $\delta_S = 1.02$ $\alpha\text{CH}_3 = 2.15 \pm 0.04$ δ_{S_2} $\beta\text{CH}_3 = 5.40$ δ_S $\beta\text{CH}_3 = 8.8 \pm 0.1$ δ_{S_2} $\text{CO} = 131.99$ δ_S $\text{CO} = 135.6 \pm 0.1$ δ_{S_2}

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^aChemical shifts are reported relative to TMS in acetone-d₆.^bChemical shifts are reported relative to the methyl carbon of acetone-d₆.

interactions are stronger than the MeCN-CCl₄ interactions.

Using the equilibrium constants obtained from the carbon-13 NMR chemical shift data of the MeCN-CCl₄ system, an alpha (α) plot was constructed, where α_i is the concentration of the i^{th} species divided by the total concentration. From the alpha plot, shown in Figure 18, it can be seen that the maximum alpha value for SC occurs at $X_{AN}=0.4$ (the azeotrope occurs at $X_{AN}=0.41$ (39)). Based on these results it is possible to suggest probable structures for the S₂, SC and S₂C species. These structures are shown in Figure 19.

Infrared spectra were obtained for solutions of acetonitrile in CCl₄. Figures 20 and 21 show ν_1 , the C-H stretch between 2960-2940 cm⁻¹, and ν_2 , the C-N stretch between 2270-2250 cm⁻¹, as a function of the mole fraction of the solute. Both of these vibrations have A_{1g} symmetry. The changes observed for ν_1 and ν_2 as a function of acetonitrile concentration, therefore, must be due to different species arising from the MeCN-MeCN and MeCN-CCl₄ interactions occurring in solution. This is in agreement with the Raman studies done by Whittenberg and Wang (192) and Yarwood, et al. (31).

2. ACETONITRILE IN BENZENE. Figure 21 shows a plot of the carbon-13 chemical shifts of MeCN and C₆H₆ as a function of the mole fraction of acetonitrile, X_{AN} . In benzene solutions, the chemical shifts for the methyl and

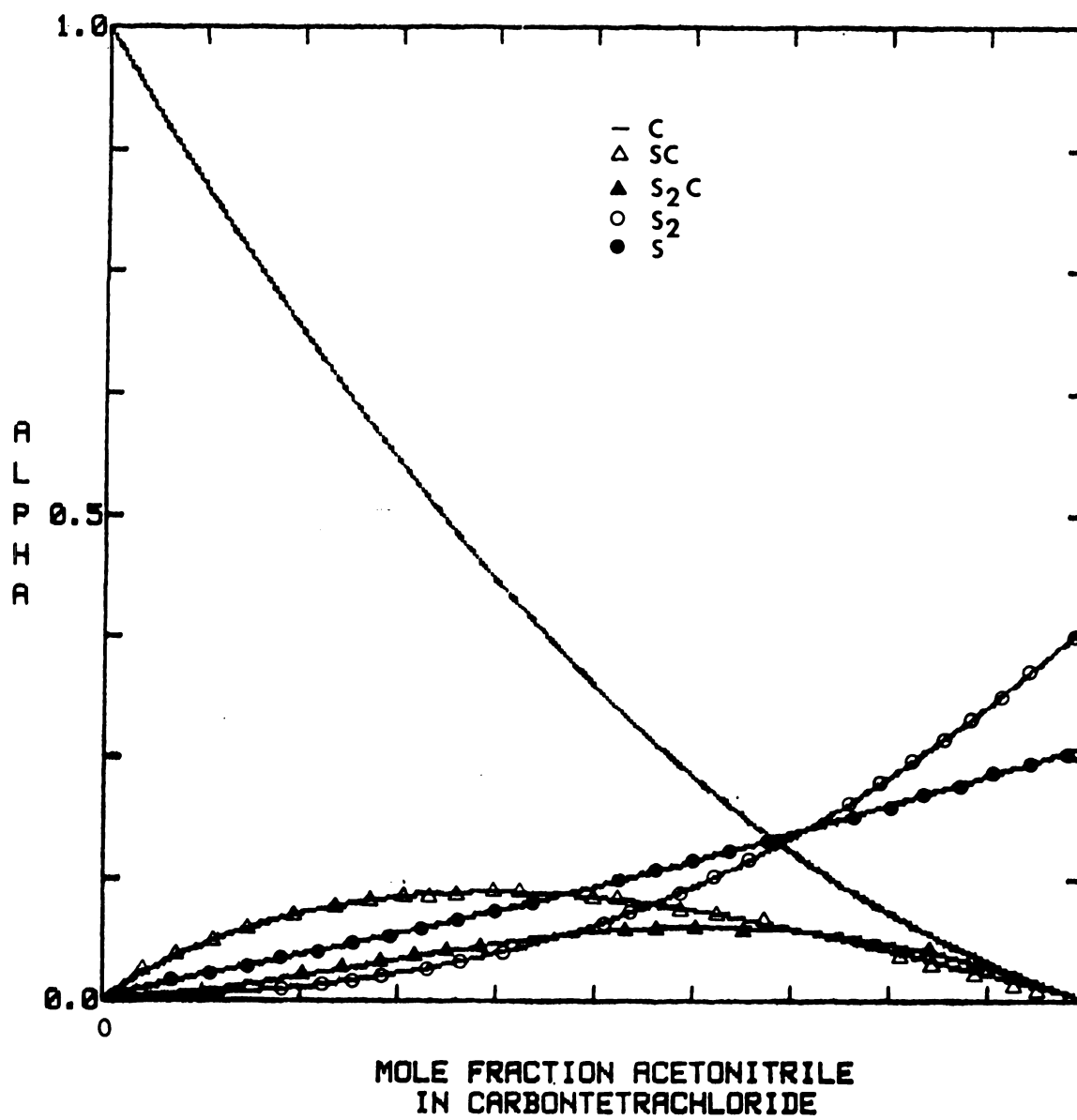


Figure 18. Alpha plots of the MeCN-CCl₄ system.

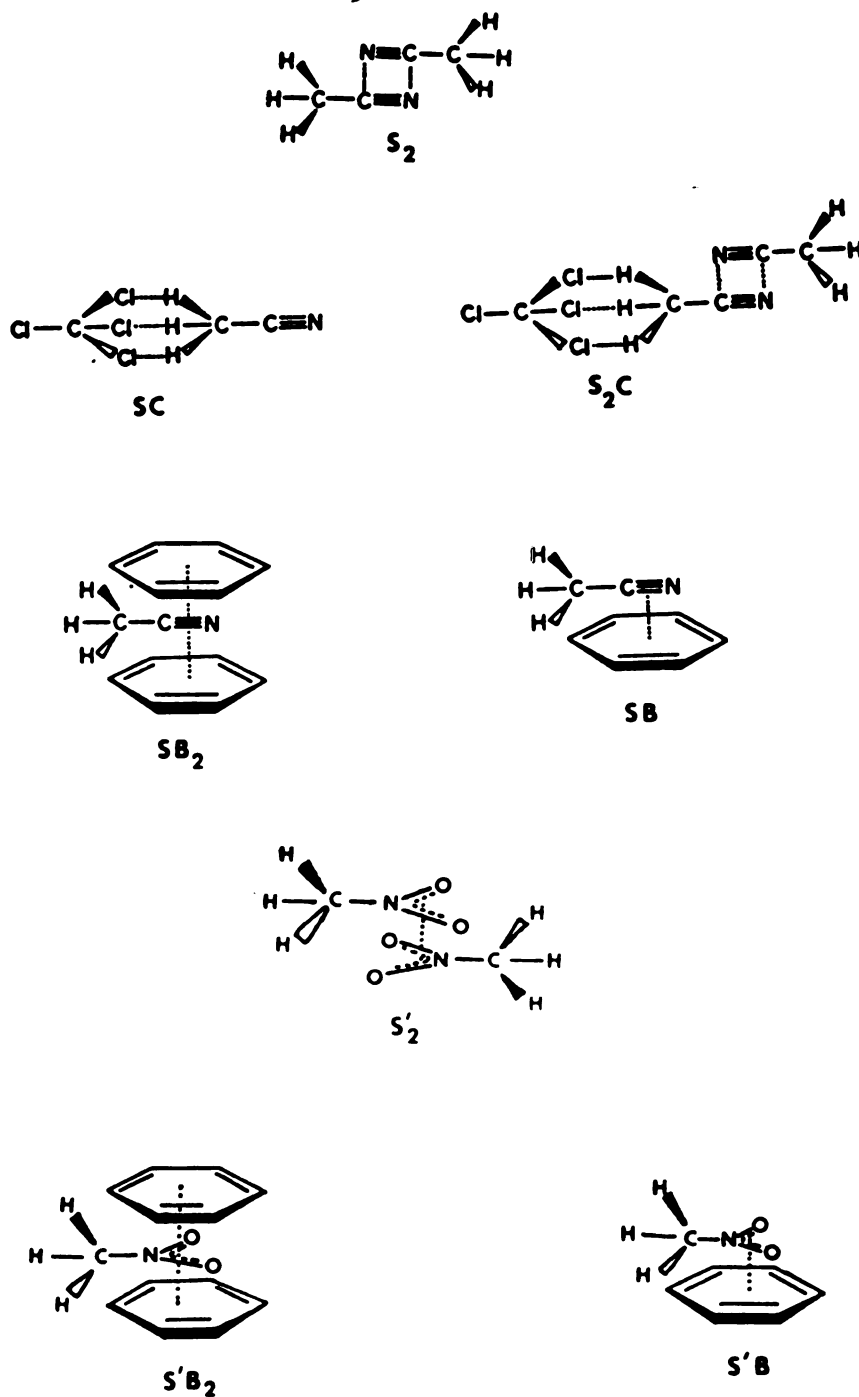


Figure 19. Structures proposed for the AN dimer, S_2 ; $CCl_4 \cdot CH_3CN$, SC ; $CCl_4 \cdot (CH_3CN)_2$, S_2C ; $C_6H_6 \cdot CH_3CN$, SB ; $(C_6H_6)_2 \cdot CH_3CN$, SB_2 ; the NM dimer, S'_2 ; $C_6H_6 \cdot CH_3NO_2$, $S'B$; and $(C_6H_6)_2 \cdot CH_3NO_2$, $S'B_2$.

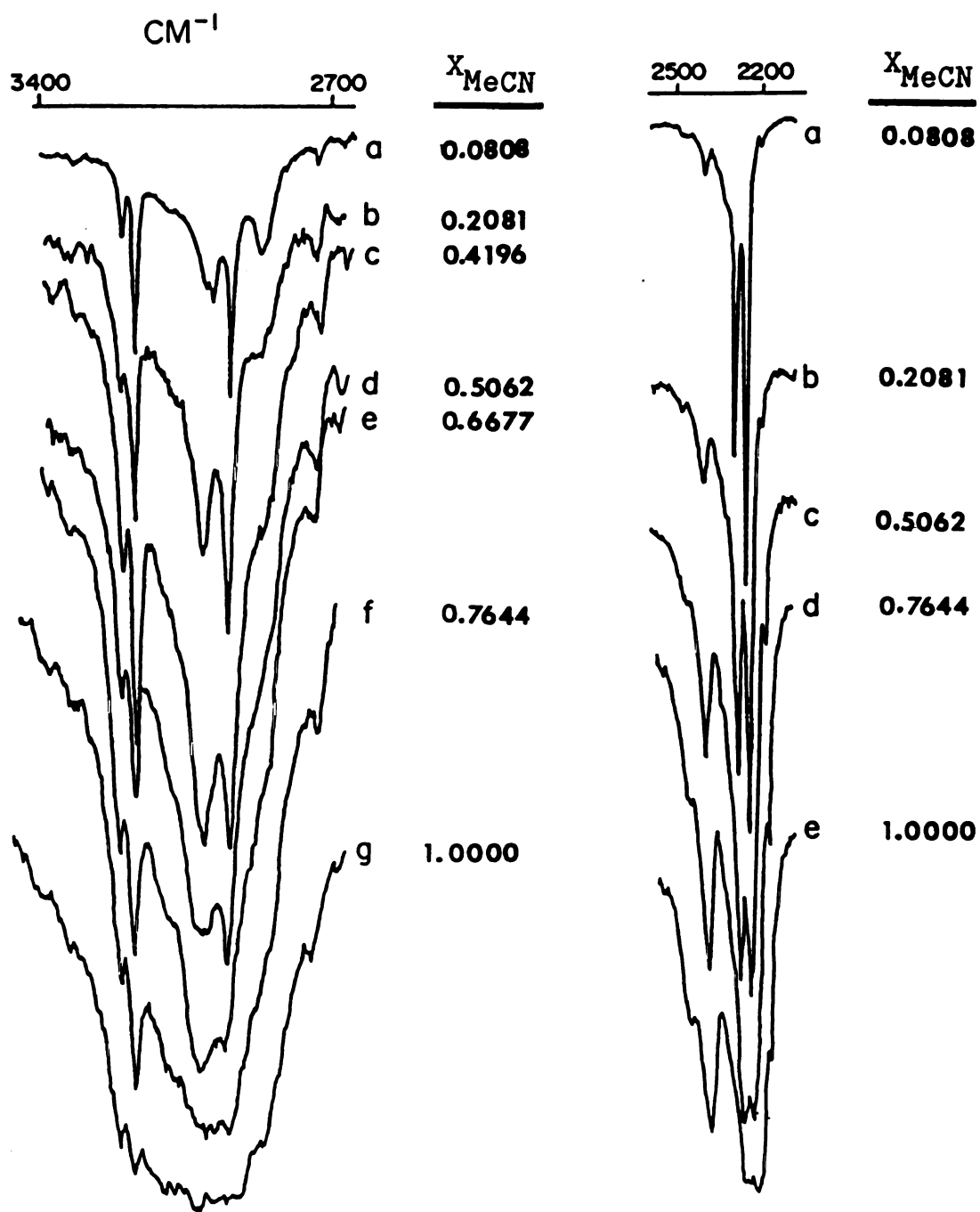


Figure 20. Infrared spectra of the C-H stretch and C≡N stretch of AN in carbon tetrachloride.

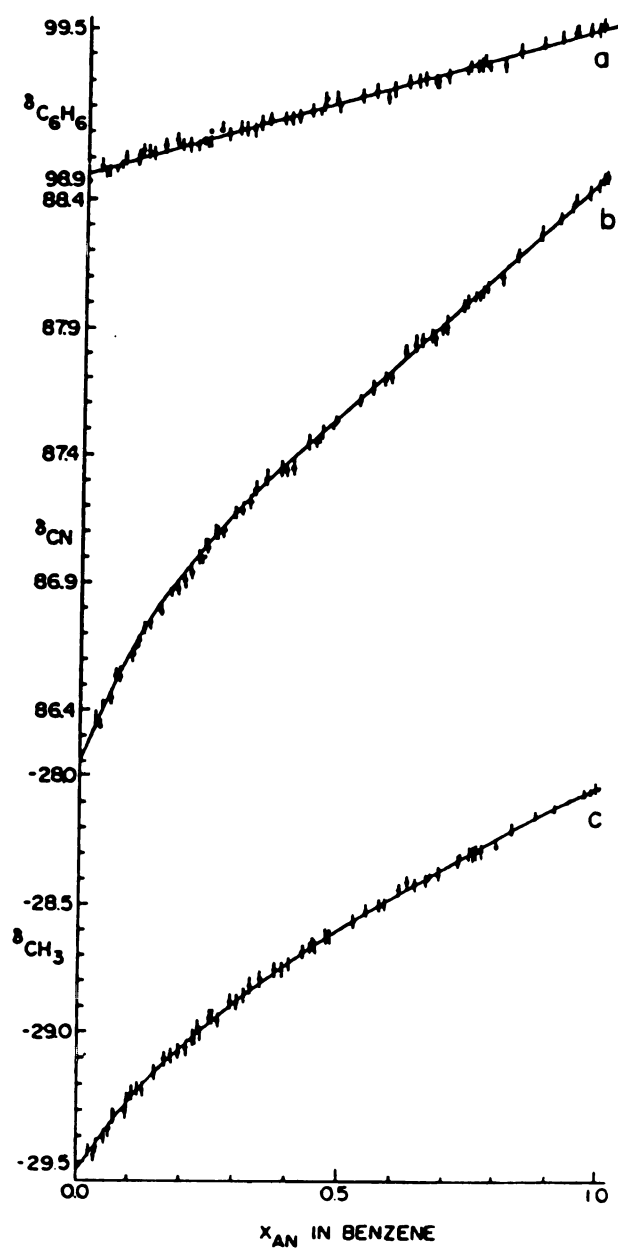


Figure 21. Plots of the carbon-13 chemical shifts of acetonitrile and benzene as a function of mole fraction of AN.

nitrile carbons of acetonitrile exhibit the same curvature. Furthermore, the nitrile carbon chemical shift - X_{AN} plot does not show as much curvature in benzene as it did in carbon tetrachloride. Generally, the stronger the interaction, the more curvature is observed in the chemical shift-concentration plots. Therefore, the self association of acetonitrile appears to be weaker in benzene than in carbon tetrachloride. Since the curvature of the δ vs. concentration plot for the methyl carbon of acetonitrile is the same as that observed for the nitrile group, it can be concluded that the self-association of acetonitrile and its interaction with benzene occur through the nitrile group. Proposed structures for the $MeCN \cdot C_6H_6$ and $MeCN \cdot (C_6H_6)_2$ species are shown in Figure 19.

The lack of curvature observed in the chemical shift vs. concentration plot for benzene is probably due to the symmetry of the benzene ring and to the fact that the nitrile group interacts with each carbon equivalently. Because the benzene carbon-13 chemical shift variation with concentration has a constant slope, it is not possible to separate the $MeCN-MeCN$ and $MeCN-C_6H_6$ interactions as it is for the CCl_4 system. A proton NMR study was done to see if it would be feasible to separate these interactions; the results are plotted in Figure 22. Although the proton chemical shifts of both the methyl group of $MeCN$ and the protons of benzene showed a

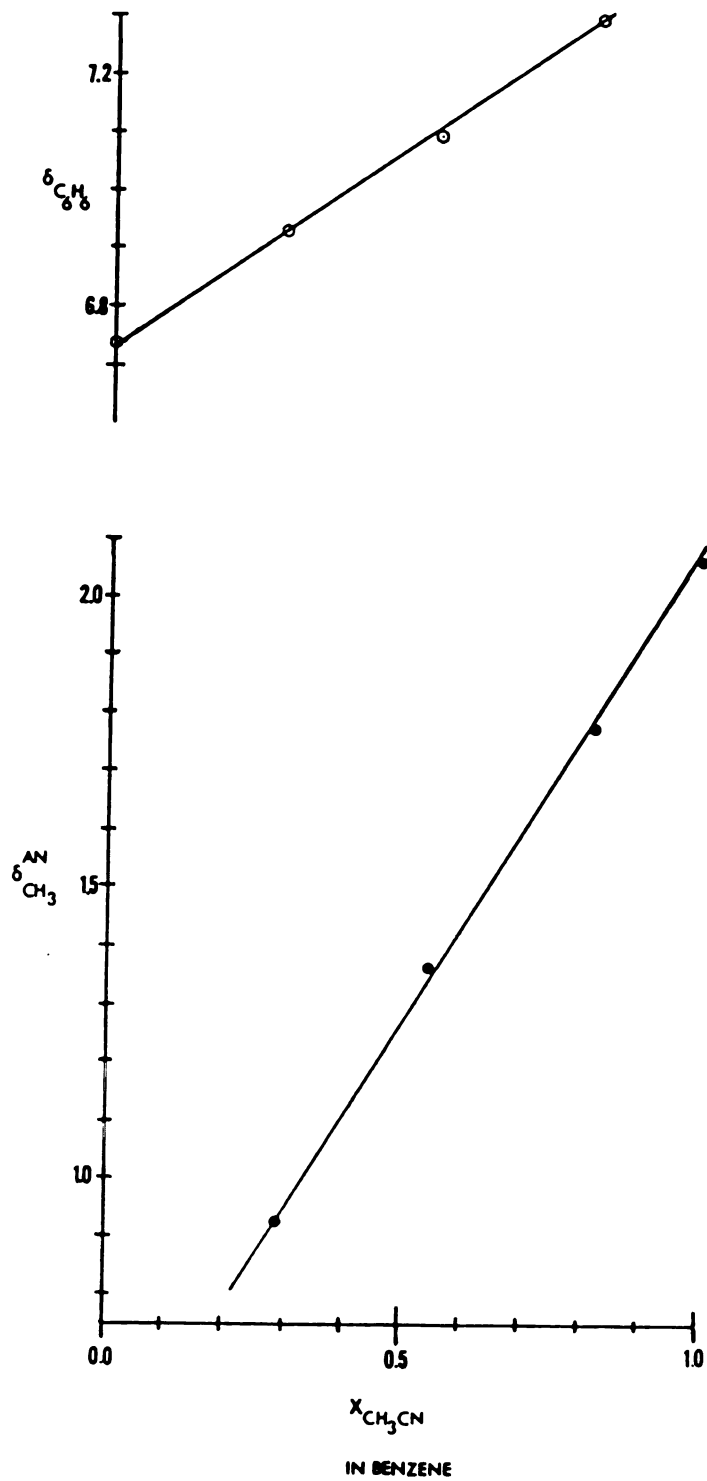
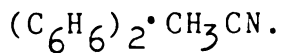


Figure 22. Plots of the proton chemical shifts of benzene and acetonitrile as a function of mole fraction of acetonitrile.

concentration dependence, no curvature was observed. Therefore, these interactions could not be separated by proton NMR.

The carbon-13 chemical shift variation for the MeCN-C₆H₆ system shows that the self-association of acetonitrile is the dominant reaction. The chemical shift data for the methyl and nitrile carbons were computer analyzed using a dimerization model. The equations and computer subroutine used are discussed in Appendix I. The results of the computer analysis are shown in Table 12. It should be emphasized that the K_d value obtained is a conditional constant since it is not possible to separate the MeCN-MeCN interaction from the MeCN-C₆H₆ interaction.

These results are in agreement with vapor-pressure studies on these systems. The MeCN-benzene system forms a low boiling azeotrope (azeotrope b.p.=73°C, b.p. of MeCN=81.57°C and b.p. of C₆H₆=80.1°C (193)); therefore, the self-association of MeCN should be the dominant reaction. Furthermore, the boiling point of the MeCN-CCl₄ azeotrope deviates more greatly from the boiling points of its pure components than does the boiling point of the MeCN-C₆H₆ azeotrope. This suggests that the MeCN-C₆H₆ interactions are stronger than the MeCN-CCl₄ interactions. It should be noted that in a study of the MeCN-C₆H₆ system, Goates and his co-workers (30) were able to isolate, at 249°K, a solid compound with the composition



3. ACETONITRILE IN ACETONE. Unlike the MeCN-CCl_4 and $\text{MeCN-C}_6\text{H}_6$ systems, the MeCN-acetone system does not form an azeotrope (194). Therefore, it is probable that the intermolecular forces between MeCN-MeCN , $\text{Me}_2\text{CO-MeCN}$ and $\text{Me}_2\text{CO-Me}_2\text{CO}$ are approximately the same. As Figure 23 shows, no curvature is observed in the chemical shift plots as a function of concentration for either the methyl and nitrile carbons of acetonitrile or for the methyl and carbonyl carbons of acetone. Therefore, no particular reaction is dominant. The interaction between acetonitrile and acetone is undoubtedly a dipole-dipole one through the nitrile and carbonyl groups. The chemical shift dependence on concentration can be described by the following relationship:

$$\delta_{\text{OBS}} = \delta_{\infty} + (\delta_{1.0} - \delta_{\infty})mX_{\text{AN}} \quad [8]$$

where δ_{∞} is the chemical shift of MeCN in Me_2CO at infinite dilution, $\delta_{1.0}$ is the chemical shift of pure MeCN , m is a proportionality constant and X_{AN} is the mole fraction of MeCN . For the $\text{MeCN-Me}_2\text{CO}$ system, $m = 0.96 \pm 0.03$, $\delta_{\infty} = 39.48$ ppm vs. chloroform-d, and $\delta_{1.0} = 40.24$ ppm vs. chloroform-d.

4. ACETONITRILE IN CHLOROFORM. Figure 24 shows plots of the carbon-13 chemical shifts of MeCN and CHCl_3

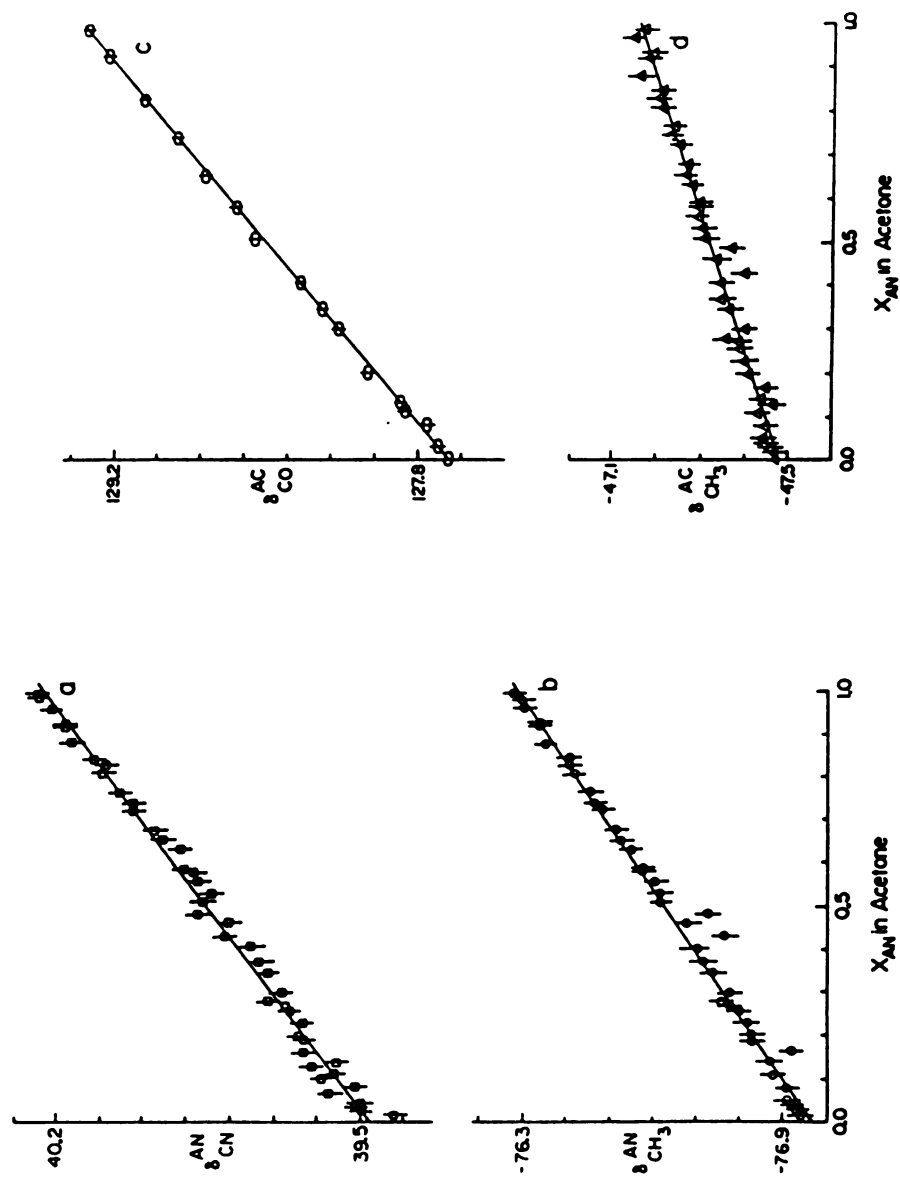


Figure 23. Plots of the carbon-13 chemical shifts of acetonitrile and acetone as a function of mole fraction of acetonitrile.

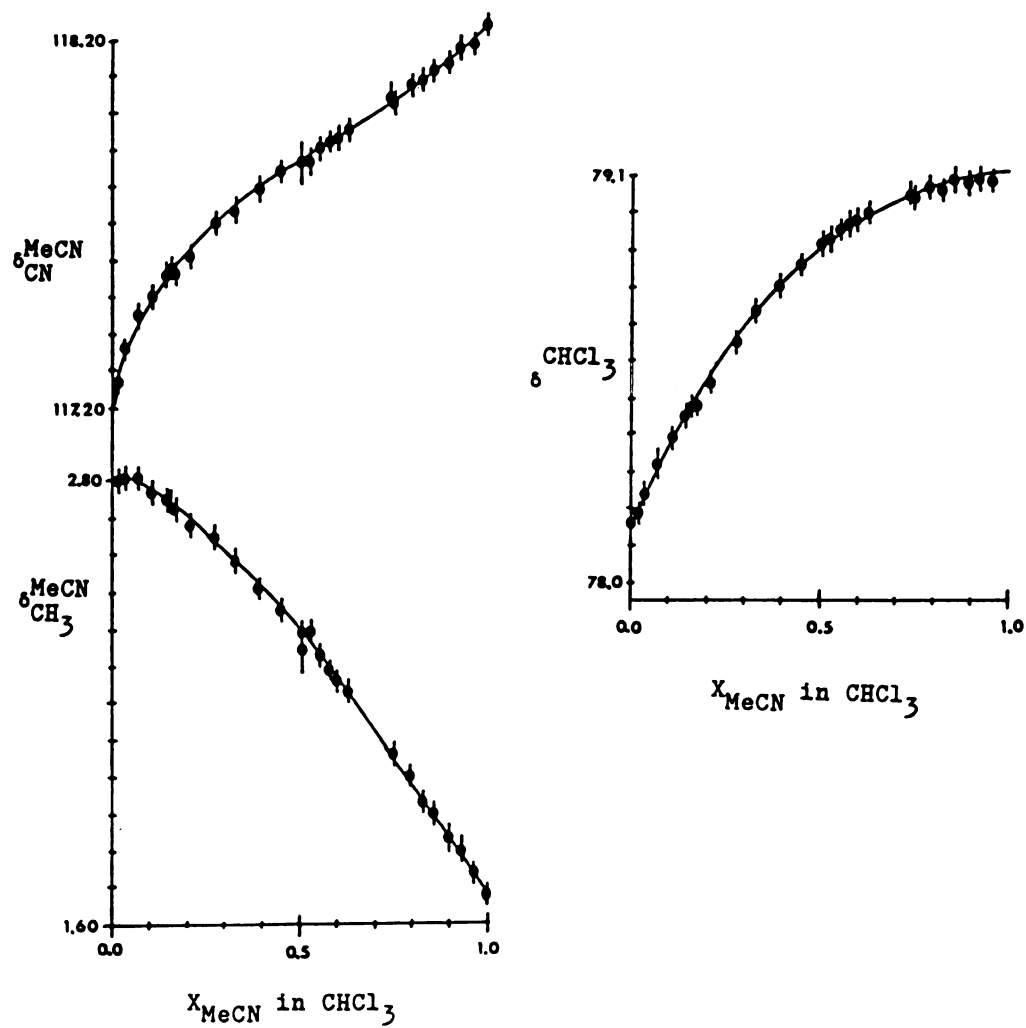


Figure 24. Plots of the carbon-13 chemical shifts of acetonitrile and chloroform vs. X_{MeCN} .

as a function of concentration. Similarities between the MeCN-CHCl_3 and MeCN-CCl_4 systems are apparent. In both systems the methyl carbon of MeCN shifts upfield with increasing concentration of acetonitrile. In the MeCN-CCl_4 system this was attributed to an interaction between the methyl group of MeCN and CCl_4 . Therefore, the same must be true of the MeCN-CHCl_3 system. The nitrile carbon of MeCN shifts downfield with increasing concentration of acetonitrile for both the MeCN-CCl_4 and MeCN-CHCl_3 systems. This has been attributed to the dimerization of acetonitrile. However, the carbon of chloroform shifts downfield with increasing concentration of MeCN and suggests dimerization of chloroform. Based on the chemical shift behavior and the similarities between the MeCN-CHCl_3 and MeCN-CCl_4 systems, two models were used to analyze the carbon-13 chemical shift data of MeCN and CHCl_3 . One model took into account dimerization of both MeCN and CHCl_3 and the formation of a 1:1 MeCN-CHCl_3 complex. The other model included dimerization of both MeCN and CHCl_3 and the formation of a 1:1 and 2:1 MeCN-CHCl_3 complexes. The equations and subroutines used are discussed in Appendix I. Multiple data sets were used. Figures 25 and 26 show the graphical plots obtained from KINFIT. From these plots it can be concluded that the second model better describes the observed carbon-13 chemical shift behavior.

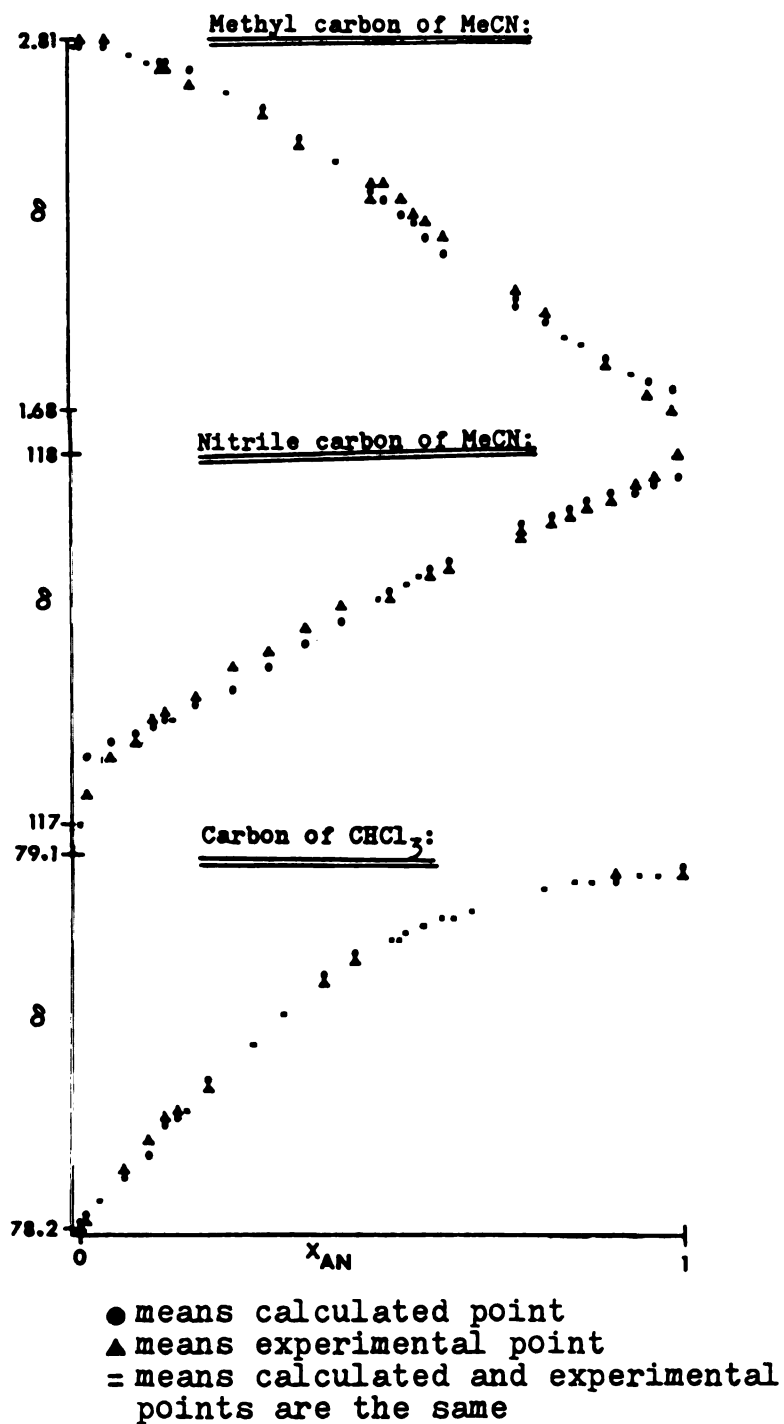
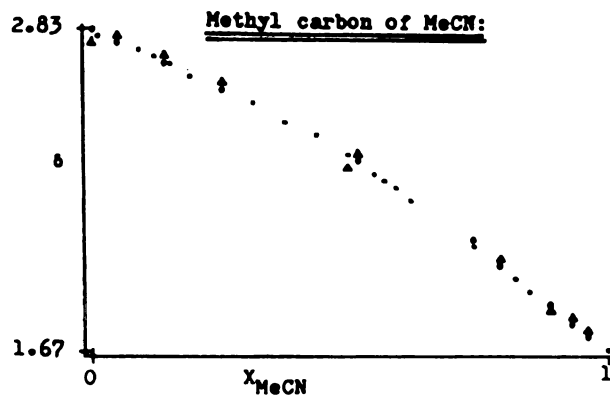
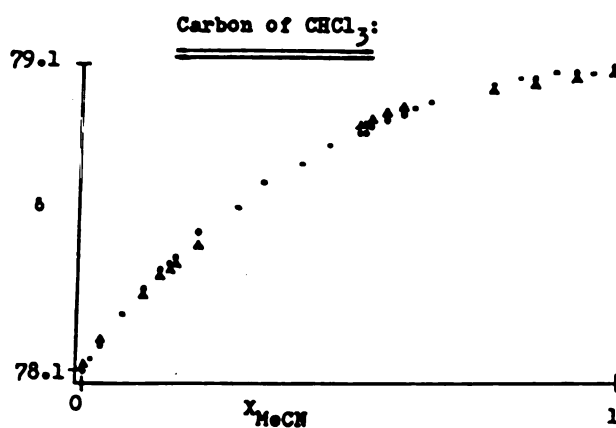
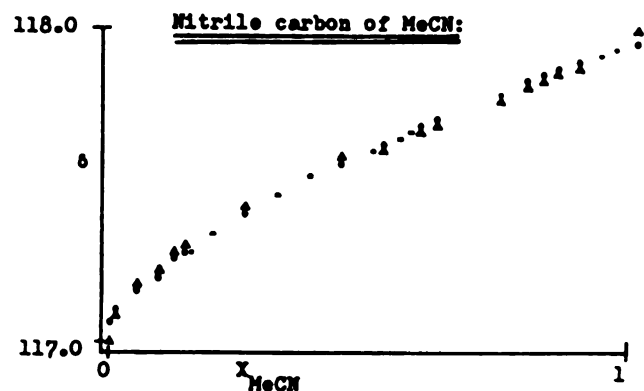


Figure 25. KINFIT outputs obtained from a multiple data fit of the MeCN-CHCl_3 system. Model included formation of S_2 , SC and C_2 .



● means calculated point
 ▲ means experimental point
 = means calculated and experimental points are the same

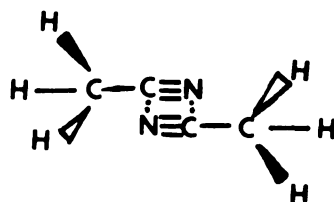
Figure 26. KINFIT outputs obtained from a multiple data fit of the MeCN- CHCl_3 system. Model included formation of S_2 , SC, S_2C and C_2 .

Table 12 tabulates the equilibrium constants obtained from the computer analysis. The uncertainties in the equilibrium constants and chemical shifts are rather large but this is not unexpected since 13 unknown parameters were obtained simultaneously. The uncertainties in the formation constants of the 2:1 MeCN-CHCl₃ species and the chemical shifts of the (MeCN)₂·CHCl₃ species are particularly large. The formation constants are also very small. Both of these conditions imply that those equilibria are not well defined. However, as the graphical plots obtained from KINFIT indicate, the formation of a (MeCN)₂·CHCl₃ species must be included to adequately describe the carbon-13 chemical shift behavior as a function of X_{AN}. One would expect the dimerization of acetonitrile to be identical in both the MeCN-CCl₄ and MeCN-CHCl₃ systems. However, as Table 12 indicates, this is not the case. This discrepancy may be the result of the assumptions made in the computer analysis of the chemical shift data. The results of this study disagree with those obtained by Lorimer and Jones ($K_{S_2} = 8.35 \pm 0.12 \text{ m.f.}^{-1}$, $K_{C_2} = 0.060 \pm 0.026 \text{ m.f.}^{-1}$ and $K_{SC} = K_{SC_2} = 1.52 \pm 0.074 \text{ m.f.}^{-1}$) (41). In their study, Lorimer and Jones analyzed the excess Gibbs energies and heats and volumes of mixing data for the MeCN-CHCl₃, MeCN-CCl₄ and CHCl₃-CCl₄ systems. In their model they assumed that dimerization of MeCN and

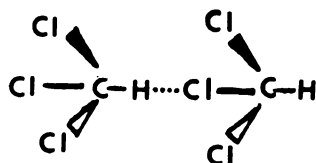
CHCl_3 only occurred in CCl_4 . Neither of these assumptions is valid. As was discussed previously, in CCl_4 , MeCN dimerizes and forms 1:1 and 2:1 MeCN: CCl_4 complexes. The proton NMR studies done by Jumper, Emerson and Howard (59) showed that chloroform and carbon tetrachloride form a weak complex ($K \approx 0.1 \text{ m.f.}^{-1}$). From the carbon-13 chemical shift data, structures shown in Figure 27 for the $(\text{MeCN})_2$, $\text{MeCN} \cdot \text{CHCl}_3$, $(\text{MeCN})_2 \cdot \text{CHCl}_3$ and $(\text{CHCl}_3)_2$ species can be proposed. For the $\text{MeCN} \cdot \text{CHCl}_3$ and $(\text{MeCN})_2 \cdot \text{CHCl}_3$, two structures can be proposed. The chemical shift behavior of the methyl carbon supports an interaction through the methyl group with chloroform. However, the proton of chloroform is fairly acidic ($\text{pK}_a = 15 \pm 1$ (58)) and could hydrogen bond to the nitrogen lone pair of electrons. It has been shown previously that MeCN forms complexes in this manner with HF and HCl (19, 20). The structure proposed for the chloroform dimer has support from the studies done by Jumper, Emerson and Howard (59) who showed that chloroform and carbon tetrachloride interact.

A proton NMR study of the $\text{MeCN}-\text{CHCl}_3$ system was carried out. The results of this study are shown in Figure 28. Plots of the proton chemical shift vs. concentration for MeCN and CHCl_3 show very little curvature. This can be easily explained. In Figure 27, in the structures proposed for the $\text{MeCN} \cdot \text{CHCl}_3$ and $(\text{MeCN})_2 \cdot \text{CHCl}_3$ species, the three methyl protons are bonded

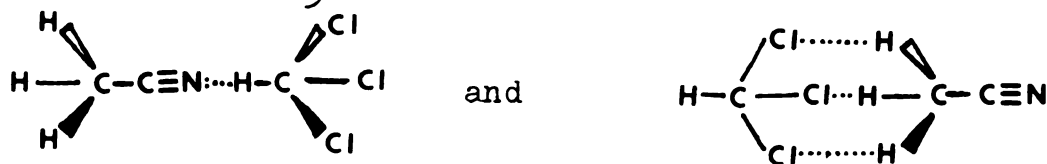
Acetonitrile dimer, S_2 :



Chloroform dimer, C_2 :



1:1 MeCN:CHCl₃ complex, SC :



2:1 MeCN:CHCl₃ complex, S_2C :

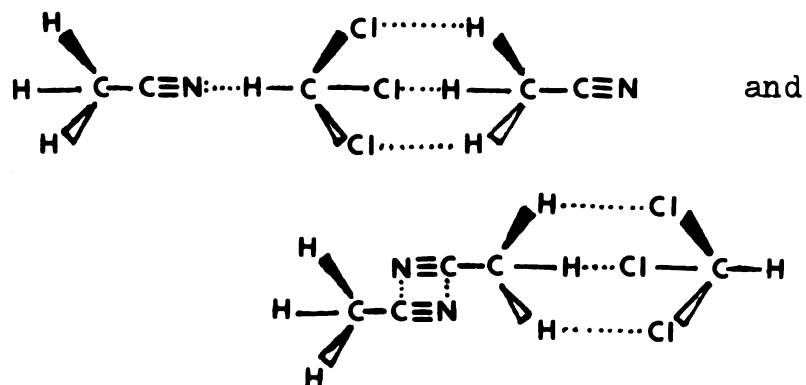


Figure 27. Structures proposed for the species occurring in the acetonitrile-chloroform system.

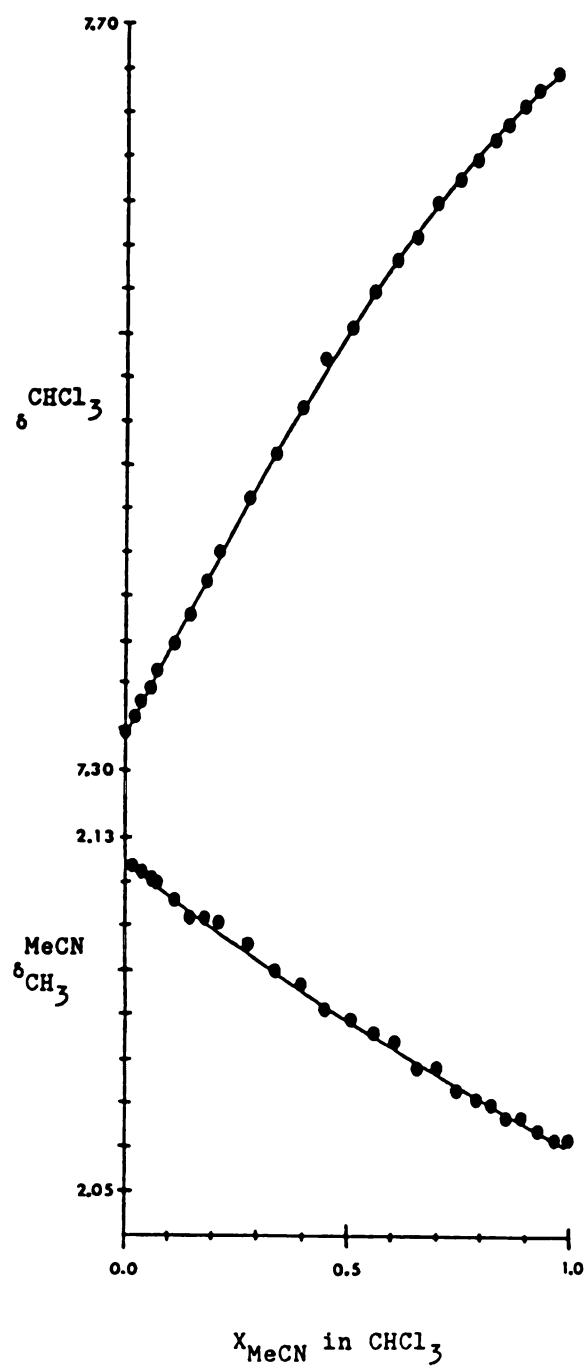


Figure 28. Plots of the proton chemical shifts of chloroform and acetonitrile vs. X_{MeCN} .

to the three chlorine atoms of chloroform. This is highly idealized. In solution, one MeCN proton could be bonded to one chlorine atom or two protons to two chlorine atoms as well as three protons to three chlorines. This is illustrated by the crystal structure of the BCl_3 MeCN complex which shows that one methyl proton hydrogen bonds to a chlorine of BCl_3 to form the lattice structure (195). If one methyl proton is bonded to one chlorine then two methyl protons are essentially "free". Due to the symmetry of the methyl group and the $-\text{CCl}_3$ of chloroform, the amount of curvature observed in the chemical shift-concentration plots is considerably less for the proton NMR study than for the carbon-13 NMR study.

5. NITROMETHANE IN BENZENE. Analogous to the $\text{MeCN}-\text{C}_6\text{H}_6$ system, the $\text{MeNO}_2-\text{C}_6\text{H}_6$ system forms a low-boiling azeotrope. As Figures 20 and 29 indicate, the curvatures in the observed chemical shift-concentration plots for these two systems are very similar. Therefore, the chemical shift data for the $\text{MeNO}_2-\text{C}_6\text{H}_6$ system were computer analyzed using a dimerization model. The results of this analysis are tabulated in Table 12.

Figure 30 shows the symmetries of the π and nonbonding orbitals of nitromethane as well as the π orbitals of benzene. Orbitals must have the same symmetry in order to overlap. Therefore the $\text{B}_1 \pi$ orbital of MeNO_2 has the appropriate symmetry to interact with the $\text{A} \pi$

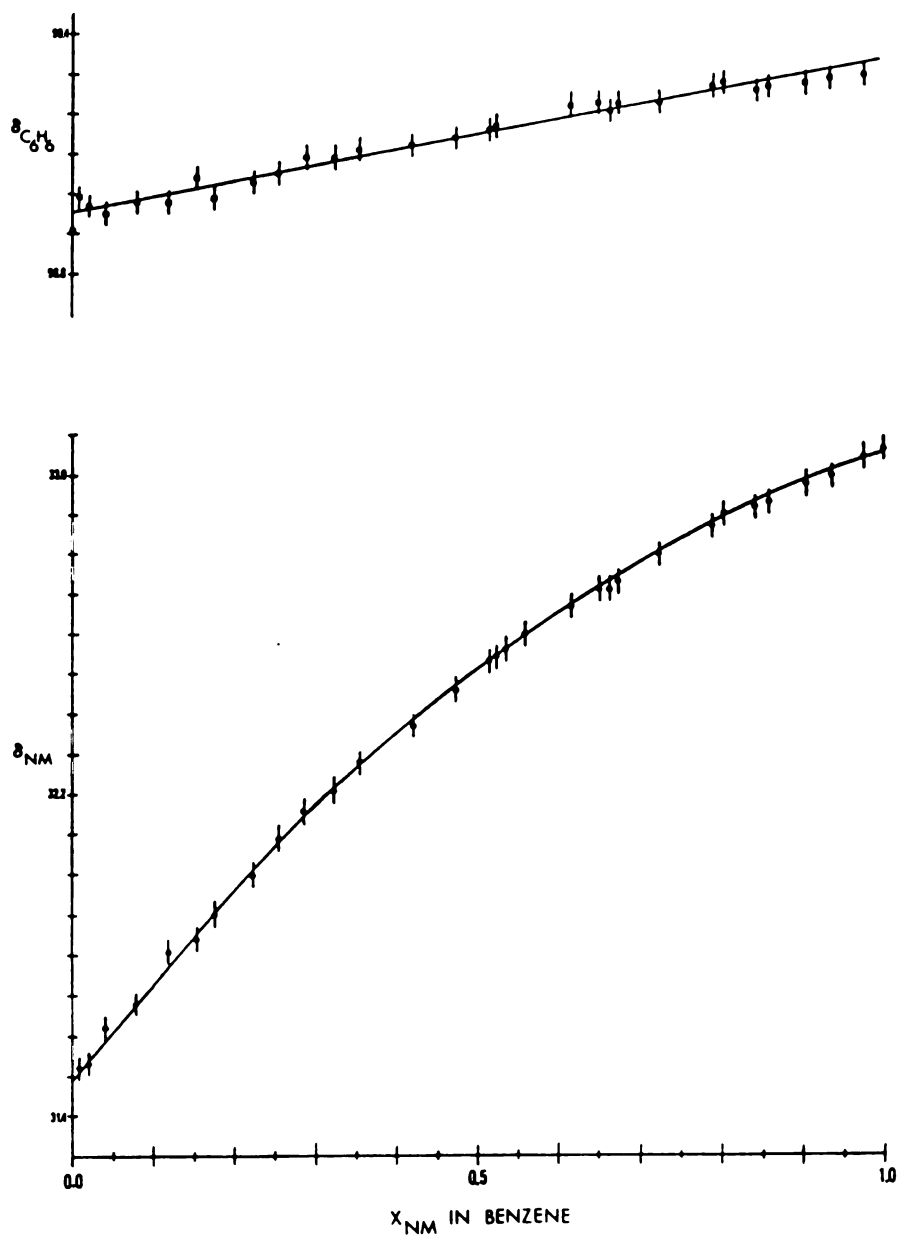


Figure 29. Plots of the carbon-13 chemical shifts of nitromethane and benzene as a function of mole fraction of nitromethane.

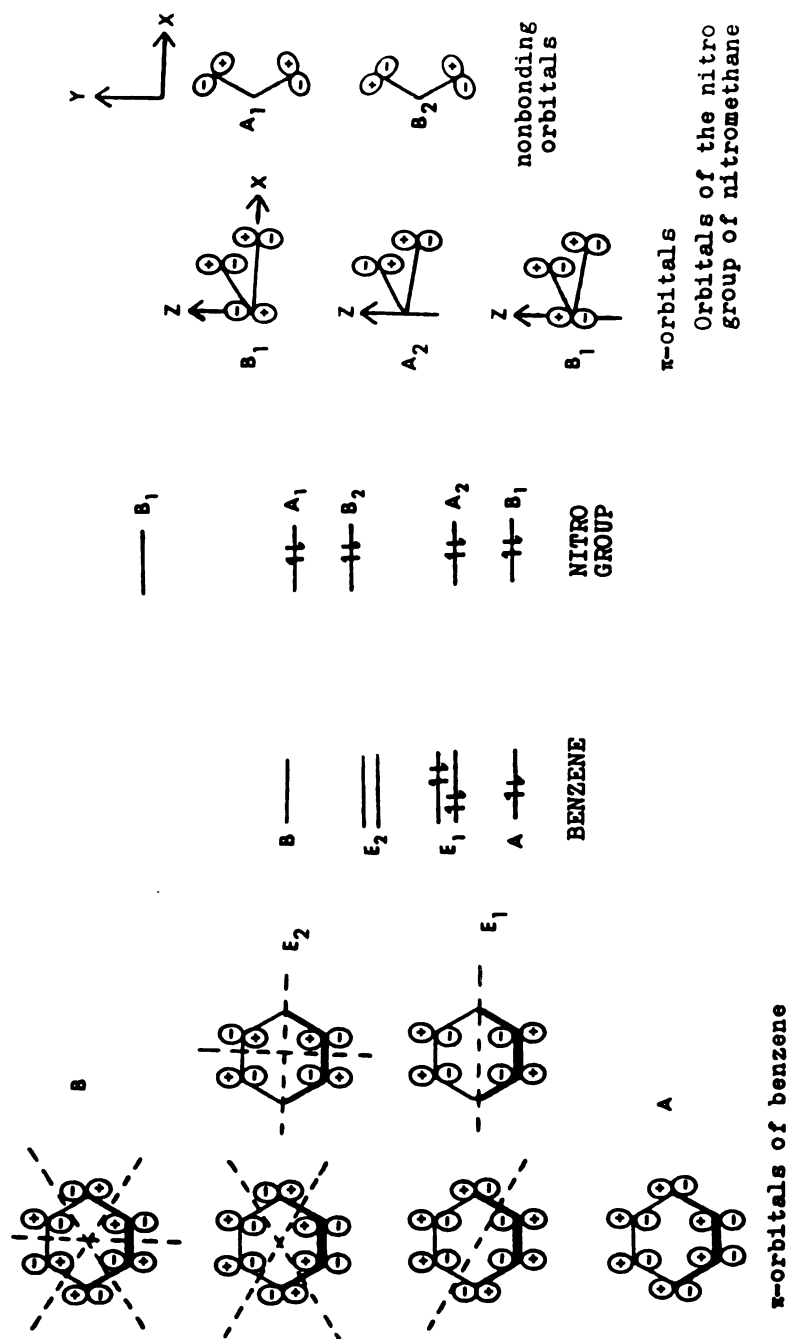


Figure 30. Diagram of the molecular orbitals of benzene and the nitro group of nitromethane.

orbitals of benzene. Likewise the A_2 of MeNO_2 matches the E_1 of benzene. However, the nonbonding orbitals of MeNO_2 do not have the appropriate symmetry to interact with the π -orbitals of benzene. Taking into account the symmetries of the orbitals of MeNO_2 and benzene as well as the carbon-13 chemical shift behavior, the structures for the dimer of MeNO_2 and $\text{MeNO}_2\text{-C}_6\text{H}_6$ complexes shown in Figure 19 can be proposed.

6. CHLOROFORM IN BENZENE. Figure 31 shows the carbon-13 chemical shift-concentration plots for chloroform and benzene. No curvature is observed in the chemical shift plots as a function of concentration for either the carbons of benzene or of chloroform. The $\text{CHCl}_3\text{-C}_6\text{H}_6$ system does not form an azeotrope (196) which implies that the intermolecular forces between $\text{CHCl}_3\text{-CHCl}_3$, $\text{C}_6\text{H}_6\text{-C}_6\text{H}_6$ and $\text{CHCl}_3\text{-C}_6\text{H}_6$ are approximately the same. The chemical shift dependence on concentration can be described by the following relationship:

$$\delta_{\text{OBS}} = \delta_{\infty} + (\delta_{1.0} - \delta_{\infty})mX_{\text{CHCl}_3} \quad [9]$$

where δ_{∞} is the chemical shift of CHCl_3 in C_6H_6 at infinite dilution, $\delta_{1.0}$ is the chemical shift of pure CHCl_3 , m is a proportionality constant and X_{CHCl_3} is the mole fraction of CHCl_3 . For the $\text{CHCl}_3\text{-C}_6\text{H}_6$ system, $m = 1.019 \pm 0.007$, $\delta_{\infty} = 48.00$ ppm and $\delta_{1.0} = 48.44$ ppm vs.

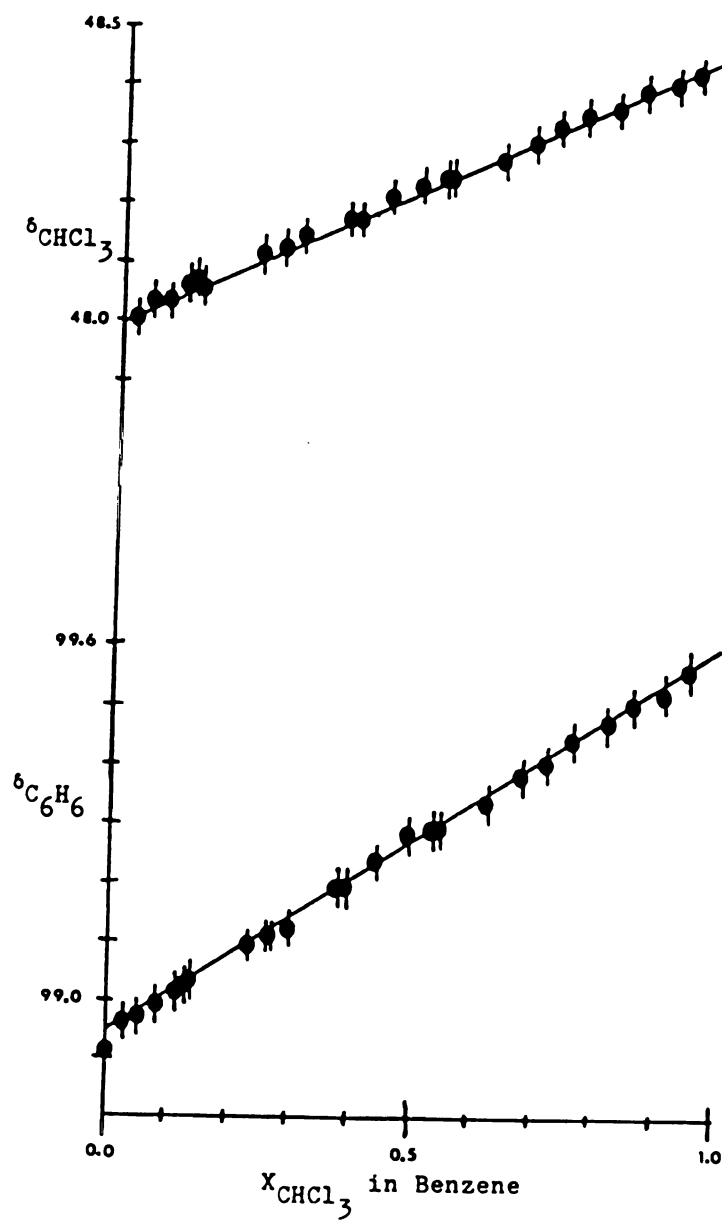
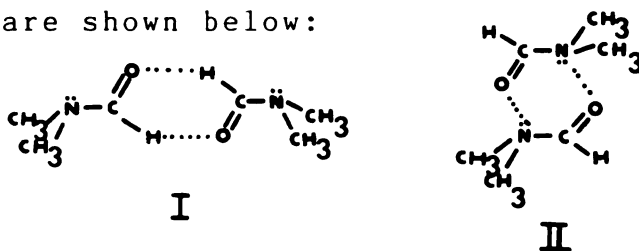


Figure 31. Plots of the carbon-13 chemical shifts of chloroform and benzene vs. X_{CHCl_3} .

acetone-d₆.

7. DIMETHYLFORMAMIDE IN BENZENE. Figure 32 shows plots of the carbon-13 chemical shifts of DMF and benzene as a function of mole fraction of DMF. The curvatures observed for the carbonyl and methyl carbons of DMF are similar to those observed for both MeNO₂ and MeCN in benzene and suggest that dimerization of DMF is the dominant reaction. The benzene chemical shift vs. concentration plot exhibits no curvature. Consequently it is not possible to separate the DMF-C₆H₆ interaction(s) from the dimerization of DMF. The chemical shift data of all three carbons of DMF were computer analyzed with a simple dimerization model. The results of this analysis are tabulated in Table 12.

Two structures have been proposed for the dimer of DMF. These are shown below:



In structure (I), the hydrogen of the carbonyl group of DMF forms hydrogen bonds to the oxygen of the carbonyl group of another DMF. Structure (II) represents a dipole-dipole interaction of the amide group. The carbon-13 chemical shift data support structure (II). In structure (I), the methyl groups on the nitrogen are four bonds away from the proposed site of interaction.

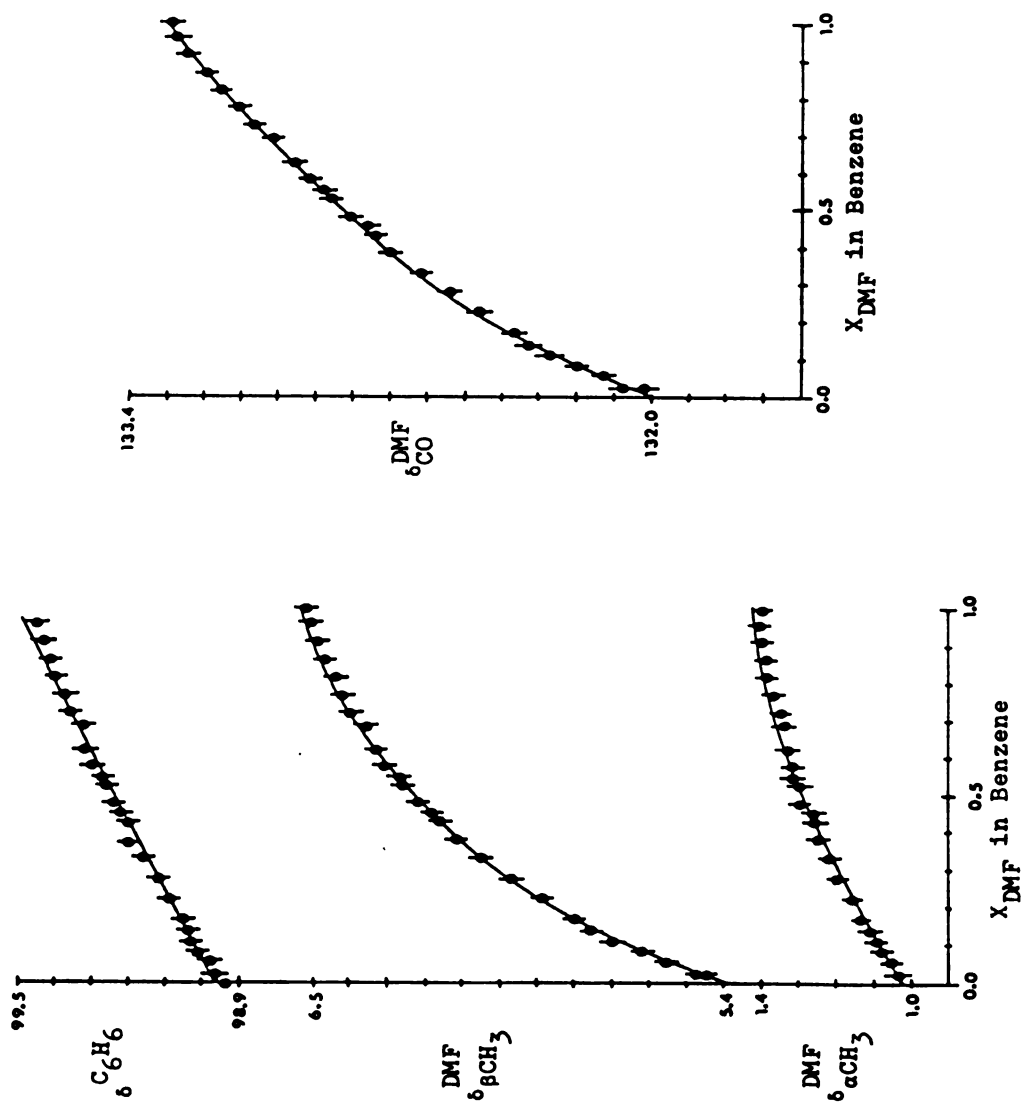


Figure 32. Plots of the carbon-13 chemical shifts of N,N-dimethylformamide and benzene vs. X_{DMF} .

Consequently, their chemical shift behavior as a function of concentration should not be affected by the dimerization. Yet Figure 32 indicates that the methyl carbons of DMF are affected by dimerization. In structure (II), the methyl groups are only one bond away from the site of dimerization. Consequently, the methyl groups are affected by the dimerization.

For a solution of two components A and B, if the intermolecular forces between A and A, B and B and A and B are all the same, then that solution is ideal. The vapor pressure of a component above the solution is a good measure of the tendency of the given species to escape into the vapor phase. The tendency of a component to escape from solution is a direct reflection of the physical state of affairs within the solution (191). For an ideal solution:

$$X_A = P_A / P_A^0 \quad [10]$$

where X_A is the mole fraction of A in solution, P_A is the partial pressure of A above the solution and P_A^0 is the vapor pressure of pure A. The relationship shown in equation [10] is Raoult's Law. A positive deviation from Raoult's Law is characterized by vapor pressures higher than those calculated for the ideal solution. The effect has been ascribed to cohesive forces between unlike components smaller than those within the pure liquids, resulting in a

trend away from complete miscibility. Negative deviations are characterized by lower vapor pressures from ideality and result when the attractive forces between the unlike molecules in solution are greater than those between the like molecules in the pure liquids. Azeotropes are formed when the deviations from Raoult's Law are large. The chemical shift data for the DMF-C₆H₆ system indicate that dimerization of DMF is the dominant reaction. At first, this was a surprising result since the DMF-C₆H₆ system does not form an azeotrope (196). However, this may simply indicate that the deviations from Raoult's Law are not large enough to form an azeotrope.

8. ACETONE IN BENZENE. The curvature observed in the carbon-13 chemical shift -concentration plot for acetone, shown in Figure 33, indicate that dimerization of acetone is the dominant reaction. Again the lack of curvature for the chemical shift-concentration plot for benzene prevents separation of the benzene-acetone interactions from the acetone-acetone interactions. The chemical shift data were computer analyzed by using a simple dimerization model. The results of this analysis are tabulated in Table 12. Like the DMF-C₆H₆ system, the AC-C₆H₆ system does not form an azeotrope (196). The fact that dimerization of AC is the dominant reaction implies that the deviations from Raoult's Law are not large enough to form an azeotrope.

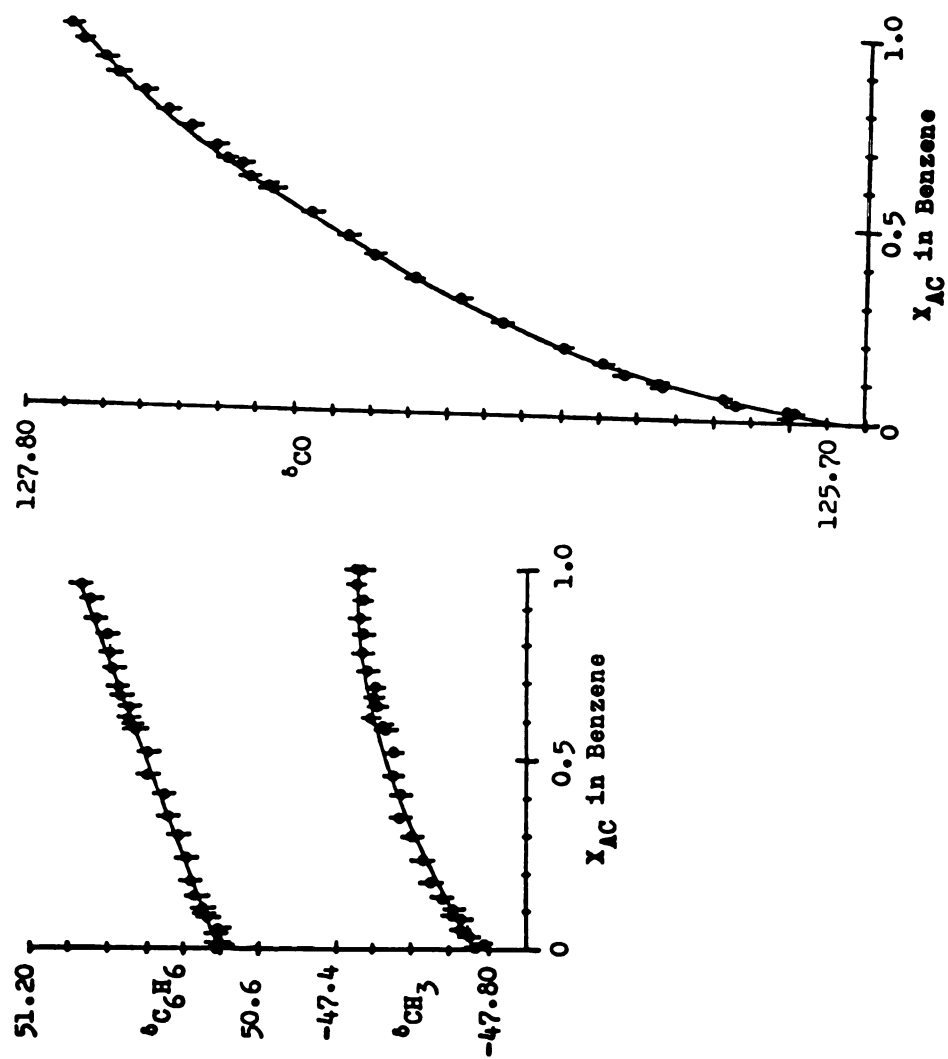


Figure 33. Plots of the carbon-13 chemical shifts of acetone and benzene as a function of mole fraction of acetone.

9. METHANOL IN CARBON TETRACHLORIDE. The MeOH-CCl₄ system was studied by both ¹H and ¹³C NMR. The chemical shift data are plotted in Figures 34 and 35. Proton spectra for solutions of MeOH in CCl₄ are shown in Figure 36.

The chemical shift-concentration plots and proton spectra indicate that multiple equilibria are occurring in solution. At 0.0215 mole fraction, the methyl group is a doublet and the hydroxyl group is a quartet. This can only occur when the proton of the hydroxyl group is not exchanging which, in turn, implies that the methanol is completely solvated. This further indicates that there is an interaction between the hydroxyl proton and carbon tetrachloride. At higher concentrations, single resonances are observed for the methyl and hydroxyl groups indicating the formation of dimers and higher aggregates. These data also show that the more hydrogen-bonding occurring between methanol molecules, the more downfield is the hydroxyl proton resonance. Besides aggregate formation of MeOH and an interaction through the hydroxyl group, interaction through the methyl group is also probable since water is soluble to 100 ppm and methanol is completely miscible. Furthermore, the curvature observed for the chemical shift-concentration plot of CCl₄ is similar to that observed for CCl₄ in the MeCN-CCl₄ system. In the MeCN-CCl₄ system, dimerization of acetonitrile and

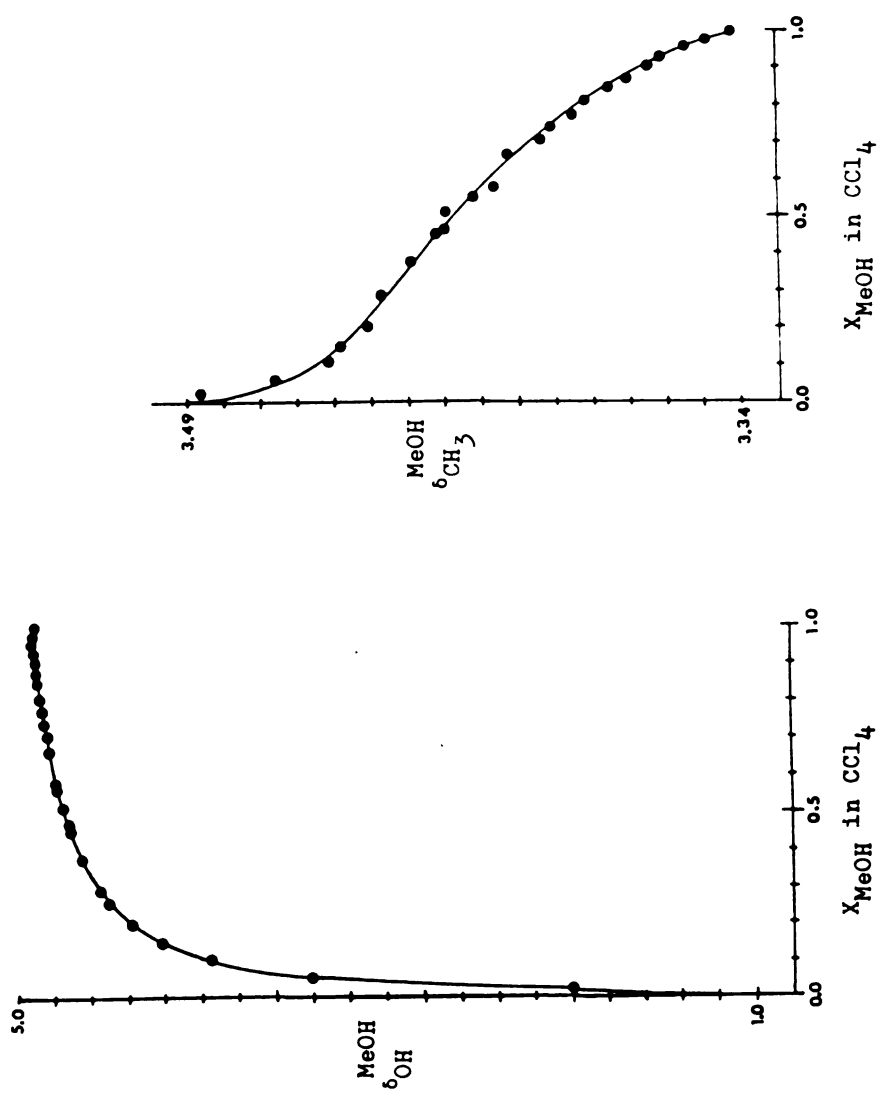


Figure 34. Plots of the proton chemical shifts of methanol vs. X_{MeOH} in carbon tetrachloride.

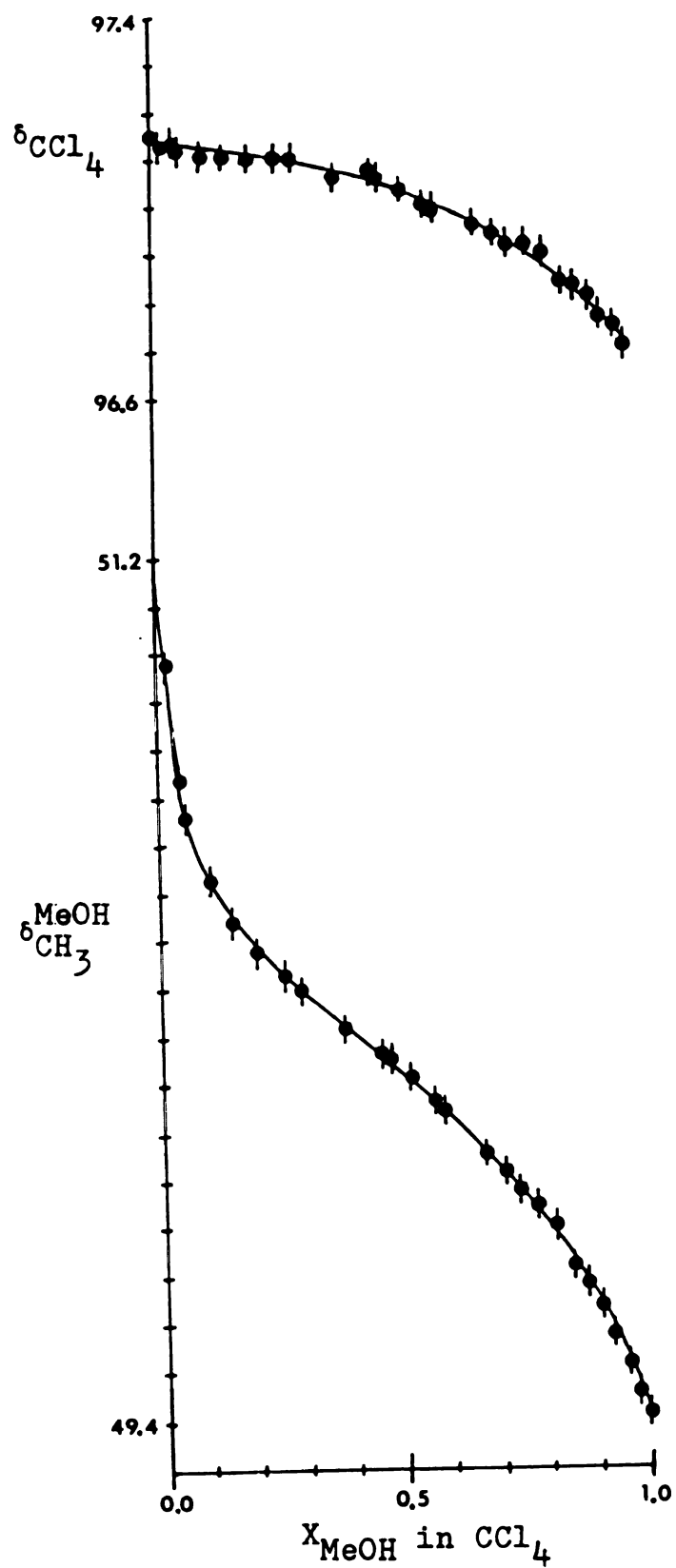


Figure 35. Plot of the carbon-13 chemical shifts of methanol and carbon tetrachloride vs. X_{MeOH} .

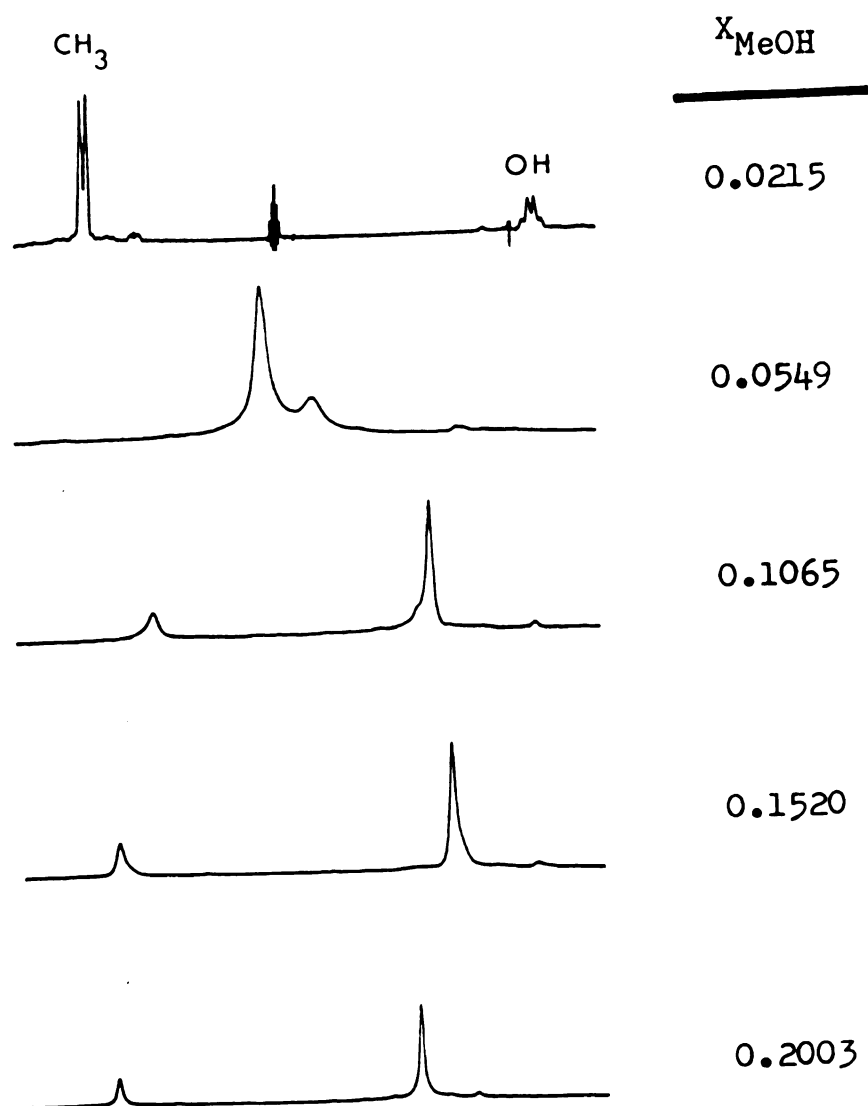


Figure 36. Proton spectra of methanol in carbon tetrachloride.

formation of 1:1 and 2:1 MeCN:CCl₄ complexes occurred. The same may be true of the MeOH-CCl₄ system. In addition, there is evidence for the formation of both cyclic and open dimers, trimers, etc. (62).

These observations are in agreement with the results of previous workers. The MeOH-CCl₄ system forms a low-boiling azeotrope (193) which indicates that the methanol self-associations are the dominant reactions. Bellamy and Pace (86) used vibrational spectroscopy to study the MeOH-CCl₄ system. They observed several bands in the OH stretching region; a band at 3642 cm⁻¹ attributed to monomeric MeOH, a band ascribed to dimer at 3542 cm⁻¹ and one ascribed to polymer at 3346 cm⁻¹. They also observed a band at 3637 cm⁻¹ which they attributed to the OH group acting as an acceptor, but not a donor. Figure 37 shows infrared spectra obtained by de Maine et al. (50). At 0.02 M MeOH methanol appears to consist primarily of monomer. With increasing concentration, the bands attributed to the dimer and polymer form.

Attempts were made to computer analyze the chemical shift data. Since the same set of equilibria must explain the chemical shift behavior for both the methanol and carbon tetrachloride, multiple data sets were used. Models used to analyze the data included formation of (1) S₂, SC, and S₂C; (2) S₂, S₃, SC, S₂C, and S₃C; (3) S₂, S₃, S₄, SC, S₂C, S₃C, and S₄C and (4) S₂, S₃, S₄, S₅, SC, S₂C,

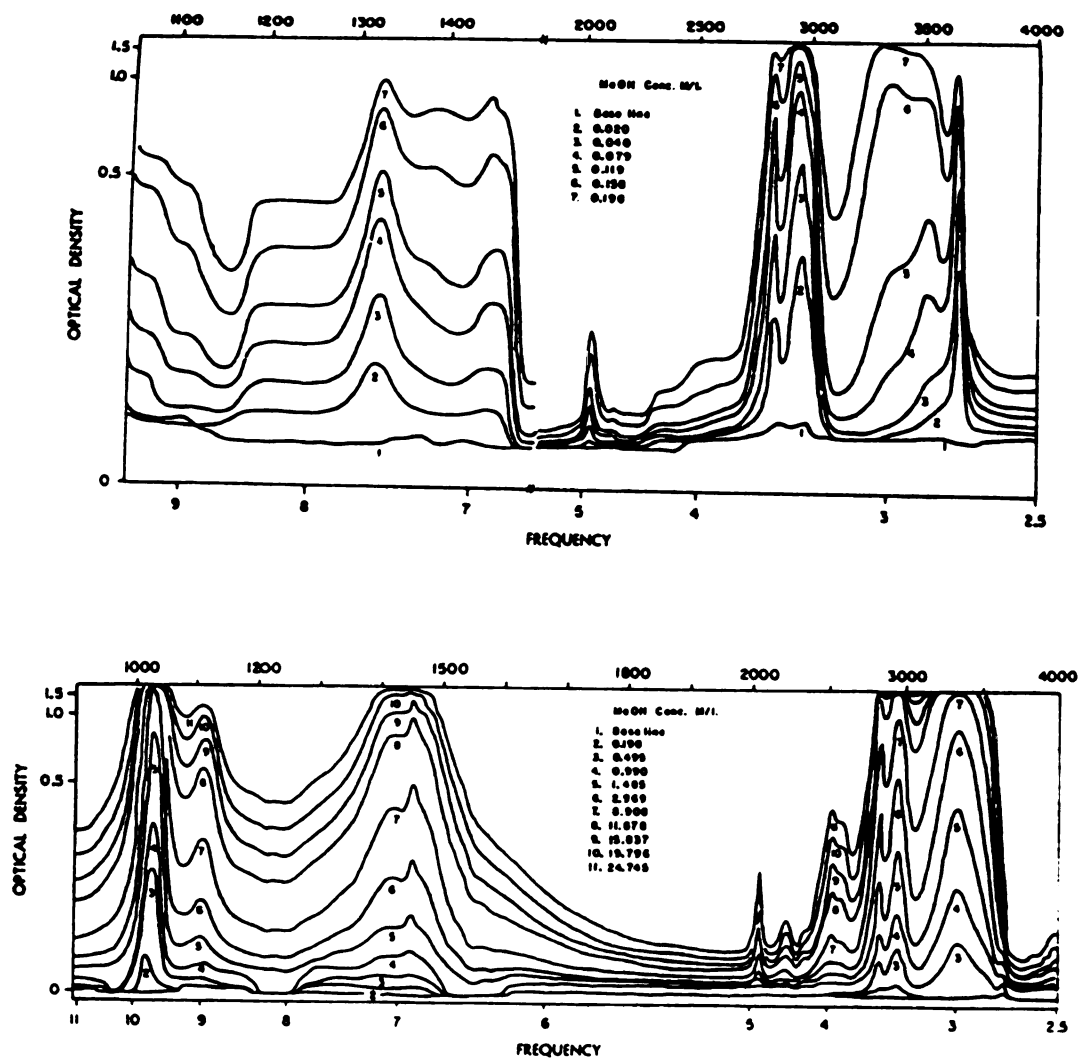


Figure 37. Infrared spectra of solutions of methanol in carbon tetrachloride (50).

S_3C , S_4C and S_5C . All four models adequately described the chemical shift behavior of the methanol but not the carbon tetrachloride. Figure 38 shows a graphical output typically obtained for these models. The values of the equilibrium constants and chemical shifts obtained using these models were extremely unreasonable and simply reflect the complexity of the system under investigation.

10. METHANOL IN BENZENE. Like the $MeOH-CCl_4$ system the $MeOH-C_6H_6$ system has multiple equilibria. The proton spectra of methanol in deuterated benzene and the 1H and ^{13}C chemical shift-concentration plots shown in Figures 39, 40, and 41, respectively, are very similar to those obtained for the $MeOH-CCl_4$ system. The proton spectra indicate an interaction between the hydroxyl group and benzene. This is in agreement with UV spectra of water and methanol solutions in benzene which indicate that complex formation between these polar solvents and benzene (105). A recent matrix isolation study of the benzene-water interaction showed the existence of a 1:1 $H_2O:C_6H_6$ complex (197). The curvature of the hydroxyl proton is similar to that observed for the $MeOH-CCl_4$ system and is due to the formation of $MeOH$ aggregates. Water is soluble in benzene to the extent of 200 ppm and methanol is miscible in all proportions. This difference in solubilities implies that an interaction between the methyl group and benzene occurs. The proton and carbon-13

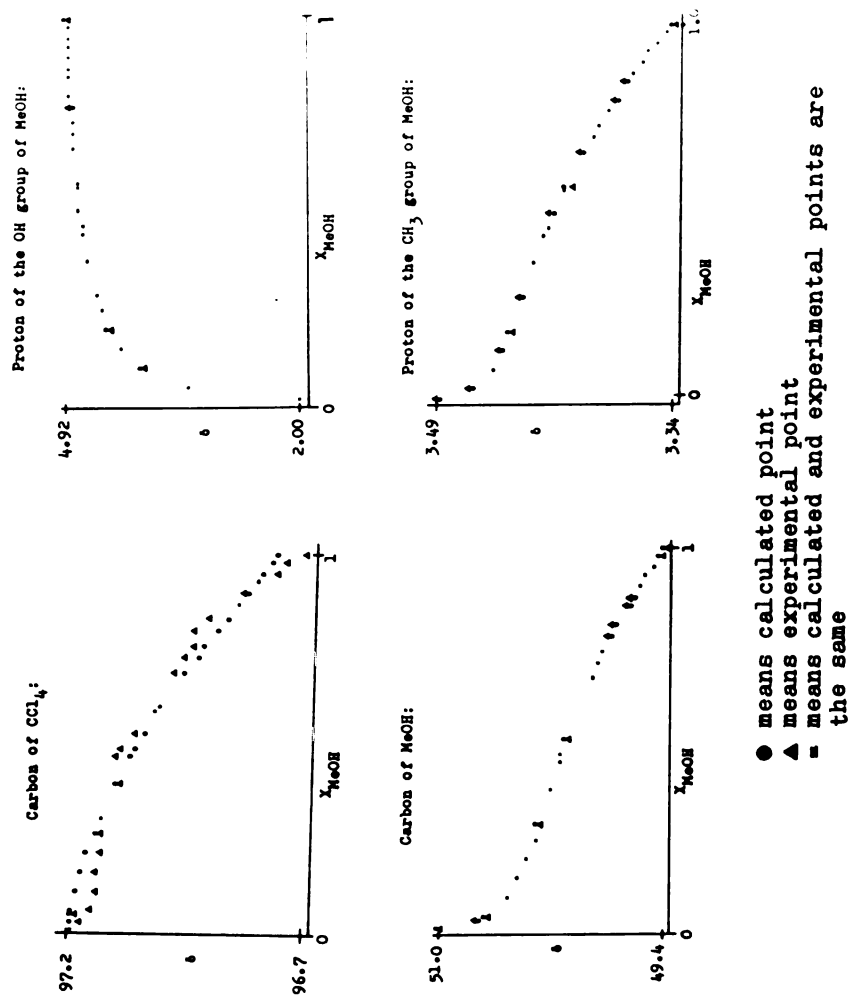


Figure 38. KINFIT outputs obtained from a multiple data fit of the MeOH-CCl₄ system.

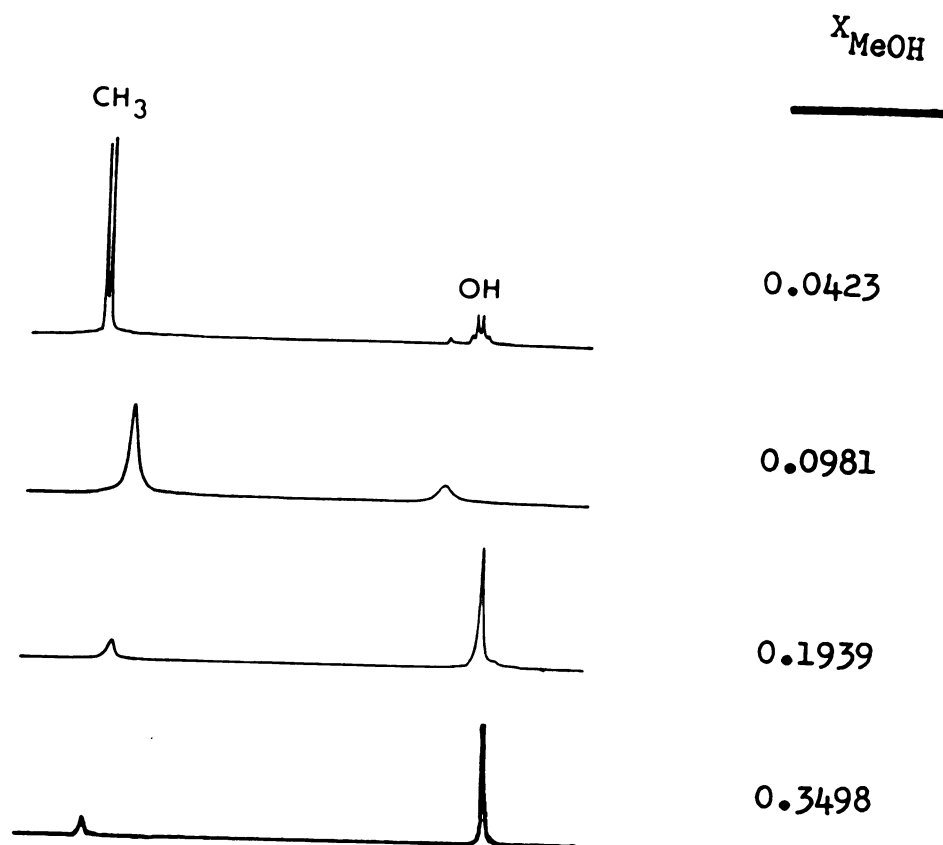


Figure 39 . Proton spectra of methanol in deuterated benzene.

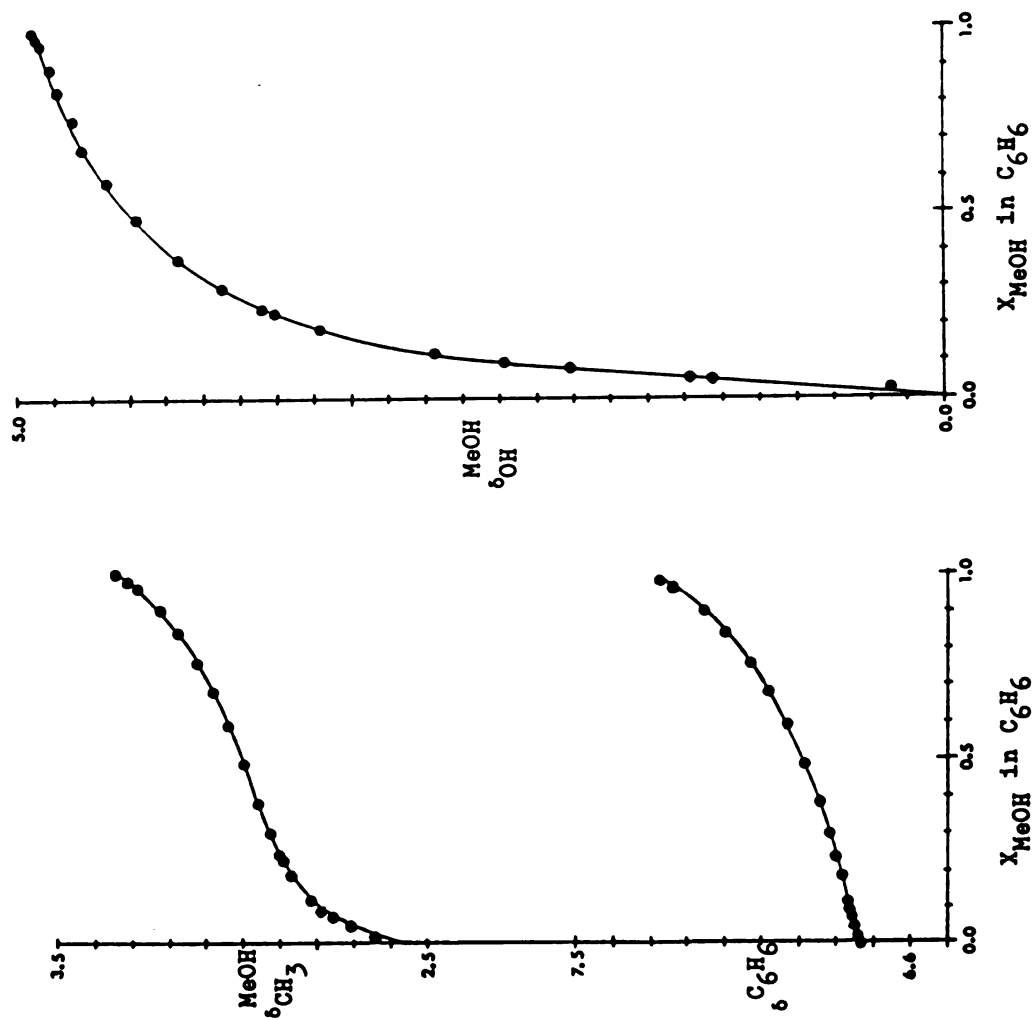


Figure 40. Plots of the proton chemical shifts of benzene and methanol vs. X_{MeOH} .

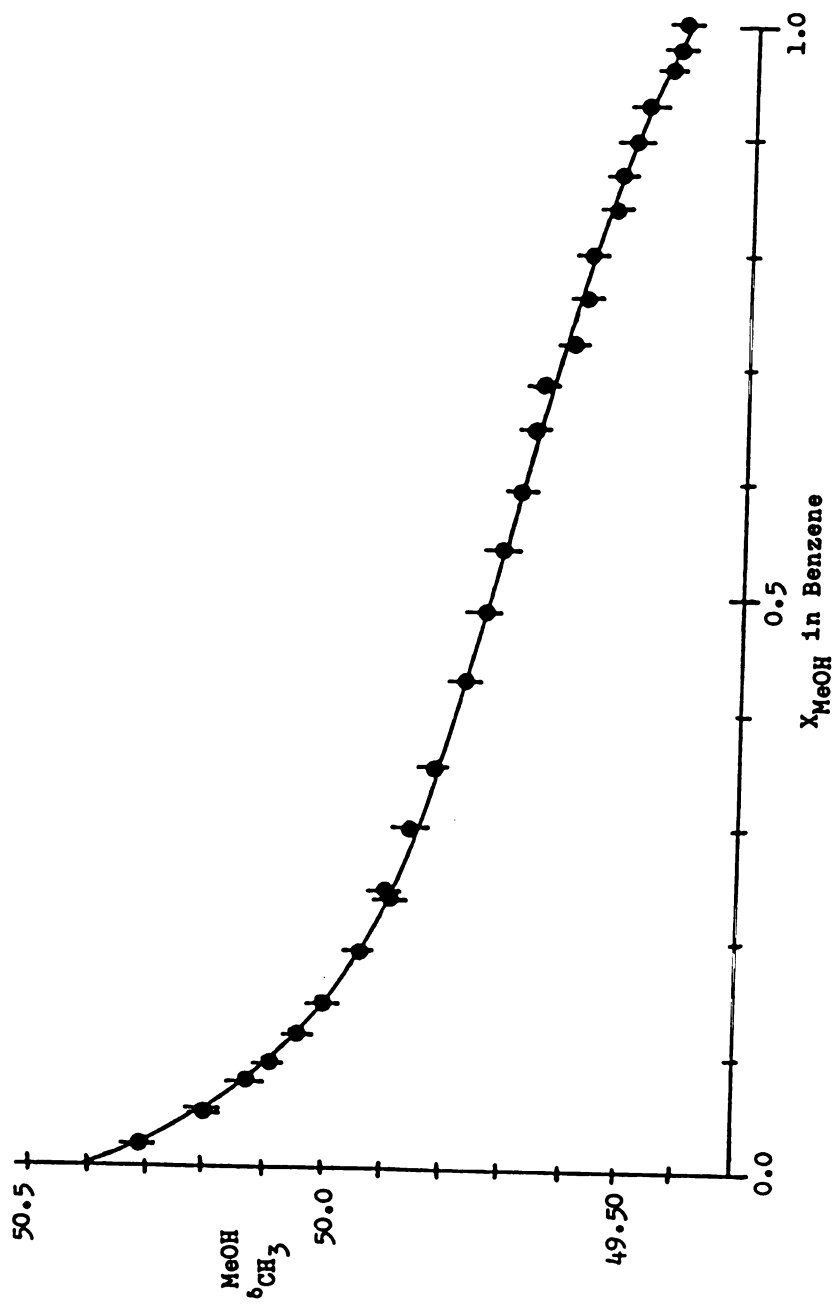
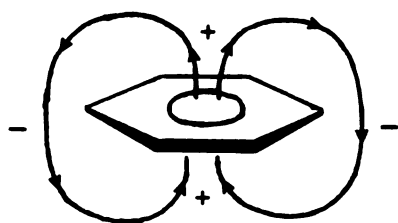
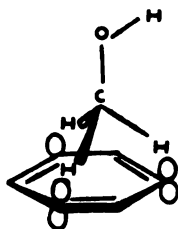


Figure 41. Plot of the carbon- 13 chemical shift of methanol vs. X_{MeOH} in benzene.

chemical shift-concentration plots support an interaction through the methyl group. The curvature obtained for the proton chemical shift data of the methyl group bends in the opposite directions from that obtained for the carbon chemical shift data. This contrasts with the observations in the MeOH-CCl₄ system and may be due to the ring current effect of benzene shown below:



Anything appearing in the "+" region is shifted upfield whereas anything in the "-" region is shifted downfield. The structure shown below would put the methyl protons and carbon in different regions of the benzene ring currents and would account for the opposite chemical shift behavior.

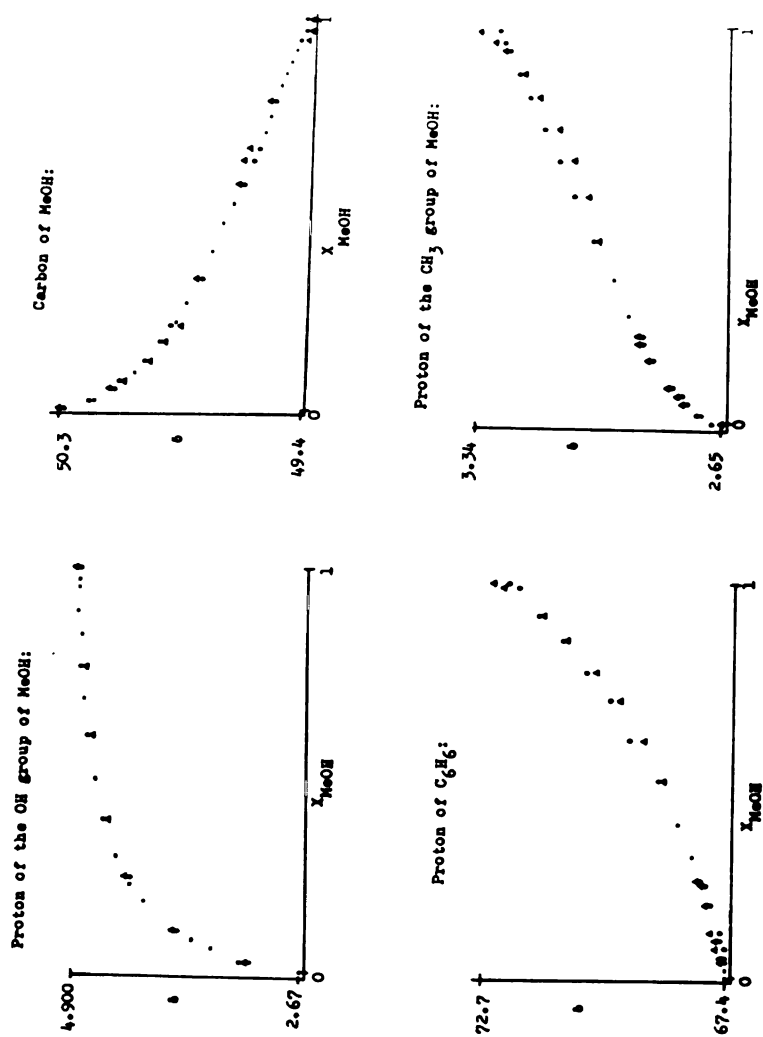


Attempts were made to computer analyze the chemical shift data with multiple data sets. Several models were used. These included formation of (1) S₂, SC and S₂C; (2) S₂, SC and SC₂; (3) S₂, SC, S₂C and SC₂; (4) S₂, S₃, SC, and S₂C; (5) S₂, S₃, SC, S₂C and S₃C; (6) S₂, S₃, SC, S₂C,

S_2C_2 and S_3C and (7) S_2 , S_3 , S_4 , SC , S_2C , S_3C and S_4C . Figure 42 shows a typical graphical output obtained from the computer analysis. The values obtained for the formation constants and chemical shifts were unreasonable and reflect the complexity of the $MeOH-C_6H_6$ system.

C. CONCLUSIONS

As was discussed in the introduction, mixed solvent systems have been widely investigated in the past. The techniques primarily used in these studies have been proton NMR and IR spectroscopy. Although these studies show that multiple equilibria occur in solution, data analysis was difficult due to the comparatively primitive instrumentation then available. Without modern computational facilities, these earlier workers linearized their data in order to obtain equilibrium constants. Consequently the values are suspect. This study primarily utilized carbon-13 NMR spectroscopy to probe solvent-solvent interactions. The chemical shift data clearly show that multiple equilibria occurred in solution. Multiple data sets were used to analyze the data. The equilibrium constants obtained agree with vapor pressure data and better reflect what occurs in solution. From the chemical shift behavior of the solvents it was possible to propose structures for the species occurring in solution.



● means calculated point
 ▲ means experimental point
 — means calculated and experimental points are the same

Figure 42. KINFIT outputs obtained from a multiple data fit of the $\text{MeOH}-\text{C}_6\text{H}_6$ system.

CHAPTER IV

SOLVATION STUDIES

OF

LINEAR AND CYCLIC

POLYETHERS

A. INTRODUCTION

The conformation of a free ligand depends on the medium and temperature, i.e. on its solvation. The extent of ligand solvation is important in understanding the "macrocyclic effect". Ligand solvation also affects metal ion complexation. The purpose of these studies, therefore, was to determine the solvent-dependence of the conformation of some cyclic and linear polyethers such as 18C6, DB18C6, B15C5, TG and DA18C6.

B. RESULTS AND DISCUSSION.

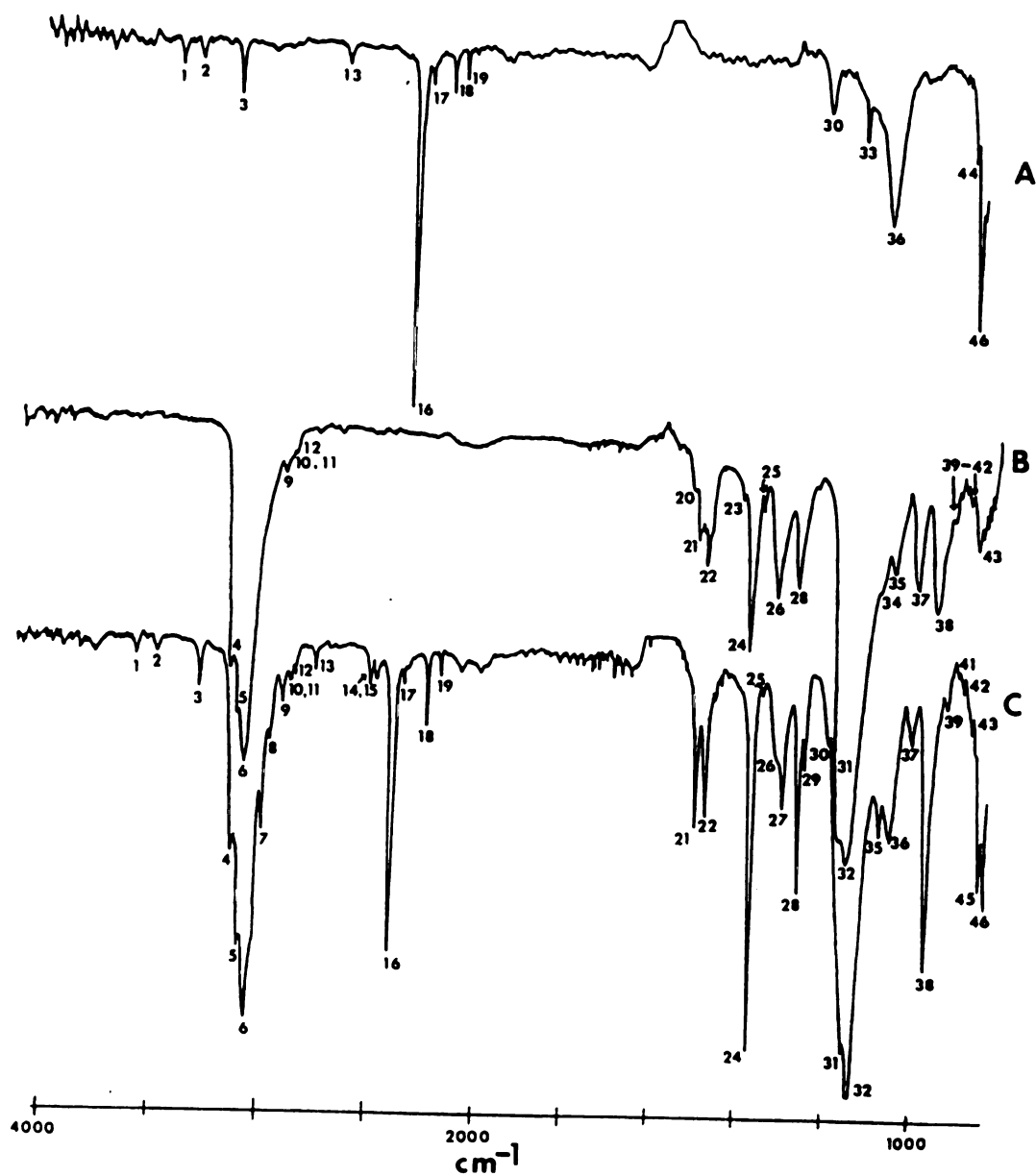
1. SOLVATION STUDIES OF 18-CROWN-6. Carbon-13 NMR concentration studies were carried out for 18C6 in AN, CCl₄, CHCl₃, benzene, AC and MeOH. The carbon-13 chemical shift data are found in Appendix III. In acetonitrile, carbon tetrachloride, benzene and chloroform, the carbon-13 chemical shift is independent of the crown concentration. In methanol, the proton chemical shift of the crown moves upfield with increasing crown concentration; however, the carbon-13 chemical shift of 18C6 does not vary with concentration. In acetone the crown carbon-13 chemical shift shifts upfield with increasing crown concentrations. A ¹³C study of acetone in acetone-benzene-18C6 systems (discussed in Chapter V) shows that the chemical shifts of the carbonyl and methyl carbons of acetone change upon the addition of 18C6. It

can, therefore, be concluded that acetone weakly complexes 18C6 and that this complexation is reflected by the concentration dependence of the crown chemical shift in acetone.

The chemical shifts of methanol, acetone and chloroform vary with crown concentration. These changes in chemical shift are indicative of perturbations of the solvent structure. This, in turn, implies interactions between these solvents and 18C6.

Figure 43 shows infrared spectra of solutions of AN-d₃, 18C6, and 18C6 and AN-d₃ in carbon tetrachloride. The assignments of the observed vibrations are tabulated in Table 13. Infrared spectra of 18C6 in CCl₄, benzene, chloroform and in a solution of AN-d₃ in CCl₄ are shown in Figure 44. The spectra indicate that the conformation of 18C6 is strongly solvent dependent. The infrared spectra of 18C6 in CCl₄ and benzene match the spectrum of liquid 18C6 at 50°C obtained by Dale and Kristiansen (136) whereas the spectrum of 18C6 and AN-d₃ in CCl₄ matches that of the crystalline KBr·18C6 complex (136). The spectrum of 18C6 in chloroform lies between the two.

At 50°C, liquid 18C6 exists as a mixture of conformers (136). Very likely, the same should be true of 18C6 solutions in CCl₄ and in benzene. In the crystalline KBr·18C6 complex, the crown has approximate D_{3d} symmetry. It can, therefore, be assumed that in CCl₄ solutions,



- (A) 0.86 M AN-d₃
 (B) 0.075 M 18C6
 (C) 0.93 M AN-d₃; 0.071 M 18C6

Figure 43. Infrared spectra of solutions of AN-d₃ and 18C6 in carbon tetrachloride.

Table 13. Assignments of the Infrared Bands for Solutions of Acetonitrile-d₃ and 18-Crown-6 in Carbon Tetrachloride.

BAND NUMBER	0.86 M AN-d ₃ ^a	0.075 M 18C6	0.93 M AN-d ₃ 0.071 M 18C6	ASSIGNMENT AND SYMMETRY
1	3377		3378	
2	3280		3283	
3	3100		3100	
4		2945	2952	
5		2910	2915	
6		2873	2886	CH ₂ stretching (asymmetrical and symmetrical)
7			2828	
8			2800	$\nu_{as} > \nu_s$
9		2745	2747	
10		2718	2720	
11		2718	2710	
12		2700	2693	
13	2608		2607	

Table 13. Continue.

BAND NUMBER	0.86 M AN-d ₃	0.075 M 18C6	0.93 M AN-d ₃ 0.071 M 18C6	ASSIGNMENT AND SYMMETRY
14			2366	
15			2340	
16	2266		2269	ν_2 =CN stretch (A_1)
17	2216		2218	ν_5 =CD stretch (E)
18	2115		2118	ν_1 =CD stretch (A_1)
19	2060		2060	$2\nu_6$ where ν_6 is CD ₃ deformation (E)
20		1484		
21		1471	1475	CH ₂ internal deformation
22		1450	1455	(scissoring)
23		1376		
24		1353	1354	CH ₂ wagging
25		1332	1334	
26		1295	1300	CH ₂ twisting
27			1286	
28		1250	1252	

Table 13. Continue.

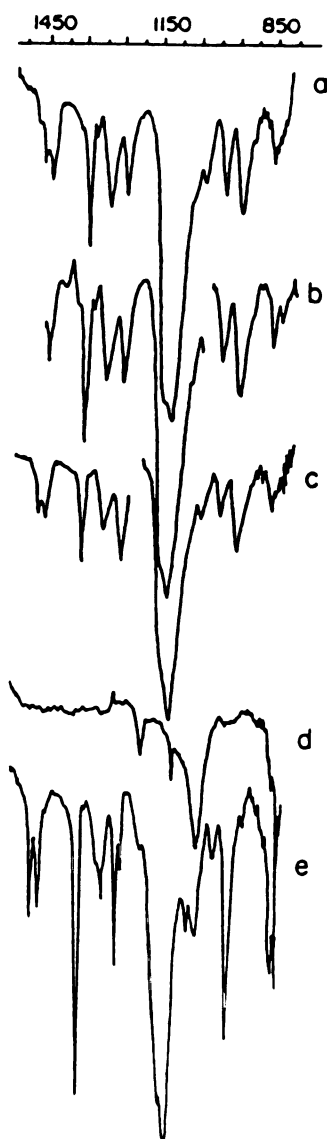
BAND NUMBER	0.86 M AN-d ₃ ^a	0.075 M 18C6	0.93 M AN-d ₃ 0.071 M 18C6	ASSIGNMENT AND SYMMETRY
29			1238	CH ₂ twisting
30	1188		1187	$\nu_7 + \nu_8$ where ν_7 is CD ₃ rock (E) and ν_8 is CCN bend (E)
31		1143	1138	C-O-C stretch
32		1127	1125	
33	1105			$\nu_3 = \text{CD}_3$ deformation (A ₁)
34		1073	1065	skeletal stretching and CH ₂ rocking
35		1045		
36	1040		1042	$\nu_6 = \text{CD}_3$ deformation (E)
37		990	994	
38		947	964	skeletal stretching and
39		917	918	CH ₂ rocking
40		905		
41		892	894	
42		880	884	

Table 13. Continue.

BAND NUMBER	0.86 M AN-d ₃ ^a	0.075 M 18C6	0.93 M AN-d ₃ 0.071 M 18C6	ASSIGNMENT AND SYMMETRY
43		868	865	skeletal stretching and CH ₂ rocking
44	849			ν_7 =CD ₃ rock (E)
45			847	CH ₂ rocking of 18C6
46	833		836	ν_4 = CC stretch (A ₁) of AN-d ₃

152

^aFrequencies are in cm⁻¹. **D**igital resolution is 2 cm⁻¹. Spectra are shown in Figures



- (a) 0.0749 M 18C6 in carbon tetrachloride
- (b) 0.07 M 18C6 in benzene
- (c) 0.0443 M 18C6 in chloroform
- (d) 0.8649 M AN-d₃ in carbon tetrachloride
- (e) 0.0711 M 18C6 and 0.9262 M AN-d₃ in carbon tetrachloride

Figure 44. Infrared spectra of 18C6 from 1500-800 cm^{-1} .

AN-d₃ complexes 18C6 and that the conformation of the crown in that complex is close to the D_{3d} symmetry. The infrared spectra show that, while neither CCl₄ or benzene complex 18C6, there is a weak interaction between 18C6 and chloroform.

2. VISCOSITIES OF SOLUTIONS OF 18-CROWN-6. The property that characterizes a fluid's resistance to flow is its viscosity, η . The viscosities of liquids are influenced by the molecular shape. Liquids with long chains are highly viscous because the chains become tangled with one another hindering flow. Strong intermolecular attractions in a liquid will also hinder flow and make the viscosity, η , large (198). Therefore, the addition of 18C6 to a solvent should change the structure of that solvent especially if the crown complexes that solvent. This in turn will be reflected in a change in the solvent viscosity. Consequently, the change in viscosity could be a measure of the "solvation" of the crown.

The crown ether, 18C6, can be thought of as a polymer composed of six $(-O-CH_2CH_2-)$ monomer linkages. The viscosity of a polymer solution depends on the size and shape (and hence on the molecular weight and the degree of compactness) of the polymer molecules in the solution. The viscosities of polymer solutions can be treated as follows. The relative viscosity is defined as the ratio

of the viscosity of a solution to that of the pure solvent, η/η_0 . Einstein showed that the viscosity of a dilute solution of uniformly suspended small rigid spheres is related to the viscosity η_0 of the pure solvent by the expression:

$$\frac{\eta}{\eta_0} - 1 = \frac{5}{2} \frac{v}{V} \quad [9]$$

where v is the volume occupied by all the spheres and V is the total volume. The quantity $(\eta/\eta_0 - 1)$ is called the specific viscosity η_{sp} .

The intrinsic viscosity, denoted by $[\eta]$, is defined as the ratio of the specific viscosity to the weight concentration of solute, in the limit of zero concentration:

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c = \lim_{c \rightarrow 0} \left(\frac{1}{c} \ln \eta/\eta_0 \right) \quad [10]$$

where c is usually defined as the concentration in grams of solute per 100 ml of solution. The intrinsic viscosity depends upon the molecular weight of the polymer as shown by the Houwink Law:

$$[\eta] = aM^b \quad [11]$$

where M is the molecular weight and a and b are empirical parameters characteristic of both the polymer itself and the solvent. The exponent b varies from about 0.5, for well-coiled polymer molecules in a poor solvent, to as

much as 1.7, for a rigidly extended "rod-like" polymer molecule. The constant a usually lies between 10^4 and 10^7 for concentrations measured in g/ml (199, 186). Therefore, the intrinsic viscosity can be thought of as a measurement of the solvation of the crown.

The viscosities of 18C6 in acetonitrile, water and carbon tetrachloride were measured and treated using equations [9]-[11]. Plots of η vs. M_{18C6} and η_{sp}/c vs. c_{18C6} are shown in Figures 45-47. The curvature of the η vs. M_{18C6} plots is very solvent dependent. For both AN and water, the viscosity of the solvent gradually increases with the addition of 18C6. In carbon tetrachloride, however, the viscosity of the solution sharply increases between 0.0 and 0.2 M and then levels off. Previous studies have shown that both water and acetonitrile are structured solvents. Furthermore, it has been shown that water and acetonitrile form complexes with 18C6. On the other hand, carbon tetrachloride is not a structured solvent. Furthermore, the infrared studies discussed earlier indicate that 18C6 forms no complexes with carbon tetrachloride.

The addition of 18C6 to either water or acetonitrile should break up the structure of these solvents. One would, therefore, expect the viscosity of these solvents to decrease with the addition of 18C6. However, the viscosity of the solutions slightly increases which may

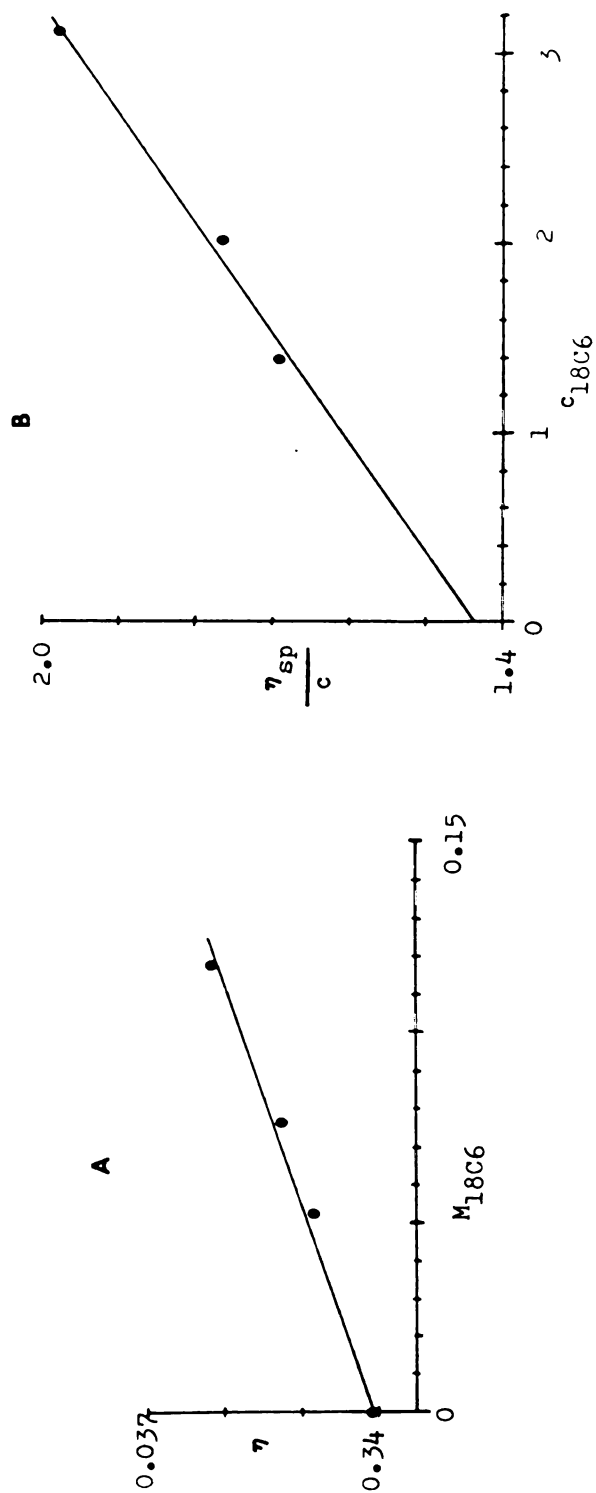


Figure 45. Plots of the viscosity data for solutions of 18C6 in acetonitrile at 26°C:
 (A) Plot of η vs. M_{18C6} .
 (B) Plot of η_{sp}/c vs. c_{18C6} (c has the units g/100 ml).

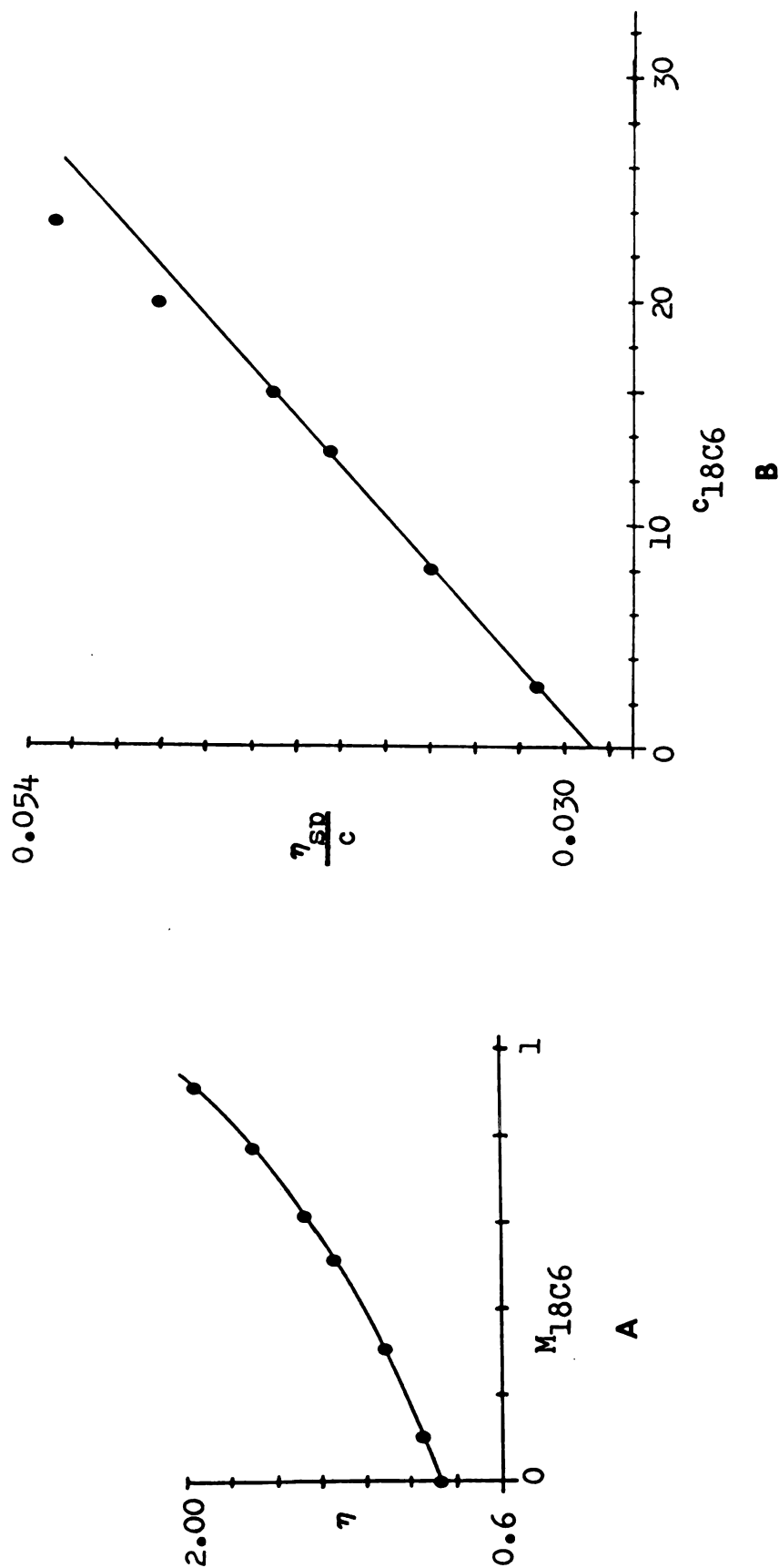


Figure 46. Plots of the viscosity data for solutions of 18C6 in water at 26°C:
 (A) Plot of η vs. M_{18C6} .
 (B) Plot of η_{sp}/c_{18C6} (c has units of g/100 ml).

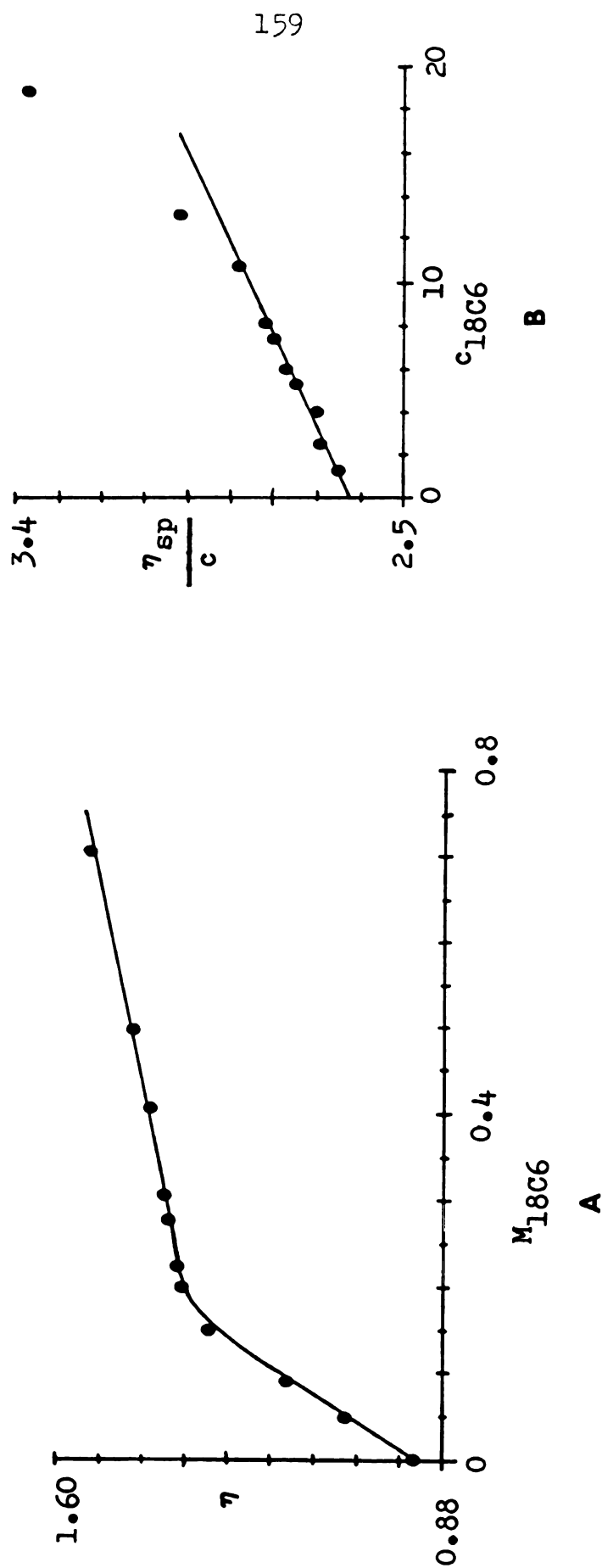


Figure 47. Plots of the viscosity data for solutions of 18C6 in carbon tetrachloride at 26°C:

(A) Plot of η vs. M_{18C6} .

(B) Plot of η_{sp}/c vs. c_{18C6} (c has units of g/100 ml).

indicate that the complexation of 18C6 with both water and acetonitrile reinforces the structure of these systems. The sharp increase in the viscosity of CCl_4 with the addition of 18C6 is not due to CCl_4 -18C6 interactions. Because of the fairly low crown concentrations, it is unlikely that the increase in viscosity is due to weak hydrogen-bonding between the crown molecules, although Smetana (200) did show that 18C6 forms an adduct with 12C4. Therefore such ligand-ligand interactions in solution are not unlikely.

The plots of η_{sp}/c vs. c are linear at low concentrations. This is to be expected since the relationships used only apply to dilute solutions. From these plots, the intrinsic viscosities, $[\eta]$, of 18C6 at 26°C in water, AN and CCl_4 were evaluated:

$$[\eta]_{\text{H}_2\text{O}}^{26^\circ\text{C}} = 2.893 \times 10^{-2}$$

$$[\eta]_{\text{AN}}^{26^\circ\text{C}} = 1.437 \times 10^{-2}$$

$$[\eta]_{\text{CCl}_4}^{26^\circ\text{C}} = 2.621 \times 10^{-2}$$

No conclusions can be made regarding the physical significance of these values of intrinsic viscosities. However, if one measured the viscosities of several crown analogues; e.g., 12C4, 15C5, 21C7, etc.; and the viscosities of the corresponding linear polyethers,

perhaps more definite conclusions could be made. The intrinsic viscosity is defined as:

$$[\eta] = aM^b \quad [11]$$

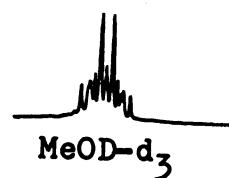
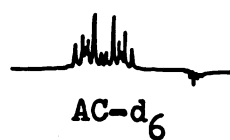
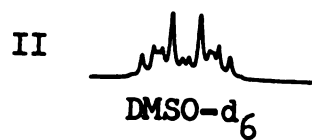
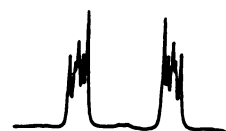
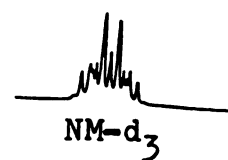
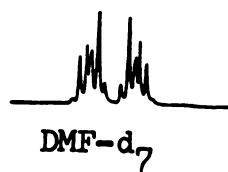
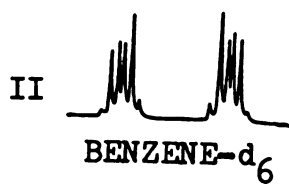
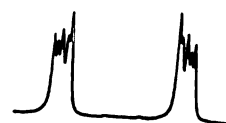
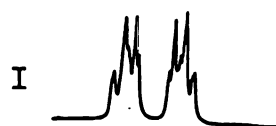
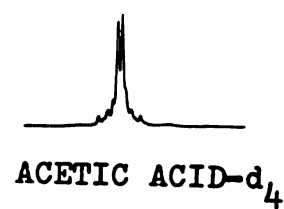
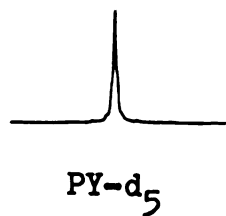
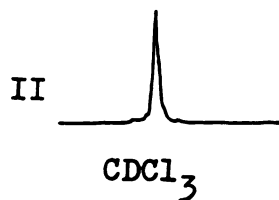
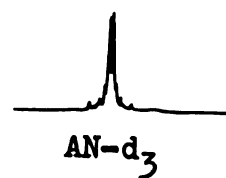
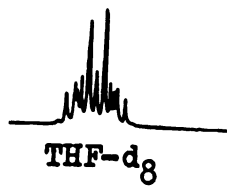
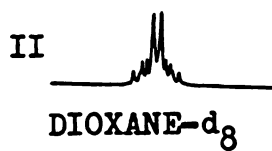
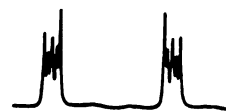
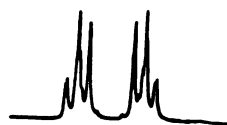
where M is the molecular weight of the solute and a and b are empirical parameters. Taking the natural logarithm of both sides gives:

$$\ln[\eta] = \ln a + b \ln M \quad [12]$$

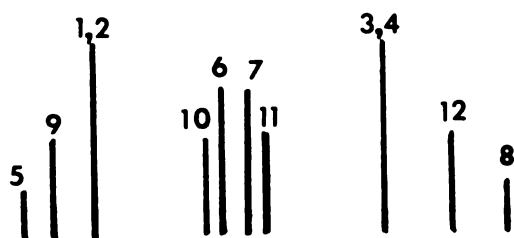
which implies that a plot of $\ln [\eta]$ vs. $\ln M$ should be linear with slope b and intercept $\ln a$. By measuring an analogous series of crown ethers, the a and b parameters could be evaluated. Comparisons between solvents and ligand types could then be made.

3. SOLVATION OF DIBENZO-18-CROWN-6. Figure 48 shows proton spectra of the ether and aromatic protons of DB18C6 in several deuterated solvents. The ether protons of DB18C6 are characterized by the presence of two multiplets corresponding to the AA'BB' spin system. A simpler subcase of the AA'BB' spin system is the AA'XX' spin system. In the AA'XX' spin system, the chemical shift, δ , between A and X is large compared to the coupling, J. In this system, ten lines are observed as shown in Figure 49. These lines are defined by four "coupling constants" K, L, M and N, which in turn are defined by the vicinal couplings, J_{AX} and $J_{AX'}$, and geminal couplings, $J_{AA'}$ and

Figure 48 . Proton spectra of DB18C6 in several deuterated solvents. In these spectra I and II refer to the ether and aromatic protons of DB18C6, respectively.



General case:



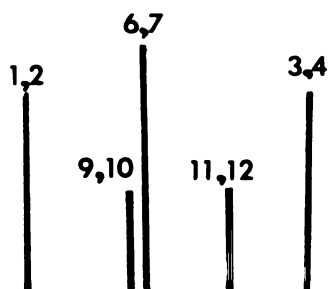
$$K = J_{AA'} + J_{XX'} = (\nu_5 - \nu_6) \text{ or } (\nu_7 - \nu_8)$$

$$L = J_{AX} - J_{AX'}$$

$$M = J_{AA'} - J_{XX'} = (\nu_9 - \nu_{10}) \text{ or } (\nu_{11} - \nu_{12})$$

$$N = J_{AX} + J_{AX'} = (\nu_{1,2} - \nu_{3,4})$$

M=0 subcase:

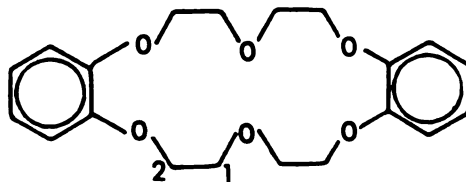


M small subcase:



Figure 49. Couplings of the special subcases of the AA'XX' spin system.

Table 14. Proton Chemical Shift Data for Solutions of DB18C6 in Several Deuterated Solvents.



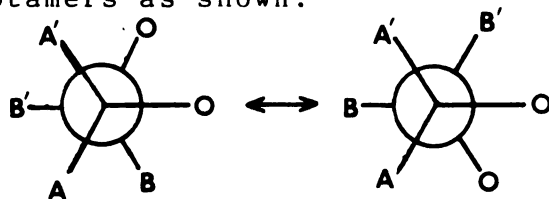
SOLVENT	^a		^b
	δ_1	δ_2	δ_{aromatic}
Py-d ₅	3.91	4.28	7.11
AcOD-d ₃	4.06	4.20	6.92
Dioxane-d ₈	3.98	4.11	6.88
THF-d ₈	4.04	4.16	6.92
DMF-d ₇	3.96	4.19	6.98
MeOD-d ₃	3.93	4.12	6.88
AN-d ₃	3.87	4.11	6.92
AC-d ₆	3.98	4.16	6.92
DMSO-d ₆	3.87	4.09	6.93
NM-d ₃	3.88	4.12	6.90
CDCl ₃	4.03	4.17	6.88
C ₆ D ₆	3.80	3.91	6.81

^aChemical shifts are reported relative to TMS in acetone-d₆ in ppm. Uncertainty in the chemical shifts is ± 0.01 ppm.

^bThe chemical shift reported is the center of the multiplets.

$J_{XX'}$. Depending on the magnitudes of the coupling constants, special cases of the $AA'XX'$ spin system are observed. From Figure 48, it can be seen that two special cases are observed for the ether protons of DB18C6 -- "M=0" and "M small". Figure 49 illustrates the splitting pattern observed for these two cases. The "M=0" case is observed in $AN-d_3$, $NM-d_3$ and $MeOD-d_3$ whereas the "M small" case is observed for 1,4-dioxane- d_8 , THF- d_8 , $CDCl_3$, $Py-d_5$, Acetic acid- d_4 , benzene- d_6 , DMF- d_7 and $AC-d_6$.

These results are in agreement with those obtained by Live and Chan (129). These authors measured the coupling constants of the ether protons of DB18C6, both free and complexed by KSCN, in acetone- d_6 . According to their results, the ether multiplet of uncomplexed DB18C6 in acetone- d_6 is typical of what is observed for a XCH_2CH_2Y fragment undergoing rapid rotamer conversion. From their coupling constants, they concluded that the ether fragments are undergoing conversion between the syn- and anti-gauche rotamers as shown:



Therefore, in the "M small" case, the ether fragments are in an all gauche configuration with rapid conversion between the anti- and syn-gauche rotamers. When KSCN is added to the DB18C6-acetone- d_6 system, the ether

multiplet observed belongs to the "M=0" case of the AA'XX' spin system. The changes observed in the proton spectrum upon addition of KSCN obviously result from the complexation of DB18C6 by K^+ . Since the splitting pattern of the ether protons in such solvents as $NM-d_3$, $AN-d_3$ and $MeOD-d_3$ is similar to that obtained for the K^+ complex of DB18C6 in acetone- d_6 , it can be concluded that the ether protons in these solvents have the same conformation as the ether protons in the K^+ complex. The x-ray structure of the Na^+ and Rb^+ complexes with DB18C6 show that the six oxygen atoms of DB18C6 are nearly coplanar. A coplanar conformation in polar solvents has also been proposed by Grunwald and Ting-Po I (133) from their dipole moment measurements.

The splitting patterns of the aromatic protons of DB18C6 are more difficult to explain. The multiplets of the aromatic protons are also characteristic of a four-spin AA'BB' coupled system. As Figure 48 illustrates, in solvents like acetone- d_6 , the splittings of the aromatic protons are well resolved and spread out. In other solvents such as THF- d_8 and DMF- d_7 , some of the peaks are lost. However, in $CDCl_3$ and $AN-d_3$ the peaks have collapsed upon one another. The exact nature of this complex coupling behavior of the aromatic rings will be discussed in greater detail later.

Dynamic proton NMR studies of DB18C6 in $CDCl_3$, $NM-d_3$,

AN-d₃ and DMF-d₇ were conducted at room temperature and higher. Figures 50-53 show the proton spectra obtained for the ether and aromatic protons as a function of temperature. No conformational change is observed for the ether protons of DB18C6 in CDCl₃ and NM-d₃. In AN-d₃, a conformational change appears to be occurring near 56°C. However, a conformational change does occur in DMF-d₇ with a coalescence temperature between 36 and 47°C. No significant changes were observed for the aromatic protons of DB18C6 with increasing temperature in either solvent.

The solvation of DB18C6 was also studied by carbon-13 NMR spectroscopy in several solvents. Dibenzo-18-crown-6 has five nonequivalent carbon atoms. Figure 54 shows a typical carbon-13 spectrum of DB18C6 and the chemical shift assignments. The results shown in Table 15 indicate that the carbon-13 chemical shifts are solvent dependent. Likewise the difference in the carbon-13 chemical shifts of the ether carbons, ($\delta_2 - \delta_1$), and the aromatic carbons, ($\delta_5 - \delta_4$), is also solvent dependent. The more acidic the solvent, the greater the splittings of the carbon-13 resonances of DB18C6. A plot of ($\delta_2 - \delta_1$) vs. ($\delta_5 - \delta_4$) is shown in Figure 55. For the solvents studied, the plot is linear.

The carbon-13 chemical shifts of DB18C6 were measured in acetonitrile and nitromethane-d₃ as a function of temperature. The results are plotted in Figures 56 and

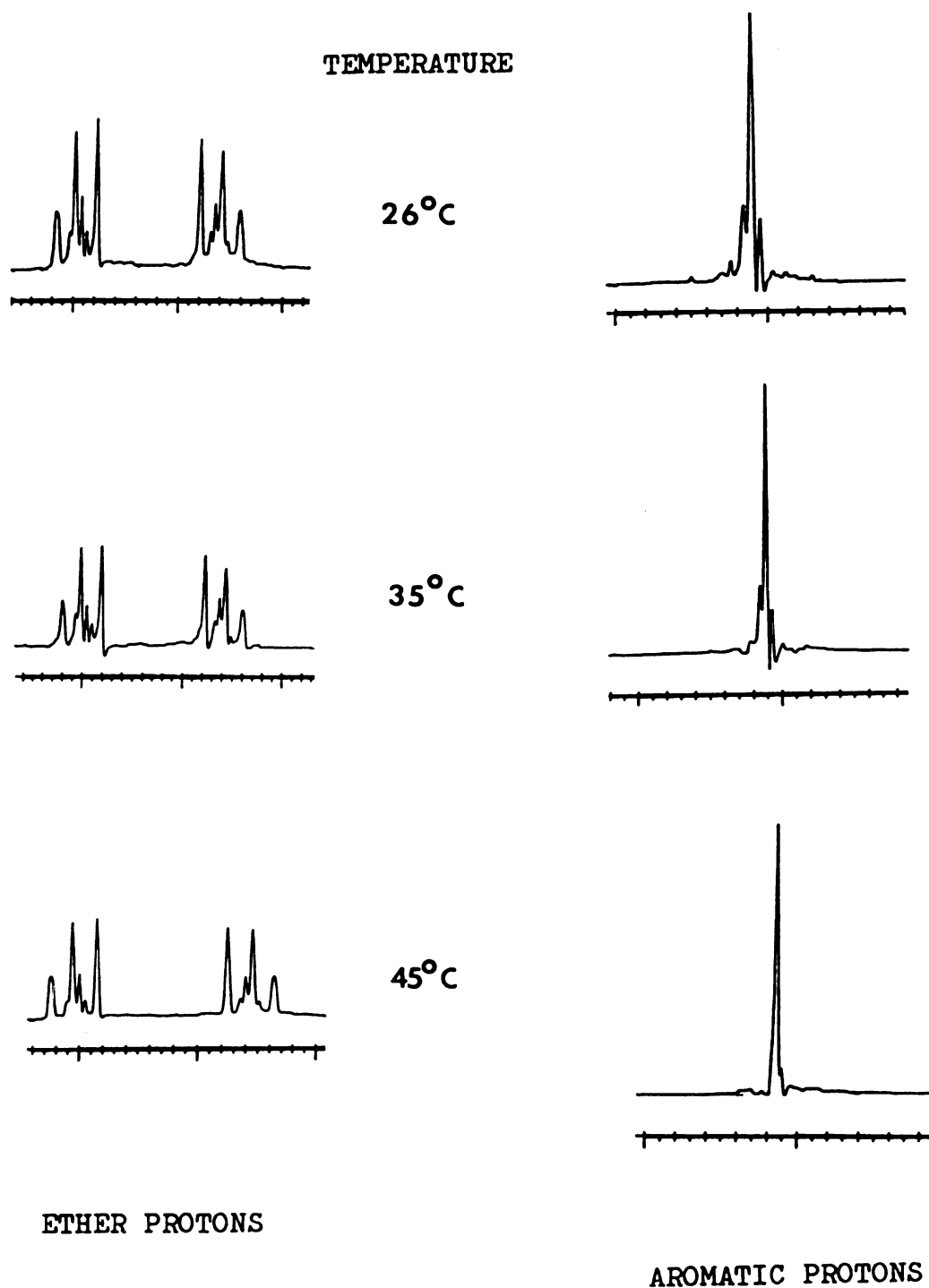


Figure 50. Proton spectra of DB18C6 in CDCl_3 as a function of temperature.

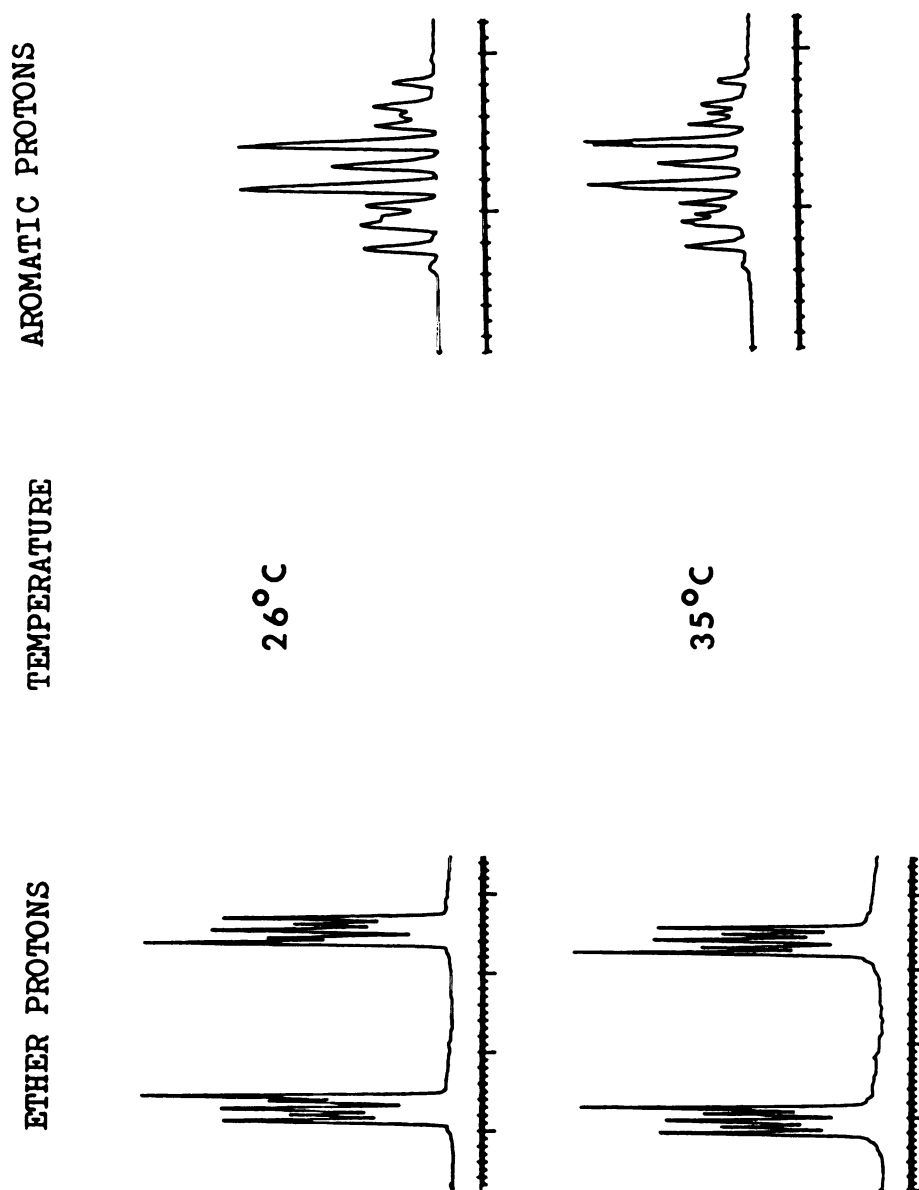


Figure 51 . Proton spectra of DB18C6 in NM-d_3 as a function of temperature.

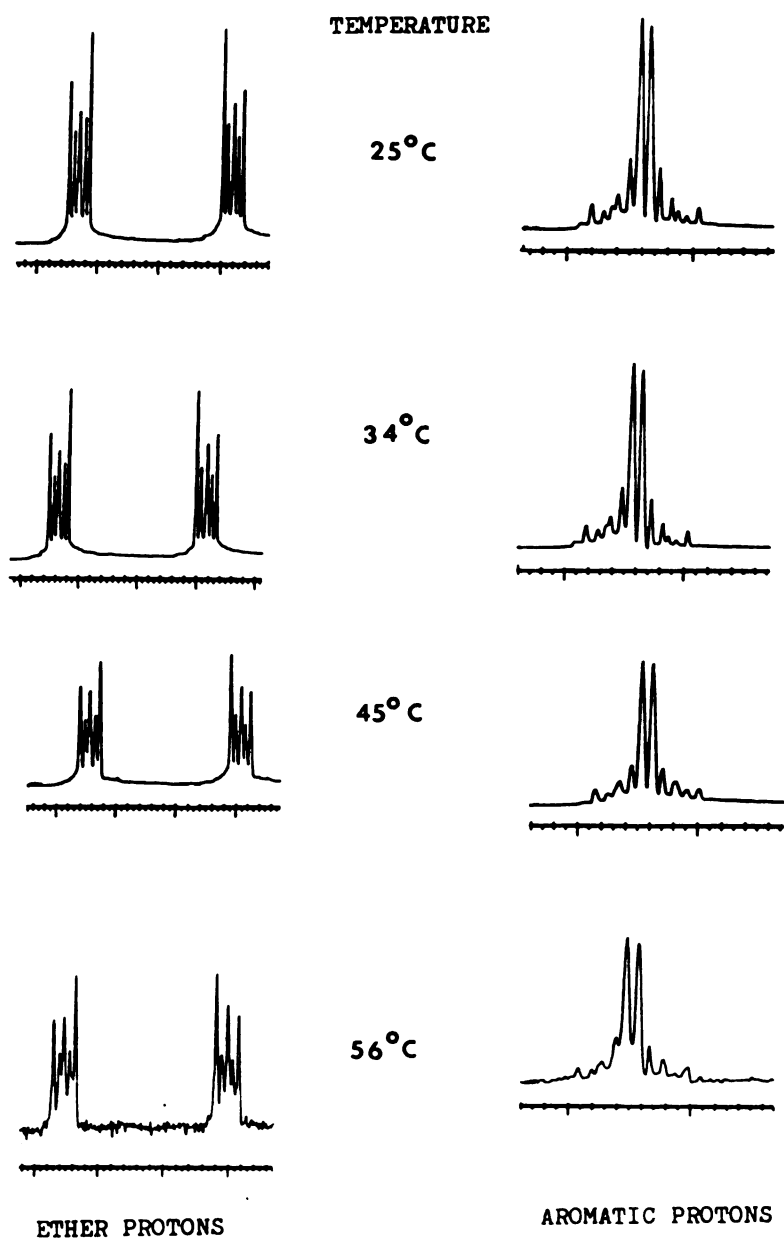


Figure 52. Proton spectra of DB18C6 in AN-d₃ as a function of temperature.

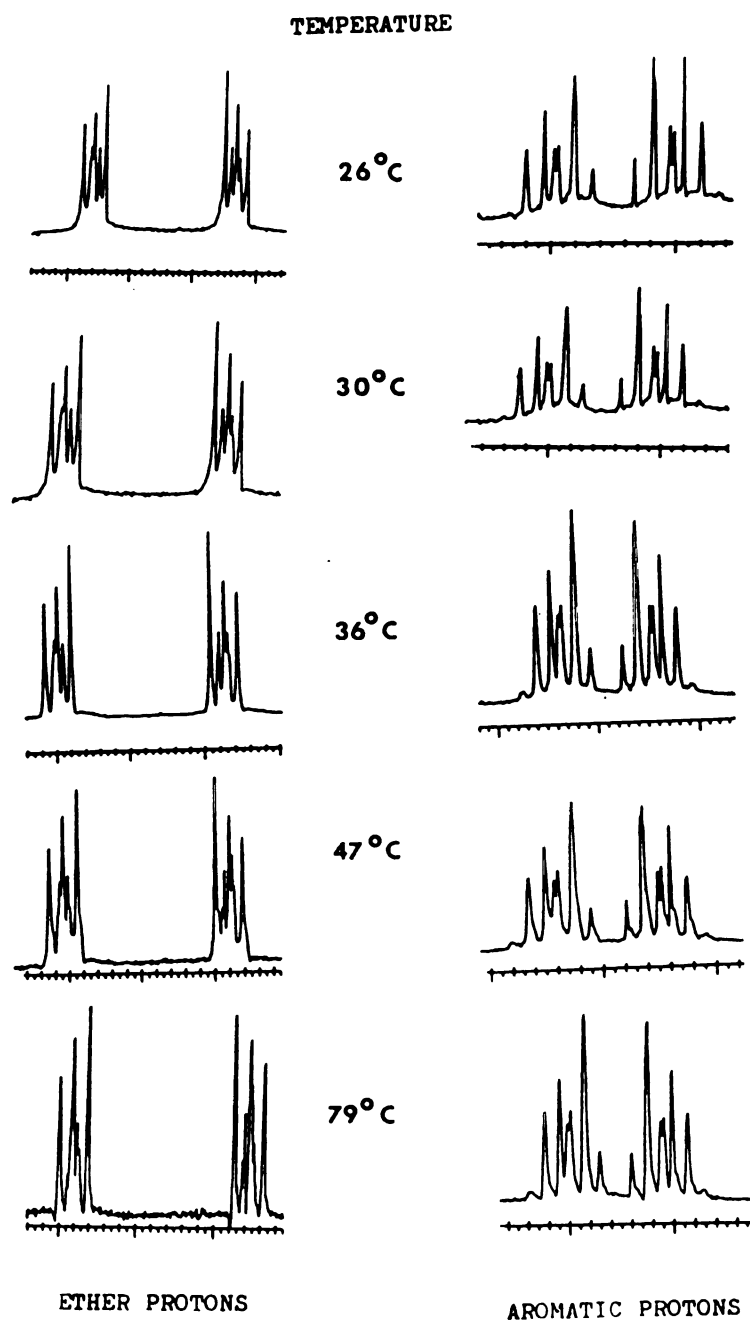


Figure 53 Proton spectra of DB18C6 in DMF-d₇ as a function of temperature.

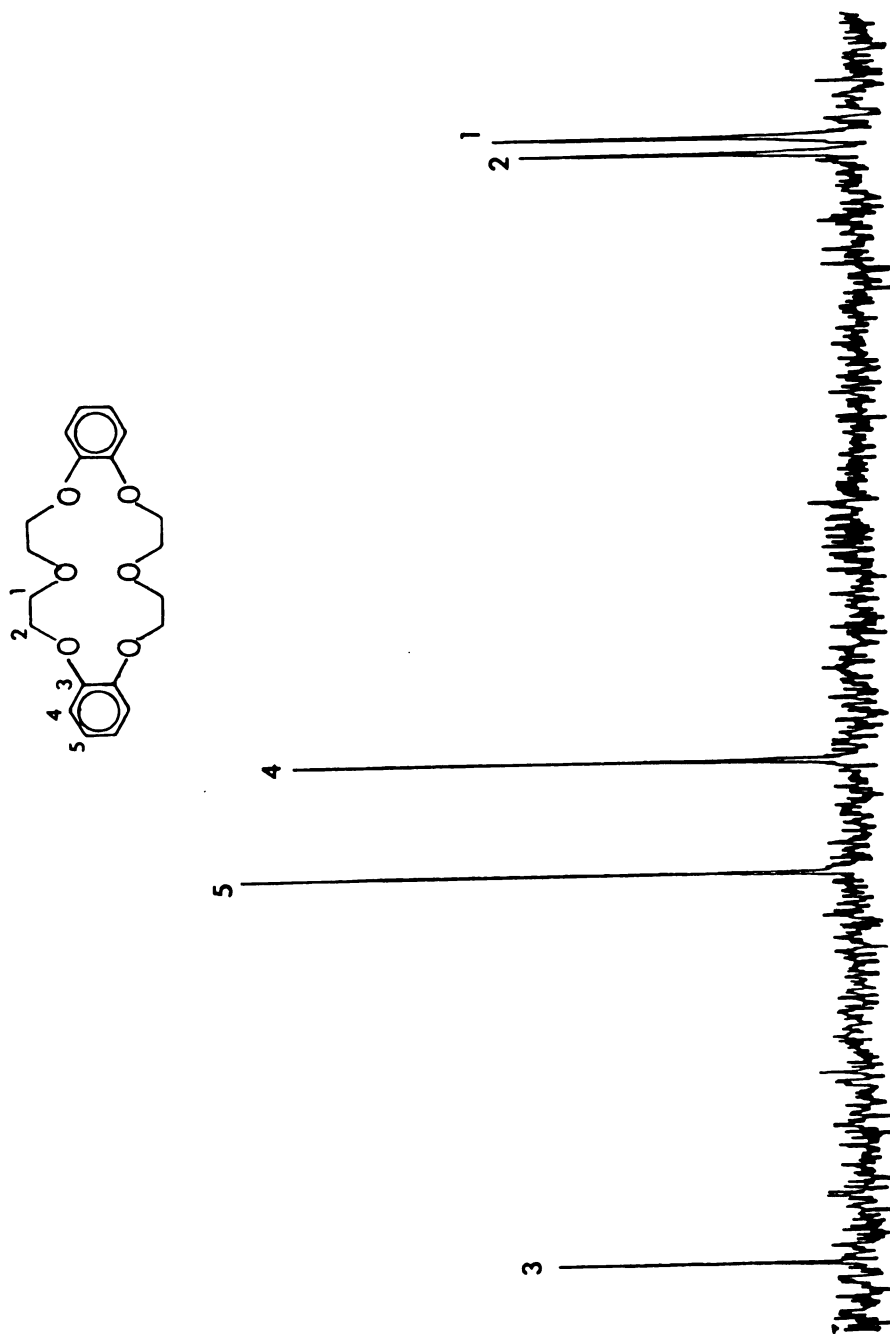
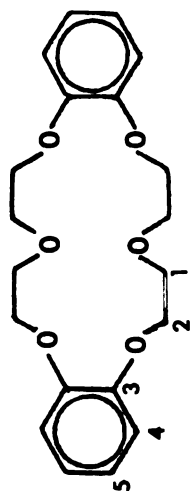


Figure 54. Carbon-13 spectrum of dibenzo-18-crown-6 in dimethylformamide.

Table 15. The Effect of Solvent on the Carbon-13 Chemical Shifts of Dibenzo-18-Crown-6.



SOLVENT ^c	$\delta_1^{a,b}$	δ_2	δ_3	δ_4	δ_5	$(\delta_2 - \delta_1)$	$(\delta_5 - \delta_4)$
MeCN	68.37	70.06	148.95	112.76	121.59	1.69	8.84
DMF	68.89	70.09	149.25	113.47	121.39	1.21	7.92
AC-d ₆	70.44	71.32	150.72	115.38	122.69	0.88	7.31
CDCl ₃	69.98	71.01	149.86	114.99	122.37	1.03	7.38
C ₆ H ₆	69.13	70.13	149.75	113.83	121.40	1.00	7.57
DMSO	69.06	70.41	149.46	113.93	122.22	1.35	8.29
p-Dioxane	69.77	70.66	150.08	114.53	121.76	0.88	7.23
PC	68.71	-----	149.28	113.59	121.72	-----	8.13
THF	69.82	70.63	150.05	114.44	121.56	0.81	7.12

^aChemical shifts are reported relative to TMS in acetone-d₆ in ppm.

^bUncertainty in the chemical shifts is ± 0.03 ppm.

^cConcentration of DB18C6 ≤ 0.05 M.

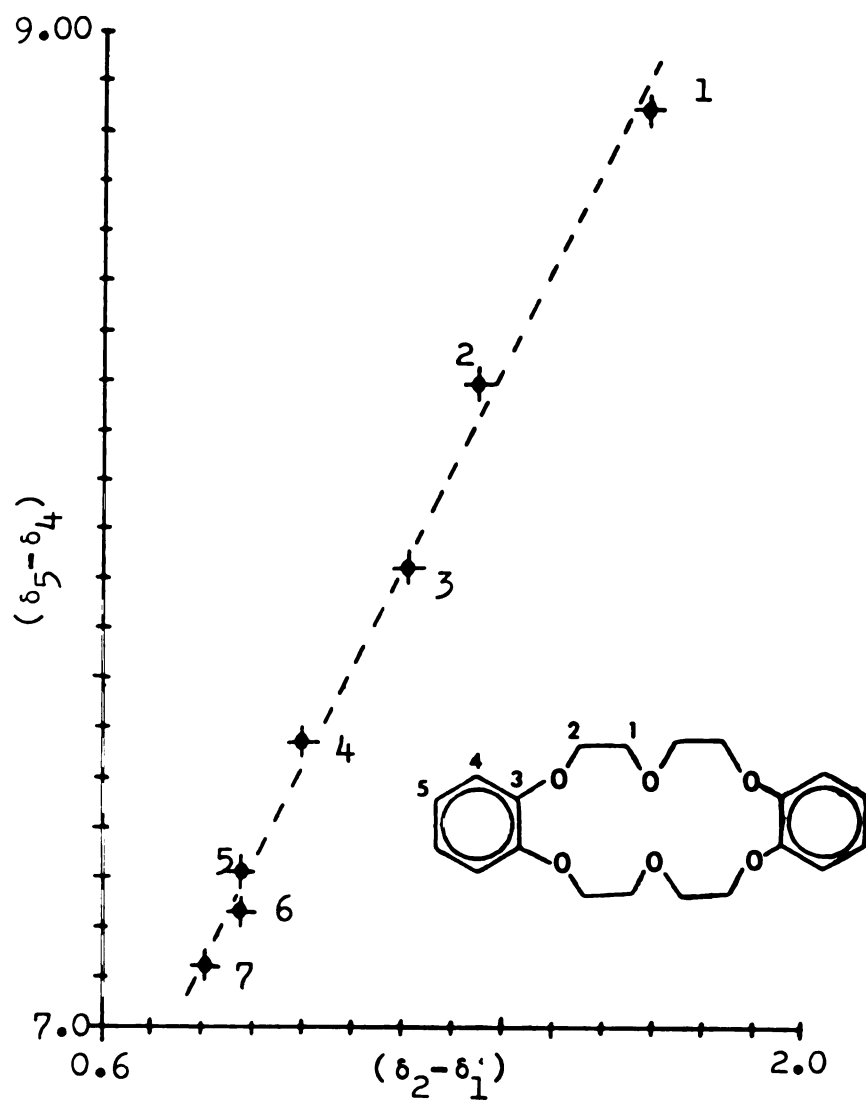


Figure 55. Plot of $(\delta_5 - \delta_4)$ vs. $(\delta_2 - \delta_1)$ of DB18C6 for solutions of DB18C6 in the following solvents: (1) AN, (2) DMSO, (3) DMF, (4) Benzene, (5) AC-d₆, (6) 1,4-Dioxane and (7) THF.

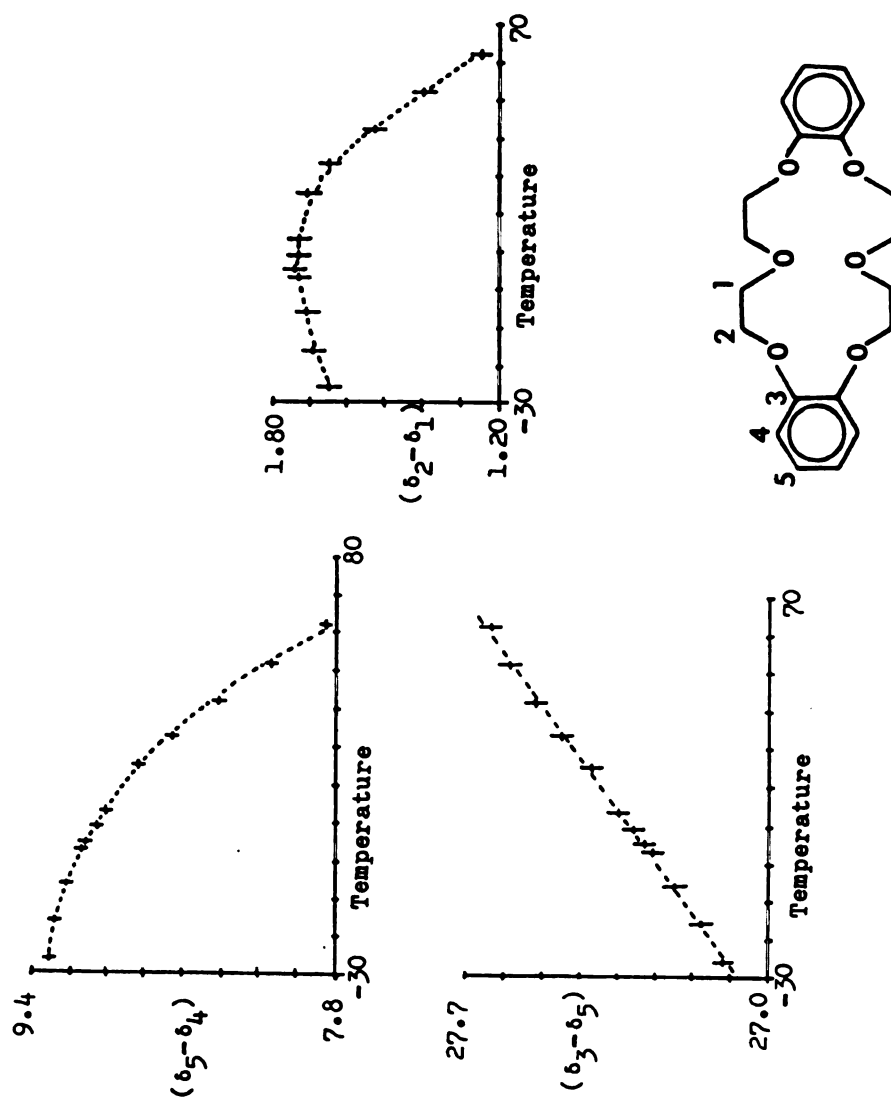


Figure 56. Plots of $(\delta_3 - \delta_5)$, $(\delta_2 - \delta_1)$ and $(\delta_5 - \delta_4)$ vs. temperature (in $^{\circ}\text{C}$) for DB18C6 in acetonitrile.

57. The results clearly show that the carbon-13 chemical shifts of DB18C6 are temperature dependent. If the change in chemical shifts is reflective of DB18C6 going from one conformation to another, one would expect a plot of $\Delta\delta$ vs. T, (where $\Delta\delta$ refers to either $(\delta_2 - \delta_1)$, $(\delta_5 - \delta_4)$ or $(\delta_3 - \delta_5)$ and T to temperature) to be monotonic. This is true of the $(\delta_5 - \delta_4)$ vs. T and $(\delta_3 - \delta_5)$ vs. T plots, where δ_4 , δ_5 and δ_3 are the carbon-13 chemical shifts of the aromatic rings. However, the $(\delta_2 - \delta_1)$ vs. T plots are not monotonic. The carbon-13 chemical shifts δ_2 and δ_1 are those of the ether oxygens. This discrepancy may be indicative of either (1) a conformational change between three or more conformers or (2) an interaction between the ether oxygens and the solvent as well as a change in conformation. The latter possibility is probably the more likely explanation. The $\Delta\delta$ vs. T plots for the aromatic carbons imply a change from one conformation to another. Therefore, the $\Delta\delta$ vs. T plots for the ether carbons should reflect a conformational change. The fact that the plots for the ether carbons are not monotonic suggests that something else is occurring in solution -- probably a specific solvent-ligand interaction.

4. SOLVATION STUDIES OF BENZO-15-CROWN-5. Proton spectra were measured for B15C5 in several deuterated solvents. These spectra are shown in Figure 58 and are very similar to those obtained for DB18C6 (Figure 48).

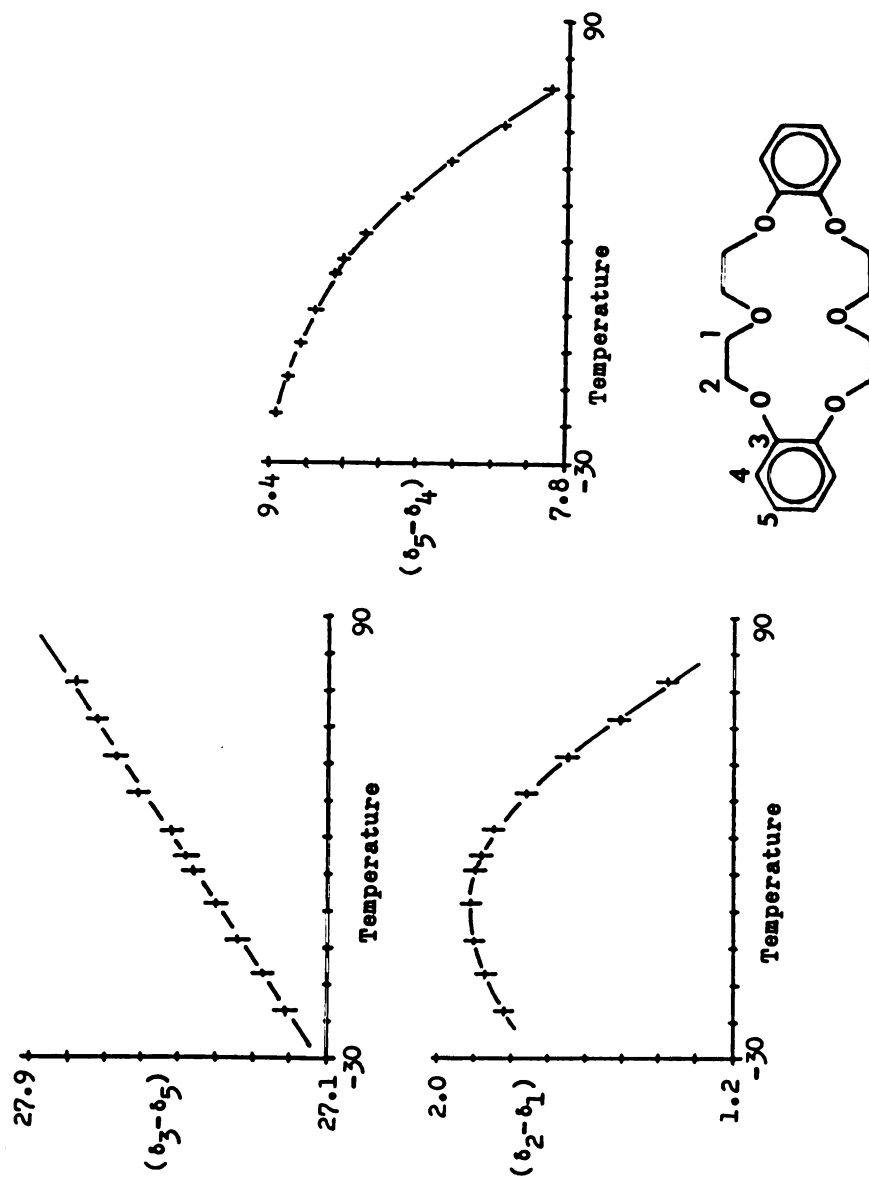
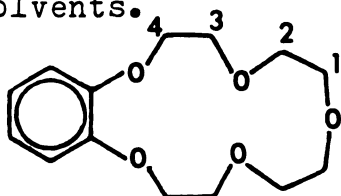


Figure 57. Plots of $(\delta_3 - \delta_5)$, $(\delta_2 - \delta_1)$ and $(\delta_5 - \delta_4)$ vs. temperature (in °C) for DB18C6 in nitromethane-d₃.

Table 16. Proton Chemical Shifts of B15C5 in Several Solvents.

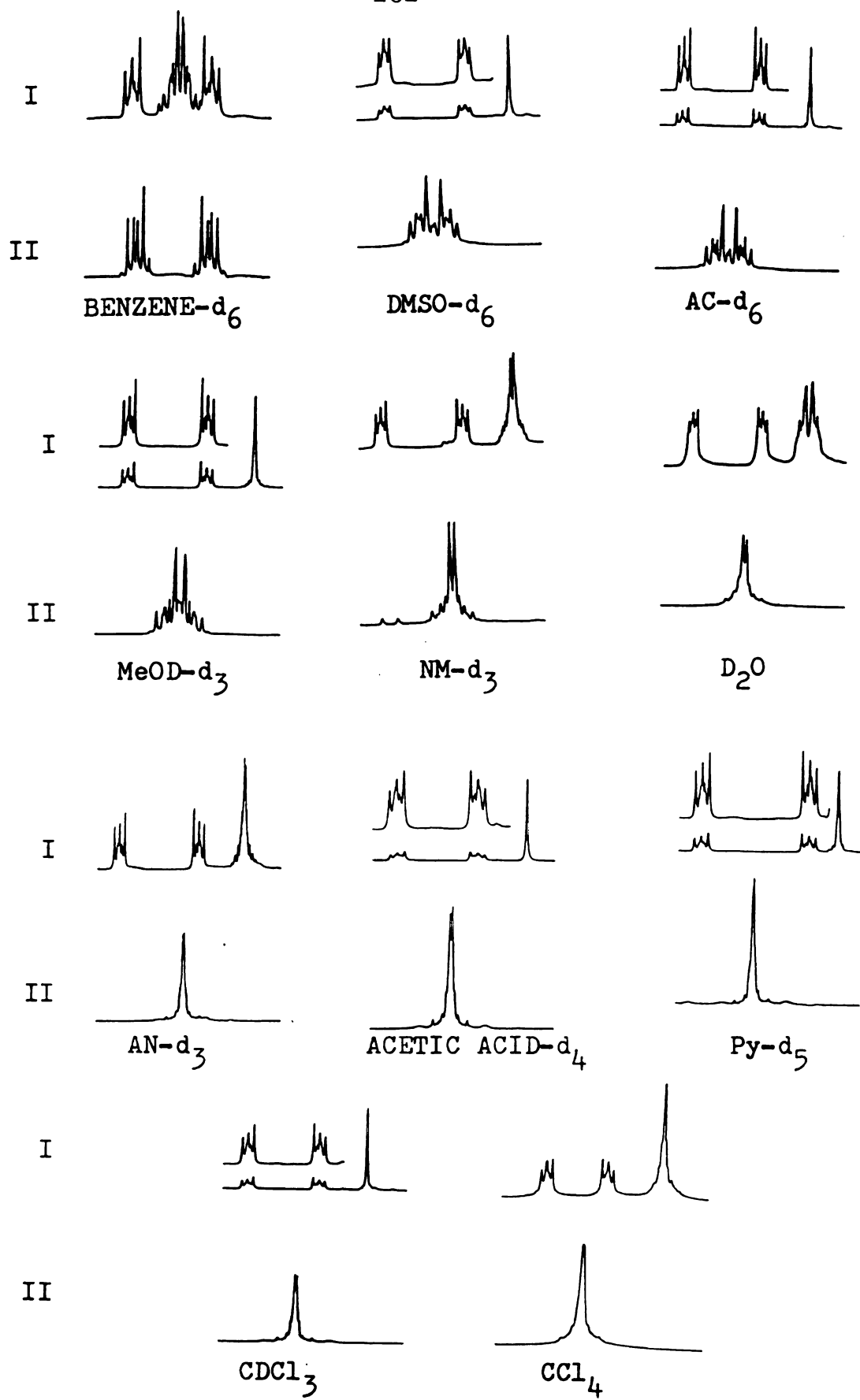


SOLVENT	^{a, b} δ_1, δ_2		δ_3	δ_4	^b δ_{aromatic}
CCl ₄	3.74	3.92		4.11	6.85
NM-d ₃	3.62	3.79		4.06	6.89
MeOD-d ₃	3.66	3.82		4.06	6.87
AN-d ₃	2.66	3.81		4.08	6.93
D ₂ O	3.56	3.74		4.01	6.86
DMSO-d ₆	3.61	3.77		4.03	6.91
AC-d ₆	3.69	3.86		4.11	6.93
AcOD-d ₃	3.83	3.95		4.15	6.92
Py-d ₅	3.59	3.67		3.96	6.81
C ₆ D ₆	3.73	3.65		3.84	6.83
CDCl ₃	3.76	3.91		4.13	6.88

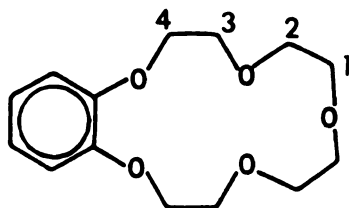
^aChemical shifts are reported relative to TMS in ppm.
Uncertainty in the chemical shifts is ± 0.01 ppm.

^bThe chemical shift reported is the center of the multiplet.

Figure 58. Proton spectra of B15C5 in several deuterated solvents. In these spectra I and II refer to the ether and aromatic protons of B15C5, respectively.



Unlike DB18C6, B15C5 has four kinds of ether protons:

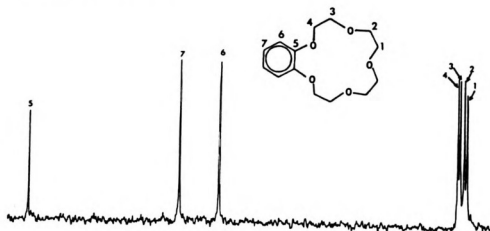


The ether multiplets of protons 3 and 4 behave in the same manner as the ether multiplets of DB18C6. The same is true of the splitting patterns of the aromatic protons of B15C5 and DB18C6. The ether multiplets of protons 1 and 2 belong to the AA'BB' spin system. However the splitting pattern of these protons is not fully understood. This may in part result from the fact that there are many subcases of the AA'BB' spin system -- depending on the magnitudes of the coupling constants and chemical shifts. However, it can be seen that in AC-d₆, CDCl₃, CD₃COOD, Py-d₅, DMSO-d₆ and MeOD-d₃ protons 1 and 2 appear as a single peak whereas in benzene-d₆, D₂O, AN-d₃ and NM-d₃ the proton resonances are split apart.

Benzo-15-crown-5 has seven inequivalent carbon atoms. Figure 59 shows a carbon-13 spectrum of B15C5 in DMF and gives the peak assignments. The carbon-13 chemical shifts of B15C5 were measured in several solvents. The results in Table 17 show that the carbon-13 chemical shifts are strongly solvent dependent. These results further indicate that the extent of solvation of B15C5 varies with the nature of the solvent.

5. SOLVENT INTERACTIONS OF THE AROMATIC RING OF

Benzo-15-Crown-5:



Tetraglyme:

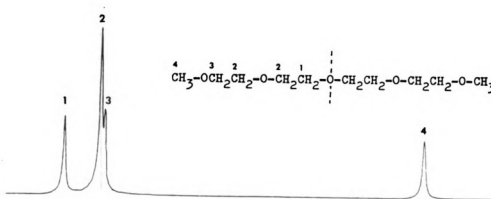
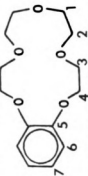


Figure 59 Carbon-13 spectra of benzo-15-crown-5, B15C5, and tetraglyme, TG, in dimethylformamide.

Table 12 Carbon-13 Chemical Shift Data for Solutions of B15C5 in Several Solvents.



SOLVENT	δ_1^a	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7
AN	69.53	70.03	70.88	71.41	149.98	114.87	122.11
NM	69.08	69.67	70.40	71.02	149.71	114.27	121.80
AC	69.78	70.22	71.28	71.81	150.20	115.01	121.92
MeOH	69.48	70.01	70.75	71.13	149.88	114.95	122.06
CHCl ₃	70.10	70.66	71.54	72.07	150.23	115.33	122.41
C ₆ H ₆	69.44	70.12	71.47	71.94	150.19	114.64	121.58
DMF	69.75	70.16	71.14	71.75	150.09	114.95	122.01
CCl ₄	70.01	71.75	71.92	72.39	150.38	115.06	122.06
H ₂ O	68.78	69.78	70.34	70.72	148.76	114.41	122.65

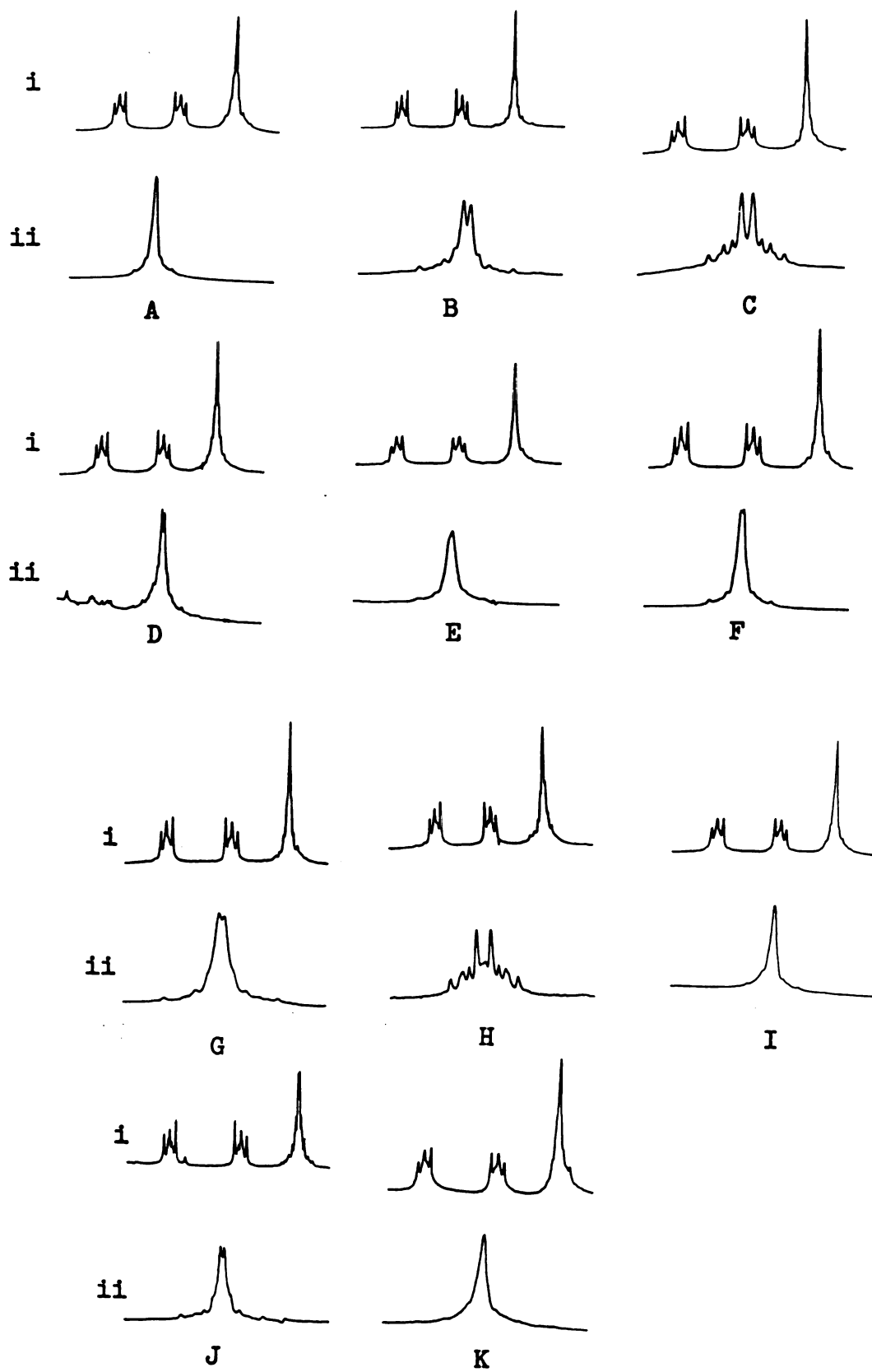
^aChemical shifts are reported relative to TMS in acetone-d₆ in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

BENZO-15-CROWN-5. It was noted in the previous sections that the splitting of the resonances of the aromatic protons of DB18C6 and B15C5 is solvent dependent. In solvents like AC-d₆, DMSO-d₆ and benzene-d₆, the protons are greatly split apart. However, in other solvents such as CDCl₃, AN-d₃ and Py-d₅ essentially one single resonance is observed. These results suggest the possibility of solvent interactions with the aromatic rings of B15C5 and DB18C6. To test this possibility, a series of solutions of B15C5 and several π acceptors and donors were prepared in carbon tetrachloride. In carbon tetrachloride, the aromatic protons are collapsed upon one another. Proton NMR spectra were measured for these solutions. The results are shown in Figure 60.

No significant changes are observed in the aromatic region of the spectra when either p-dichlorobenzene, 1,3,5-trichlorobenzene, hexachlorobenzene, nitrobenzene, benzonitrile, nitromethane or methanol is added to a solution of B15C5 in carbon tetrachloride. However, the addition of benzene, hexamethylbenzene and m-dinitrobenzene causes the aromatic proton resonances to split apart. These results can be explained in terms of π - π interactions with the aromatic ring of B15C5. The ether oxygens bonded to the aromatic ring withdraw electron density from the aromatic ring. Consequently, one would expect the aromatic ring of B15C5 to act as a

Figure 60. Proton spectra of solutions of B15C5 (where i refers to the ether protons and ii to the aromatic protons) in carbon tetrachloride. The spectra correspond to the following solutions:

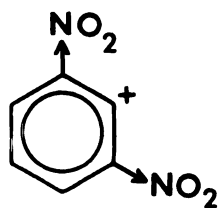
- (A) B15C5 in CCl_4 .
- (B) $[\text{Benzene}]/[\text{B15C5}] = 15.25$
- (C) $[\text{Hexamethylbenzene}]/[\text{B15C5}] = 8.84$
- (D) $[\text{p-Dichlorobenzene}]/[\text{B15C5}] = 27.27$
- (E) $[\text{1,3,5-Trichlorobenzene}]/[\text{B15C5}] = 28.69$
- (F) $[\text{Hexachlorobenzene}]/[\text{B15C5}] = 4.92$
- (G) $[\text{Nitrobenzene}]/[\text{B15C5}] = 23.28$
- (H) $[\text{m-Dinitrobenzene}]/[\text{B15C5}] = 9.02$
- (I) $[\text{Benzonitrile}]/[\text{B15C5}] = 21.01$
- (J) $[\text{Nitromethane}]/[\text{B15C5}] = 21.86$
- (K) $[\text{Methanol}]/[\text{B15C5}] = 31.02$



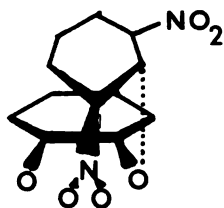
π -acceptor. Hexachlorobenzene, 1,3,5-trichlorobenzene, p-dichlorobenzene, nitrobenzene and benzonitrile are also π -acceptors due to the inductive effects of their functional groups. It is not surprising, then, that no significant changes are observed in the aromatic region of the proton spectra of B15C5 with the addition of these π -acceptors. Benzene is a weak π -donor. It has been shown to form weak adducts with tetracyanoethylene (TCNE), a strong π acid (201). There is a slight splitting of the aromatic protons of B15C5 with the addition of benzene. This implies that a weak π - π complex is formed between benzene and B15C5. Hexamethylbenzene is a much stronger π -donor than benzene. The addition of hexamethylbenzene greatly splits up the aromatic protons of B15C5 suggesting the formation of a stronger π - π complex.

The splitting of the aromatic proton resonances of B15C5 with the addition of m-dinitrobenzene is very puzzling especially since nitrobenzene and nitromethane did not significantly affect the splitting of the protons of the aromatic ring. Previous workers (202) have shown that 1,3,5-trinitrobenzene, TNB, forms complexes with B15C5, DB18C6 and DB30C10. Their results suggested that TNB is situated predominantly over the phenyl ring of the ether with one of the nitro groups projected over the cavity. These workers also showed that the nonbenzenoid ethers form very weak molecular complexes with TNB. This

was shown by the appearance of charge transfer absorptions in the electronic spectra of TNB. It was also found that the complexes of the nonbenzenoid ethers with TNB are much weaker than those with the benzenoid ethers. The results of these previous workers help explain the m-dinitrobenzene results. There is a similarity between m-dinitrobenzene and TNB. As a result of the inductive effects of the nitro groups, the carbon between the two nitro groups of m-dinitrobenzene is very electron deficient as shown below:



The ether oxygens adjacent to the aromatic ring of B15C5 are electron rich. An interaction as described by Jayathirtha and Krishnan (202) would position the electron deficient carbon over an electron rich oxygen as shown:



Such an interaction would perturb the aromatic ring of B15C5 and could explain the splittings observed.

Benzo-15-crown-5 is a stronger π -acceptor than o-dimethoxybenzene. Figure 61 shows proton spectra of the aromatic region of o-dimethoxybenzene in carbon

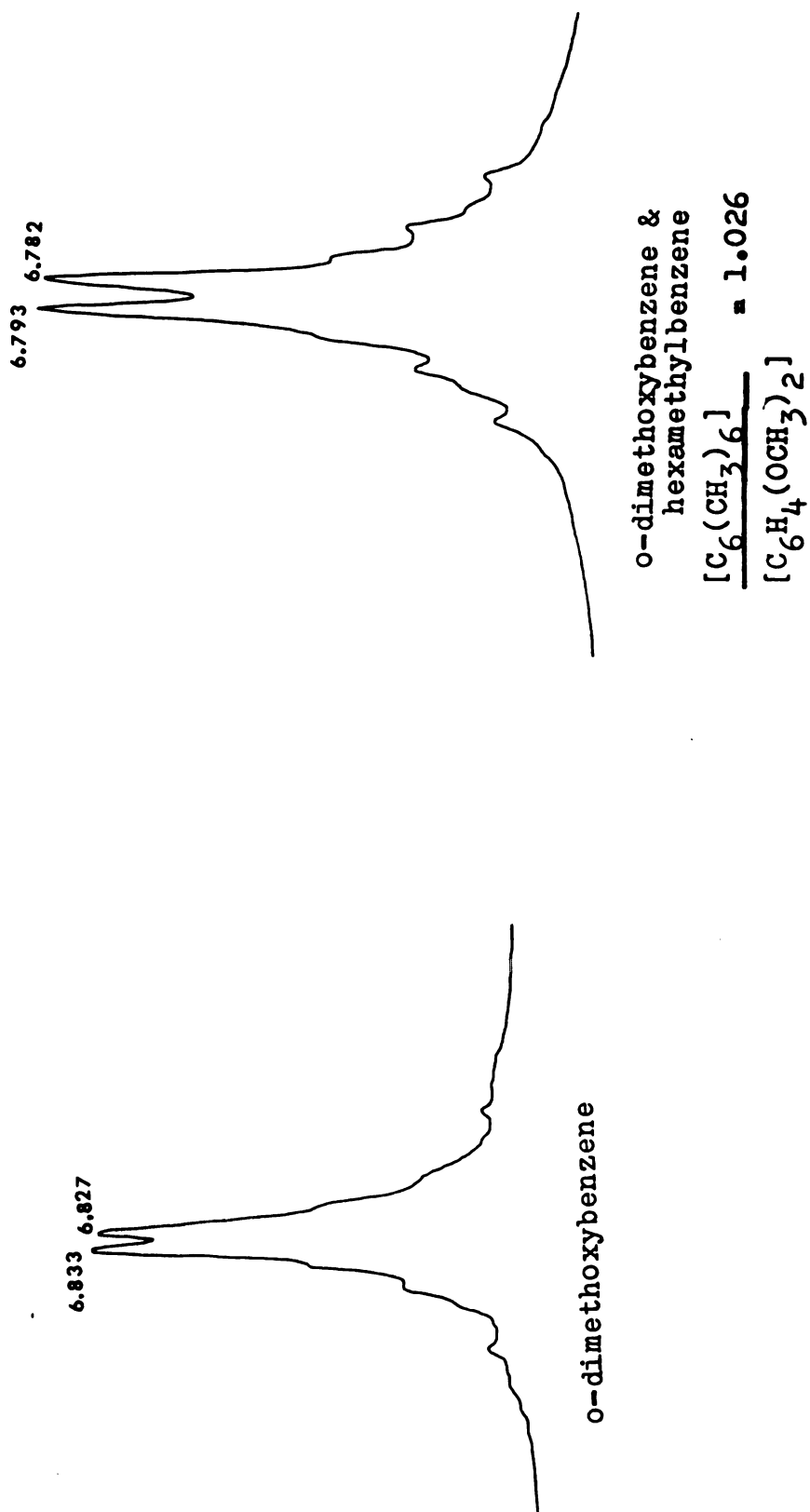


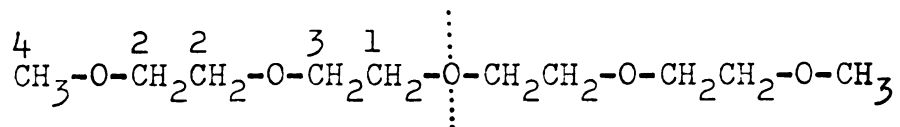
Figure 61. Proton spectra of the aromatic region of o-dimethoxybenzene in carbon tetrachloride.

tetrachloride. With the addition of hexamethylbenzene, the splitting of the aromatic protons of o-dimethoxybenzene slightly increases. However, the addition of hexamethylbenzene shifts the methyl resonance upfield by 2.05 ppm from 3.85 ppm. This may indicate an interaction between the methoxy groups and hexamethylbenzene similar to that described for benzene and methanol (Chapter III).

6. SOLVATION STUDIES OF TETRAGLYME. Proton spectra of TG were obtained. These spectra are shown in Figure 62. The differences in the spectra of TG in the different solvents is not as dramatic as observed for B15C5 and DB18C6. In benzene-d₆, pyridine-d₅ and carbon tetrachloride, the splitting pattern observed for the ethylene protons of TG is similar to that observed for B15C5 and DB18C6. This implies that in benzene-d₆, pyridine-d₅ and carbon tetrachloride the TG molecule is folding in on itself resulting in a "cyclic" conformation. This is not surprising since benzene-d₆, pyridine-d₅ and carbon tetrachloride have low dipole moments. As a result of this the ether oxygens orient themselves away from the solvent molecules.

A carbon-13 NMR study was done. The results are tabulated in Table 19. As with the previous studies, the carbon-13 chemical shifts of tetraglyme are solvent dependent indicating that the solvation of the ligand

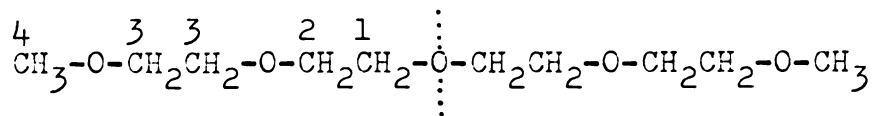
Figure 62. Proton spectra of tetraglyme in several deuterated solvents. Spectra labeled A are vertical expansions of spectra B.



SOLVENT	δ_1^a	δ_2	δ_3	δ_4
Neat	3.19	3.09	3.19	2.93
CCl ₄	3.62	3.52	3.63	3.40
D ₂ O	3.44	3.45	3.38	3.14
MeOD-d ₃	3.59	3.60	3.50	3.32
C ₆ D ₆	3.54	3.54	3.41	3.20
CDCl ₃	3.62	3.63	3.52	3.34
Py-d ₅	3.45	3.46	3.32	3.09
DOAc-d ₃	3.70	3.69	3.62	3.40
AC-d ₆	3.58	3.58	3.48	3.30
DMSO-d ₆	3.49	3.50	3.42	3.24
AN-d ₃	3.56	3.55	3.47	3.31
NM-d ₃	3.52	3.53	3.44	3.25

^aChemical shifts are reported relative to TMS in ppm.
Uncertainty in the chemical shifts is ± 0.01 ppm.

Table 19. Carbon-13 Chemical Shift Data for Solutions of Tetraglyme in Several Solvents.

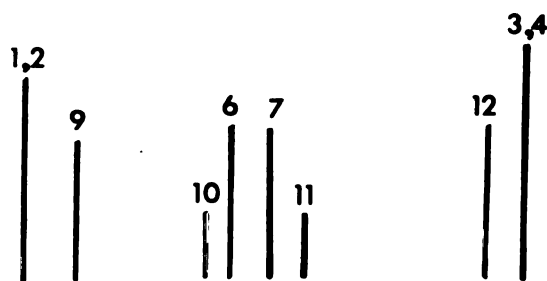


SOLVENT	^a			
	δ_1	δ_2	δ_3	δ_4
NEAT	72.40	70.84	70.99	58.67
CCl ₄	72.89	71.54	71.42	59.51
DMF	72.60	71.13	70.96	58.81
NM	72.25	70.81	70.66	58.29
MeOH	72.39	70.98	70.78	58.51
AN	72.56	71.09	70.94	58.80
C ₆ H ₆	72.50	71.17	71.03	58.79
CHCl ₃	72.92	71.57	71.57	60.01
AC	71.75	70.39	70.39	58.84
H ₂ O	71.95	70.54	70.43	59.05

^aChemical shifts are reported relative to TMS in acetone-d₆ in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

differs with the nature of the solvent.

7. SOLVATION STUDIES OF DIAZA-18CROWN-6. The N-CH₂CH₂-O protons of DA18C6 are characterized by the presence of two multiplets corresponding to the AA'XX' spin system. As was discussed earlier, ten lines are normally observed in the AA'XX' spin system. However, the multiplets observed for DA18C6 are composed of eight lines:



This suggests that the geminal couplings are on the order of -12 Hz resulting in "K" (where $K = J_{AA'} + J_{XX'} = (\nu_5 - \nu_6)$ or $(\nu_7 - \nu_8)$ being very large. Consequently ν_5 and ν_8 of the AA'XX' spin system are lost in the noise, and ν_6 and ν_7 can become degenerate. Because $J_{AA'}$ and $J_{XX'}$ are usually close together in value and sometimes even identical, the separation (M) between ν_9 and ν_{10} (ν_{11} and ν_{12}) is small or zero, so ν_9 and ν_{12} are drawn inside the two large peaks that give the sum of the vicinal couplings (K).

Because of the amine functional groups of DA18C6, the crown undergoes some acid-base chemistry. Consequently, the carbon-13 and proton spectra of DA18C6 are very dependent on pH, as shown in Figure 63. At pH's lower than 7.00, the carbon-13 and proton spectra of DA18C6

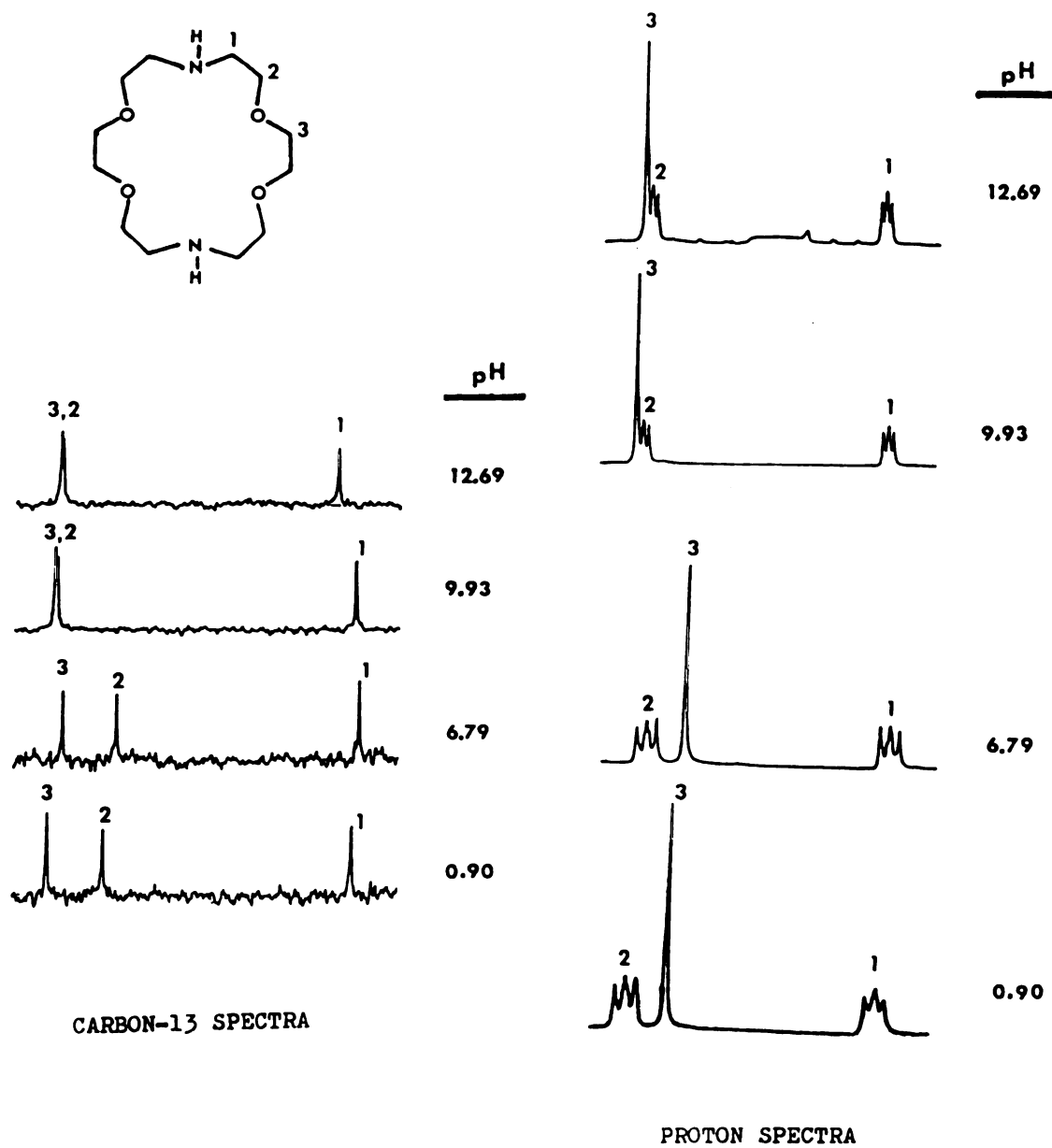
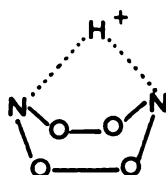


Figure 63. Proton and carbon-13 spectra of DA18C6 in deuterated water as a function of pH.

resemble those of DT18C6 obtained by Lee (203). From simulations, Lee evaluated the coupling constants and dihedral angles for DT18C6. His results suggested that, in solution, DT18C6 has its heteroatoms arranged in a boat conformation. This is primarily due to the bulkiness of the sulfur atoms. The similarity between the low pH DA18C6 ^{13}C and ^1H spectra and those of DT18C6 implies that the heteroatoms of DA18C6 are in a boat conformation. This suggests the existence of the following protonated species:



At pH's greater than 9.0, the carbon-13 resonances of carbons 2 and 3 are nearly superimposed and the proton resonance of protons 3 move downfield of those of protons 2. These results suggest that the heteroatoms of DA18C6 are arranged in a chair conformation.

Besides being dependent on pH, the proton and carbon-13 NMR spectra of DA18C6 are dependent on the nature of the solvent. Figure 64 shows proton spectra of DA18C6 in acetonitrile, acetone- d_6 , deuterated water, carbon tetrachloride and deuterated chloroform. In AN, AC- d_6 , D_2O and CCl_4 the positions of the resonances due to protons 3 and 2 suggest that DA18C6 has a chair conformation. However, in CDCl_3 , the conformation of the

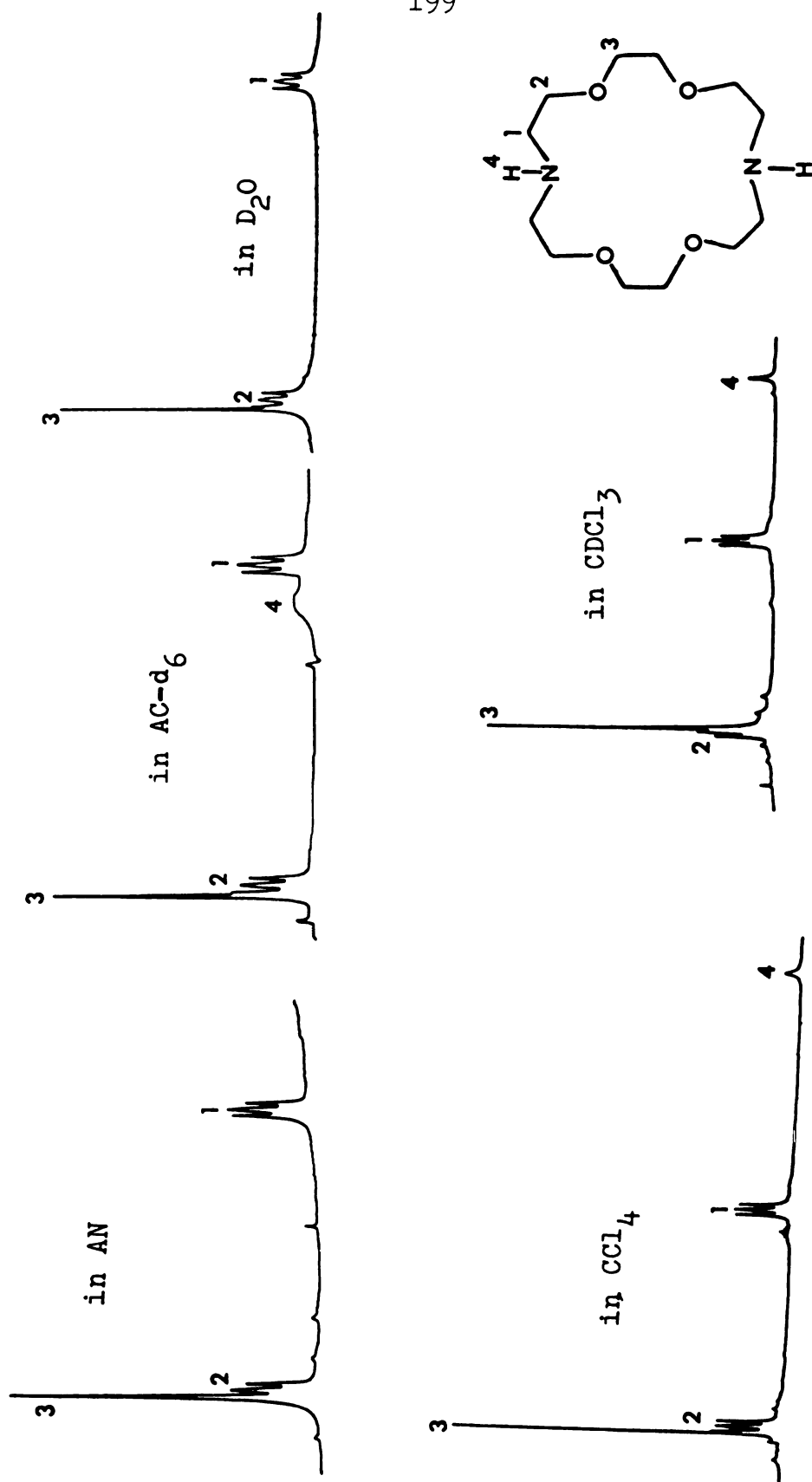
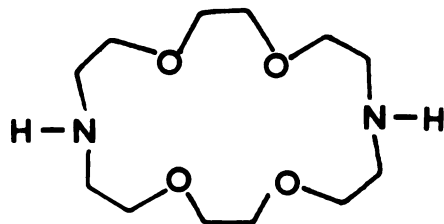


Figure 64. Proton spectra of DAL8C6 in several solvents.

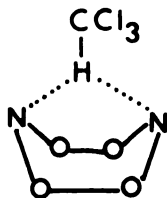
Table 20. Proton Chemical Shift Data for Solutions of DA18C6 in Several Solvents.



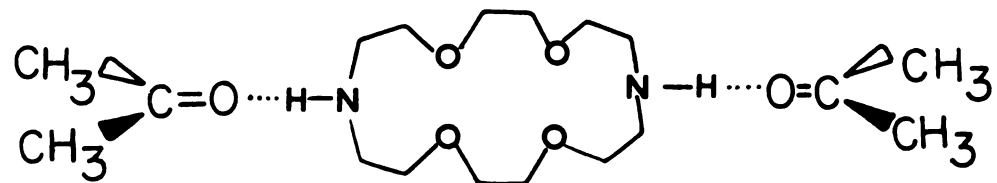
SOLVENT	δ_1^a	δ_2	δ_3	δ_4
AC-d ₆	2.77	3.60	3.63	2.88
CDCl ₃	2.75	3.55	3.54	2.34
D ₂ O	2.61	3.47	3.49	----
CCl ₄	2.78	3.59	3.62	1.89

^aChemical shifts are reported relative to TMS in ppm.
 Uncertainty in the chemical shifts is ± 0.01 ppm.

crown seems to be between a boat and chair configuration. This probably results because chloroform is slightly acidic ($pK_a = 15 \pm 1$ (58)). Consequently, the following solvent-crown interaction could be occurring in solution:



In $AC-d_6$, the proton chemical shift of the amine protons of DA18C6 is considerably downfield from those observed in CCl_4 and $CDCl_3$. The resonance is also broader than in either CCl_4 or $CDCl_3$. This implies an interaction between the carbonyl group of $AC-d_6$ and the amine protons as shown:



Such an interaction would pull the proton chemical shift of the amine downfield. The broadening is due to exchange between the carbonyl group and the nitrogen.

The carbon-13 chemical shifts of the carbons of DA18C6 vary with solvent, as shown in Table 21. This indicates that the solvation shell of the crown differs.

C. CONCLUSIONS

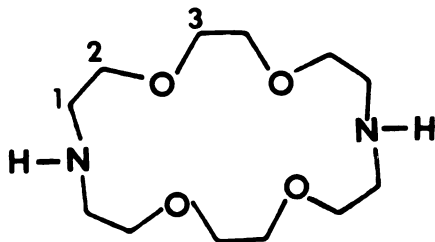
These studies indicate that the solvation of linear and cyclic polyethers is solvent dependent. It was also

Table 21. Carbon-13 Chemical Shift Data for Solutions of DA18C6 in Several Solvents.

SOLVENT	a, b		
	δ_1	δ_2	δ_3
AC-d ₆	50.34	71.14	71.20
CDCl ₃	49.30	70.24	70.32
H ₂ O	48.39	70.25	70.46
D ₂ O	48.28	70.24	70.43
AN	50.33	71.16	71.46
DMF	50.17	70.83	71.09
CCl ₄	50.52	71.42	71.42

^aChemical shifts are reported relative to TMS in acetone-d₆ in ppm. The uncertainty in the chemical shifts is ± 0.03 ppm.

^bChemical shift assignment is shown below:



possible to detect specific solvent-ligand interactions and to propose structures for the complexes formed. The solvation of B15C5 and DB18C6 is complicated by $\pi - \pi$ interactions of the aromatic rings.

CHAPTER V

SPECTROSCOPIC STUDIES

OF

SOLVENT-LIGAND COMPLEXATION

A. INTRODUCTION

Solvent-macrocyclic ligand interactions can modify the complexing abilities of the ligand by altering its conformation and/or by varying the thermodynamics of ligand desolvation. An understanding of macrocyclic complex formation and the "macrocyclic effect" cannot be complete without some quantitative knowledge of solvent-ligand interactions. This study was an attempt in this direction.

B. RESULTS AND DISCUSSION.

1. X-RAY CRYSTAL STRUCTURE OF THE ACETONITRILE 18-CROWN-6 COMPLEX AND MASS SPECTRUM OF 18-CROWN-6 IN ACETONITRILE. Figure 65 shows an X-ray crystal structure of the acetonitrile complex with 18C6. This crystal structure was obtained by Dr. Don Ward (204) on an old crystal grown and sealed in a capillary by Alfred Smetana. The crystallograph shows that the crystalline complex has a stoichiometry of two moles of acetonitrile per mole of 18C6. It also shows that the methyl groups of the acetonitrile are hydrogen-bonded to the oxygens of 18C6. This was also shown to be the case for the malonitrile (148) and nitromethane (147) complexes of 18C6.

John Rovang (205) used fast atom bombardment to obtain mass spectra of 12C4 and 18C6 in acetonitrile. These spectra are shown in Figure 66. The mass spectrum

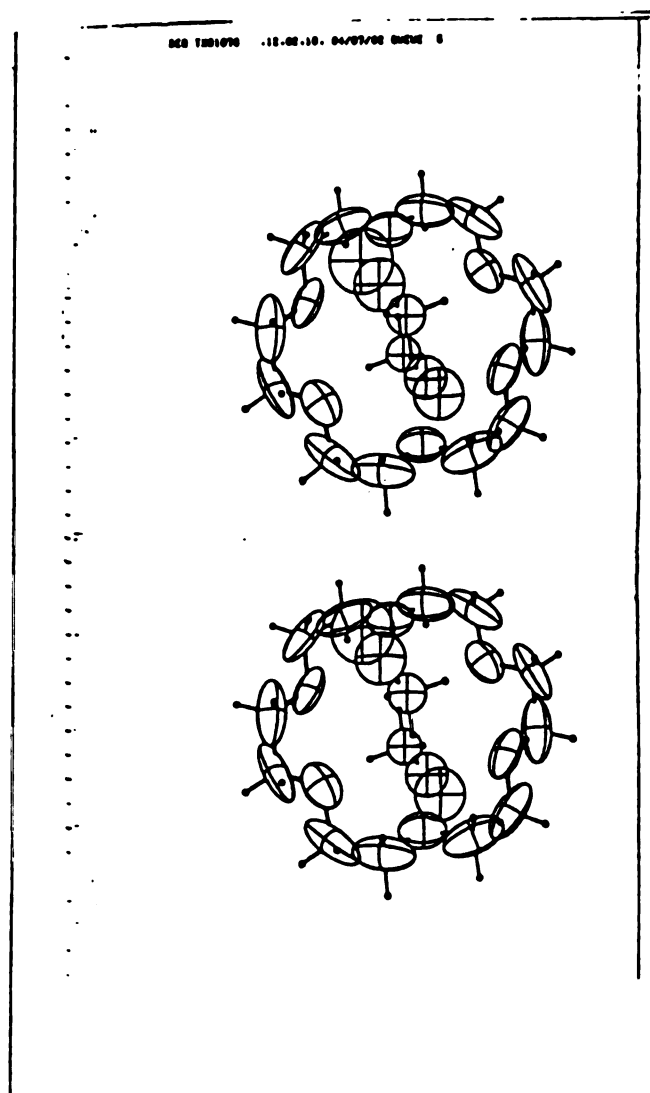
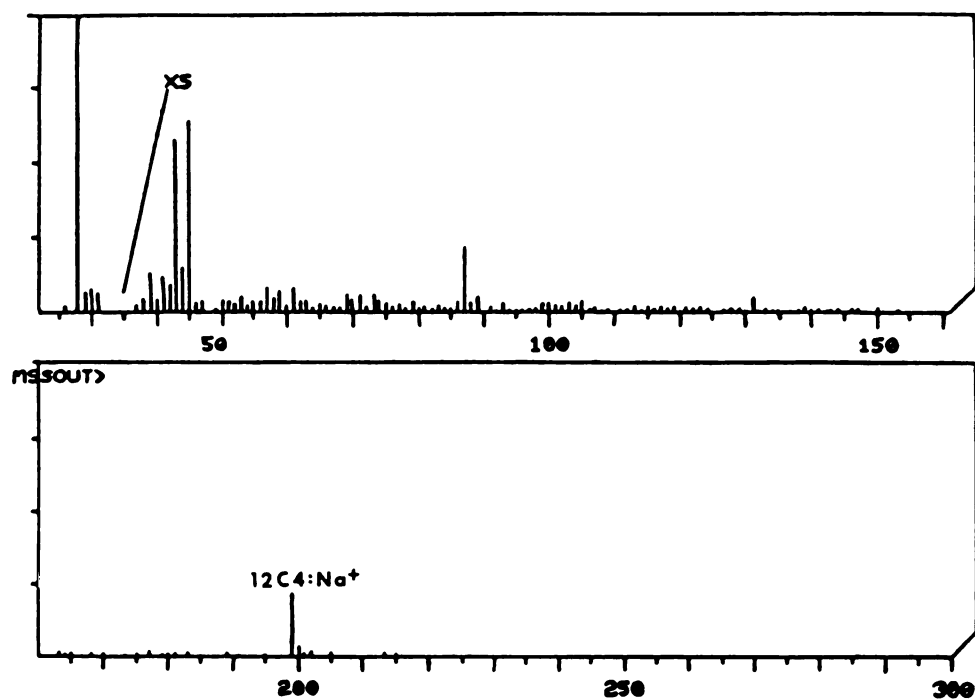


Figure 65. Crystal structure of the acetonitrile complex with 18-crown-6.

12-Crown-4 in Acetonitrile:



18-Crown-6 in Acetonitrile:

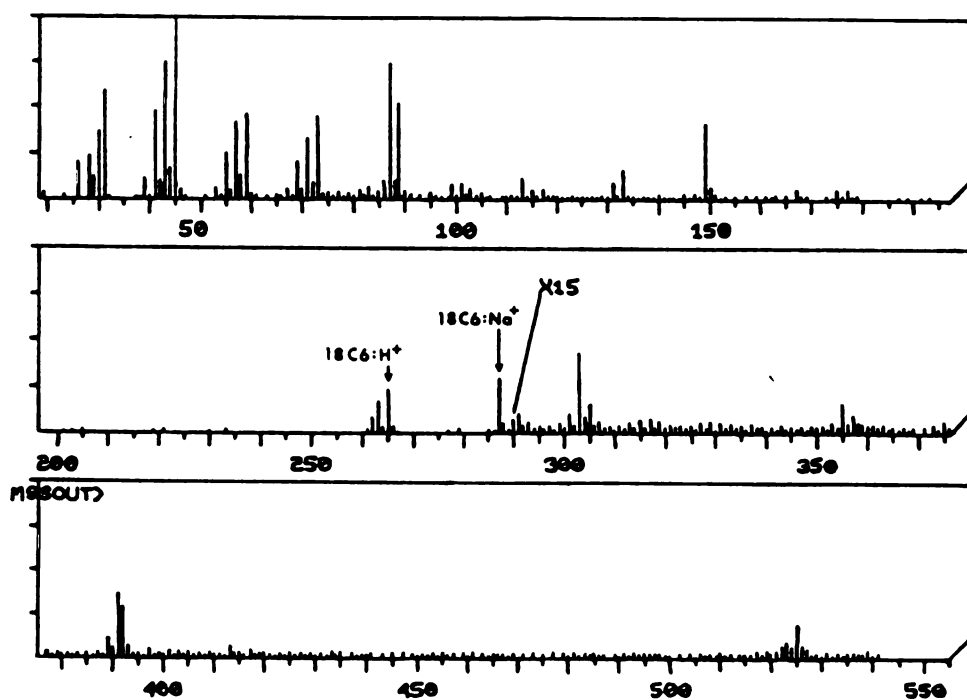
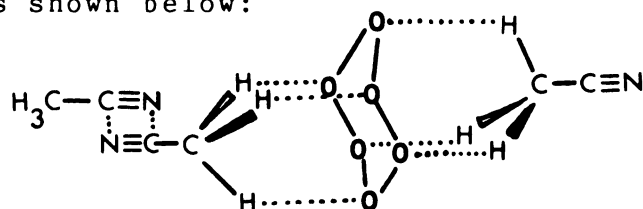


Figure 66. Mass spectra of solutions of 12-crown-4 and 18-crown-6 in acetonitrile.

of a solution of 12C4 in acetonitrile is similar to that obtained for 12C4 whereas the spectrum obtained for the solution of 18C6 in acetonitrile bears little resemblance to that obtained for pure 18C6. Lee et al. (206) found that 12C4, 15C5, 18C6 and 21C7 gave similar mass spectra. For the crowns, the parent ion is difficult to obtain and formation of small protonated cyclic ethers is the predominant reaction. This is also true of the solution of 12C4 in acetonitrile. However, for 18C6 in acetonitrile, a fairly large signal for the protonated parent ion is obtained at m/z 265. Ions with masses larger than that of the protonated parent ion of 18C6 are also observed. These have been attributed to the acetonitrile complexes of 18C6. The fact that these complexes are observed in the gas phase attest to their stability. Table 22 tabulates the fragment ion m/z values and probable composition. The results show the possible existence of both 1:1 and 1:2 18C6:MeCN complexes. They also show the presence of a species possibly composed of three MeCN and one 18C6. A probable structure for this species is shown below:



The existence of this species implies a dipole-dipole interaction between the nitrile groups of acetonitrile and

Table 22. Assignment of the High Molecular Weight Ion Fragments Obtained in the Mass Spectrum for 18-Crown-6 in Acetonitrile.

FRAGMENT ^a ION (m/z value)	PROPOSED SPECIES	MW of PROPOSED SPECIES
265	18C6:H ⁺	265
303	18C6:CH ₃ CN	305
355	CH ₃ CN:18C6:CH ₃ CN	346
391	CH ₃ CN:18C6:CH ₃ CN:CH ₃ CN	387
525	18C6:18C6 (?)	528

^aUncertainty in the m/z values is ± 5 m/z units.

that the methyl group interacts with the crown ether. The existence of this species may explain why acetonitrile forms a crystalline complex with 18C6. A solid is held together by van der Waals, covalent, ionic, hydrogen or metallic bonds or a combination thereof. The crystal lattice of the acetonitrile-18C6 complex must result from both hydrogen bonding and van der Waals interactions. The methyl protons hydrogen bond to the ether oxygens; the complex then forms chains through dipole-dipole bonding of the nitrile groups.

2. COMPLEXATION OF 18-CROWN-6 WITH ACETONITRILE, NITROMETHANE, CHLOROFORM, ACETONE, DIMETHYLFORMAMIDE AND METHANOL. The complexation of 18C6 with acetonitrile was studied in carbon tetrachloride, chloroform, benzene and acetone solutions. Although the MeCN-CCl₄ system was the best characterized (Chapter III), the limited solubility of the MeCN·18C6 complex(es) in CCl₄ made a mole ratio study difficult. However, greater solubilities were found in benzene, chloroform and acetone solutions.

The complexation of 18C6 and MeCN in carbon tetrachloride was studied by ¹³C and ¹H NMR spectroscopy. In these studies, the largest [18C6]/[MeCN] mole ratio achieved was approximately 0.3. Yet, as Figure 67 shows, the carbon-13 chemical shifts of acetonitrile change with the addition of 18C6 indicating that complexation is occurring.

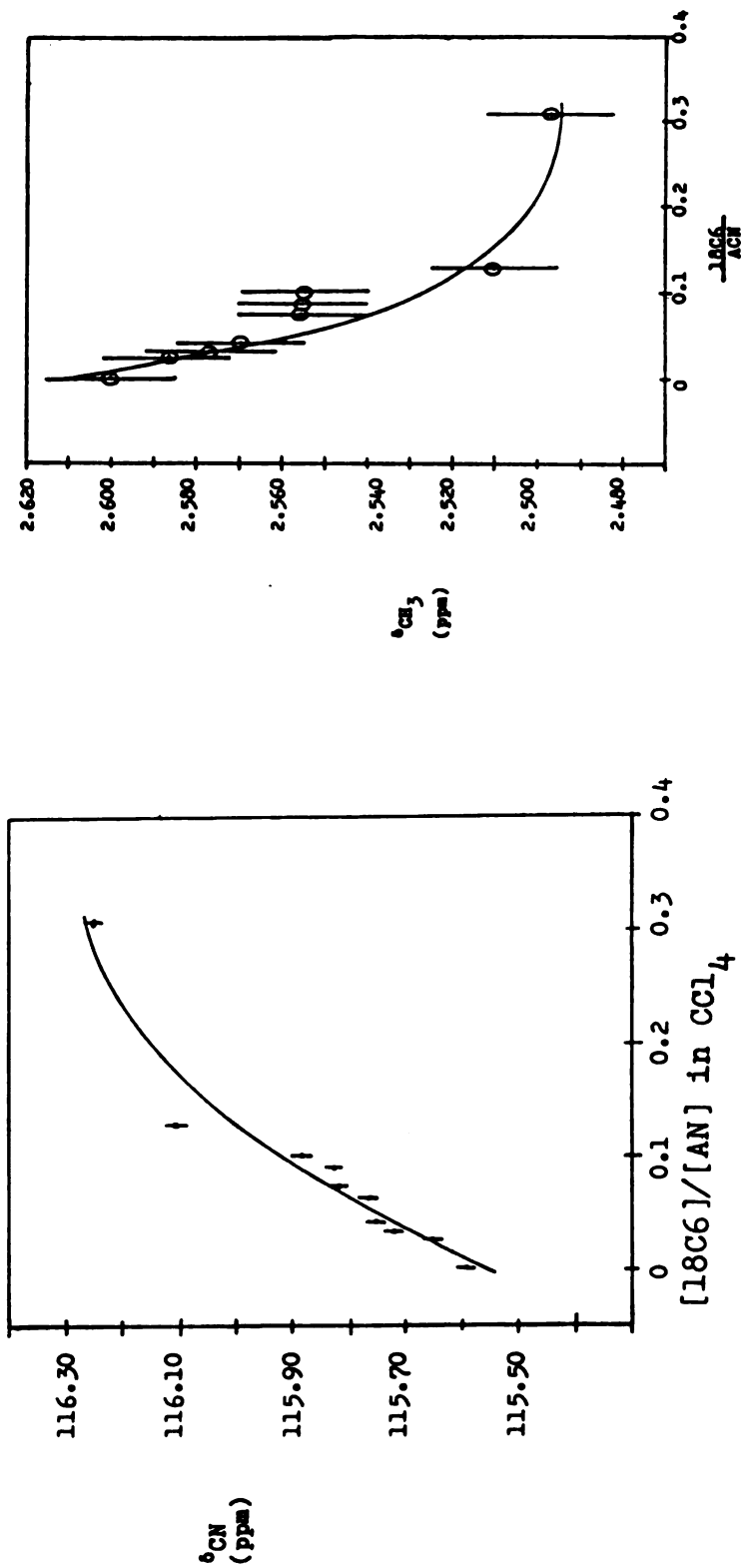
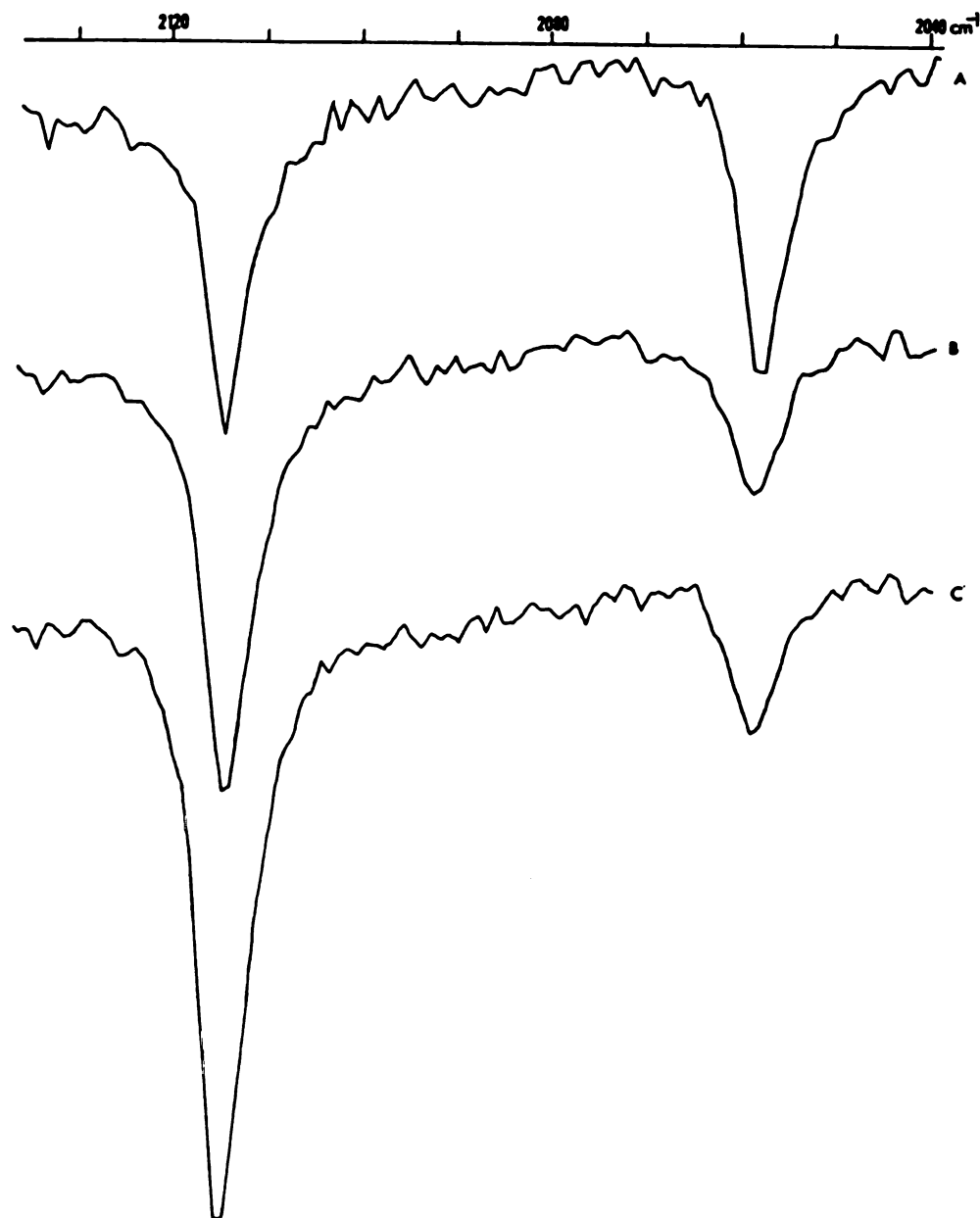


Figure 67. Plots of the carbon-13 chemical shifts of acetonitrile as a function of $[18C6]/[AN]$ in carbon tetrachloride.

An infrared study of the MeCN-18C6-CCl₄ system proved to be more valuable. Figures 68 and 69 show the infrared spectra of ν_1 vibrations of MeCN-d₃ and ν_2 vibrations of MeCN and MeCN-d₃, both free and complexed by 18C6. For MeCN-d₃, the intensity of ν_1 , the CD stretch at 2118 cm⁻¹, increases upon complexation with 18C6. No new bands appear near ν_1 . However, a new band does grow out of ν_2 , the CN stretch which occurs at 2265 cm⁻¹ for MeCN-d₃ and 2255 cm⁻¹ for MeCN (the band at 2295 is the $\nu_3+\nu_4$ combination band in Fermi resonance with the ν_2 band (207)). For both MeCN-d₃ and MeCN, the new band appears at lower frequencies. These observations agree well with those obtained by McLachlan (150) in his Raman studies of the single crystals of 18C6·2CH₃NO₂, 18C6·2CH₃CN, 18C6·2CD₃CN and 18C6·Ac₂O. They also agree with the Raman studies done by Gold and Rice (151).

The complexation of 18C6 and MeCN in chloroform was studied by both carbon-13 NMR spectroscopy and infrared spectroscopy. Figure 70 shows the plot of the MeCN chemical shift-mole ratio plots obtained. Between [18C6]/[MeCN] mole ratios of 0.0 and 3.5, the plots of the carbon-13 chemical shifts of the methyl and nitrile groups of MeCN vs. mole ratio are linear. Therefore, it can be concluded that in chloroform the complexation of 18C6 with acetonitrile is very weak since chloroform also complexes 18C6. The weakness in complexation also results from the



- (A) 0.4243 M AN-d₃; [18C6]/[AN-d₃]=0.00
(B) 0.4254 M AN-d₃; [18C6]/[AN-d₃]=0.1161
(C) 0.4232 M AN-d₃; [18C6]/[AN-d₃]=0.2012

Figure 68. Infrared spectra of the C-D stretch of AN-d₃ in solutions of AN-d₃ and 18C6 in CCl₄.

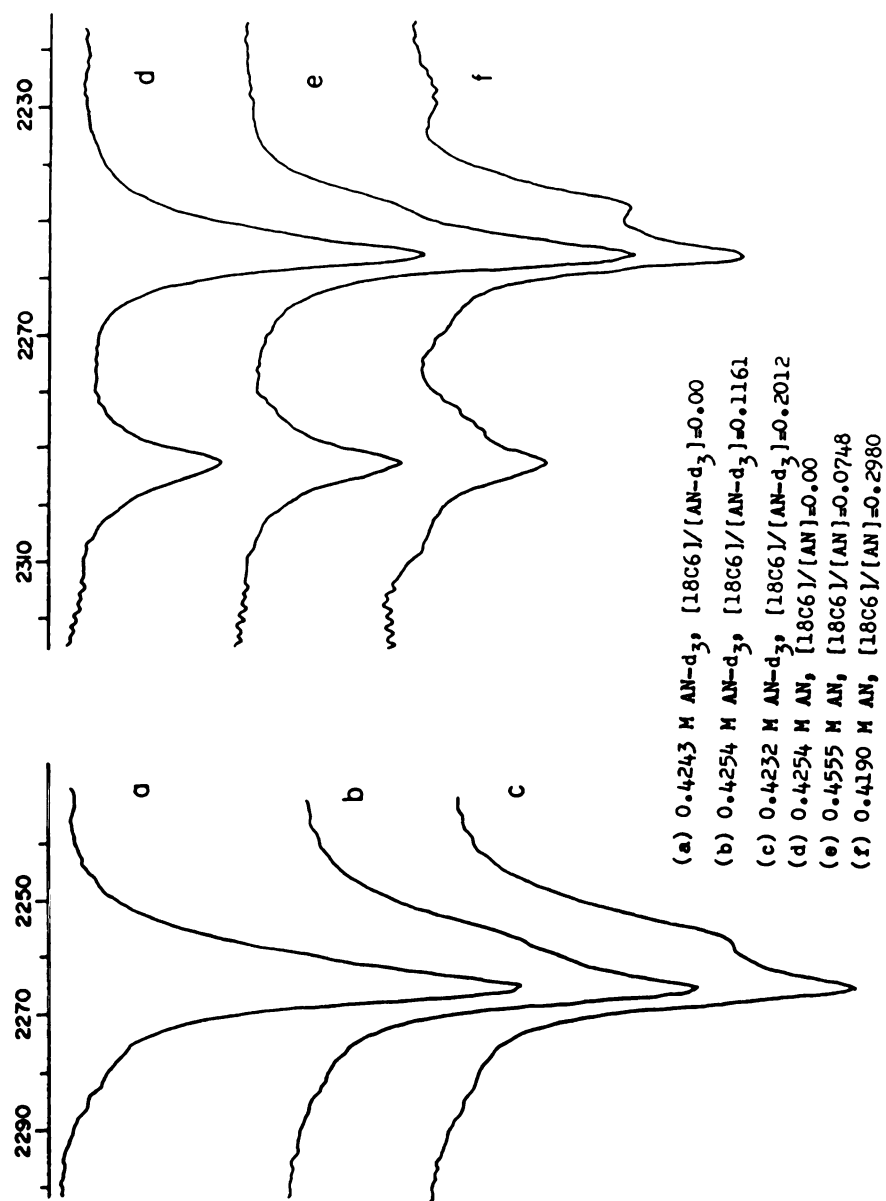


Figure 69. Infrared spectra of the CN stretch of AN and AN-d₃ for solutions of AN and 18C6 in carbon tetrachloride.

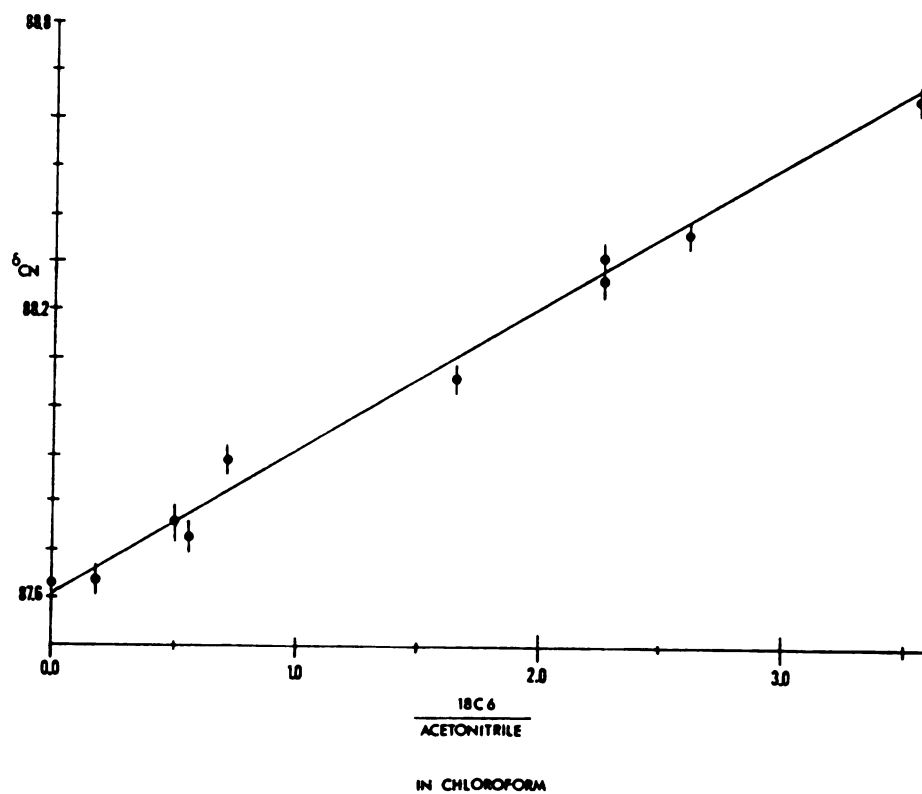
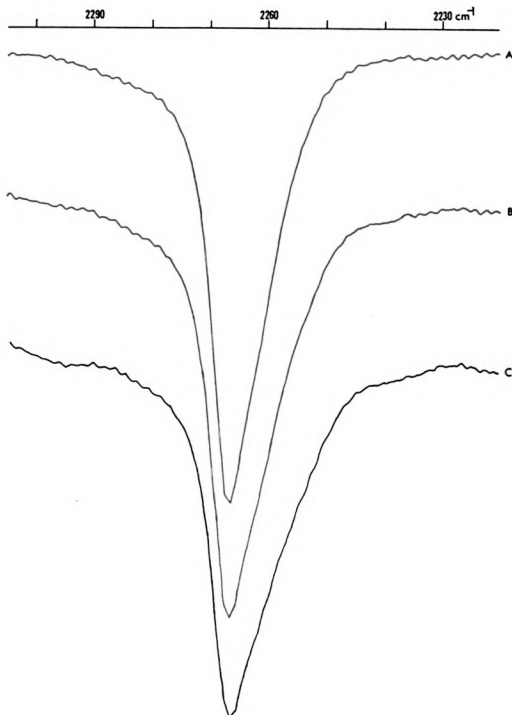


Figure 70. Plots of the carbon-13 chemical shifts of the nitrile carbon of acetonitrile as a function of $[18C6]/[AN]$ mole ratio in chloroform.

CHCl_3 -MeCN interactions which involve the methyl group of acetonitrile. The infrared spectra (Figure 71) obtained for solutions of 18C6 and MeCN-d_3 in chloroform further point out the weakness of complexation between 18C6 and MeCN-d_3 . In these spectra, no changes were observed in ν_1 . The ν_2 band due to the complexation appears as a shoulder in the CN stretch. These spectra as well as those for MeCN-d_3 and 18C6 in CCl_4 were deconvoluted. The subroutine used is discussed in Appendix II. The results of these deconvolutions are shown in Table 23.

Carbon-13 chemical shifts of acetonitrile carbons were measured in benzene and acetone solutions in the presence of 18C6 as a function of $[\text{18C6}]/[\text{MeCN}]$ mole ratio at a fixed concentration of MeCN. As Figure 72 indicates, the chemical shift plots for the methyl carbon of MeCN in benzene shows two breaks indicative of the formation of two complexes. The model used to analyze the chemical shift data took into account dimerization of acetonitrile. The equations and subroutines used are discussed in Appendix I. The results of this analysis are tabulated in Table 24. Infrared studies of MeCN and 18C6 solutions in benzene showed the same changes as observed for the same solutions in CCl_4 .

For MeCN and 18C6 in acetone solutions, only one break is apparent in the chemical shift plot shown in Figure 73. Therefore, only one MeCN-18C6 complex is



- (a) 0.4232 M AN-d₃, [18C6]/[AN-d₃]=0.00
(b) 0.4266 M AN-d₃, [18C6]/[AN-d₃]=0.5935
(c) 0.3472 M AN-d₃, [18C6]/[AN-d₃]=1.4786

Figure 71. Infrared spectra of the C≡N stretch of MeCN in solutions of MeCN and 18C6 in chloroform.

Table 23. Results of the Deconvolution of the CN Band of AN-d₃^a

Solution	Peak 1	Peak 2	Peak 3	Peak 4
0.4243 M AN 18C6/AN = 0.0 0.0 M 18C6 InCCl ₄	$\nu_0 = 2275.0$ $I_0 = 0.0145 \pm 0.0007$ $\sigma = 12.7 \pm 0.4$ $A = 0.3031$	$\nu_0 = 2264.8$ $I_0 = 0.117 \pm 0.004$ $\sigma = 3.4 \pm 0.1$ $A = 0.1395$	$\nu_0 = 2262.2$ $I_0 = 0.105 \pm 0.002$ $\sigma = 9.0 \pm 0.2$ $A = 1.561$	no complex
0.4254 M AN 18C6/AN = 0.1161 0.0494 M 18C6 InCCl ₄	$\nu_0 = 2275.0$ $I_0 = 0.007 \pm 0.001$ $\sigma = 14.0 \pm 1.0$ $A = 0.1615$	$\nu_0 = 2264.8$ $I_0 = 0.130 \pm 0.004$ $\sigma = 4.6 \pm 0.1$ $A = 0.3555$	$\nu_0 = 2262.2$ $I_0 = 0.034 \pm 0.006$ $\sigma = 14.5 \pm 0.7$ $A = 0.8169$	$\nu_0 = 2256.0$ $I_0 = 0.060 \pm 0.004$ $\sigma = 8.3 \pm 0.2$ $A = 0.8205$
0.4232 M AN 18C6/AN = 0.2012 0.0851 M 18C6 InCCl ₄	$\nu_0 = 2275.0$ $I_0 = 0.072 \pm 0.002$ $\sigma = 15.0 \pm 2.0$ $A = 0.1819$	$\nu_0 = 2264.8$ $I_0 = 0.140 \pm 0.003$ $\sigma = 4.6 \pm 0.1$ $A = 0.3850$	$\nu_0 = 2262.2$ $I_0 = 0.026 \pm 0.005$ $\sigma = 20.0 \pm 1.0$ $A = 0.8522$	$\nu_0 = 2256.0$ $I_0 = 0.095 \pm 0.003$ $\sigma = 8.0 \pm 0.2$ $A = 1.248$
0.4232 M AN 18C6/AN = 0.0 0.0 M 18C6 InCHCl ₃	$\nu_0 = 2276.0$ $I_0 = 0.0238 \pm 0.0004$ $\sigma = 14.0 \pm 0.2$ $A = 0.5464$	$\nu_0 = 2265.7$ $I_0 = 0.265 \pm 0.003$ $\sigma = 4.99 \pm 0.05$ $A = 0.9033$	$\nu_0 = 2260.0$ $I_0 = 0.100 \pm 0.001$ $\sigma = 8.1 \pm 0.2$ $A = 1.329$	no complex

Table 23. Continued.

Solution	Peak 1	Peak 2	Peak 3	Peak 4
0.4266 M AN 18C6/AN = 0.5935	$\nu_0 = 2276.0$ $I_0 = 0.022 \pm 0.004$	$\nu_0 = 2265.7$ $I_0 = 0.234 \pm 0.003$	$\nu_0 = 2260.0$ $I_0 = 0.075 \pm 0.004$	$\nu_0 = 2257.6$ $I_0 = 0.044 \pm 0.004$
0.2532 M 18C6 InCHCl ₃	$\sigma = 16.0 \pm 0.2$ $A = 0.5789$	$\sigma = 4.90 \pm 0.04$ $A = 0.7615$	$\sigma = 6.1 \pm 0.3$ $A = 0.7455$	$\sigma = 13.6 \pm 0.5$ $A = 0.9850$
0.3472 M AN 18C6/AN = 1.4786	$\nu_0 = 2276.0$ $I_0 = 0.022 \pm 0.002$	$\nu_0 = 2265.7$ $I_0 = 0.182 \pm 0.003$	$\nu_0 = 2260.0$ $I_0 = 0.051 \pm 0.003$	$\nu_0 = 2257.6$ $I_0 = 0.079 \pm 0.004$
0.5133 M 18C6 InCHCl ₃	$\sigma = 12.1 \pm 0.3$ $A = 0.4350$	$\sigma = 4.54 \pm 0.08$ $A = 0.4832$	$\sigma = 5.3 \pm 0.3$ $A = 0.4466$	$\sigma = 11.9 \pm 0.2$ $A = 1.550$

a) ν_0 = peak position in cm^{-1} ; I_0 = maximum intensity in absorbance units; σ = variance in cm^{-1} ; A = area

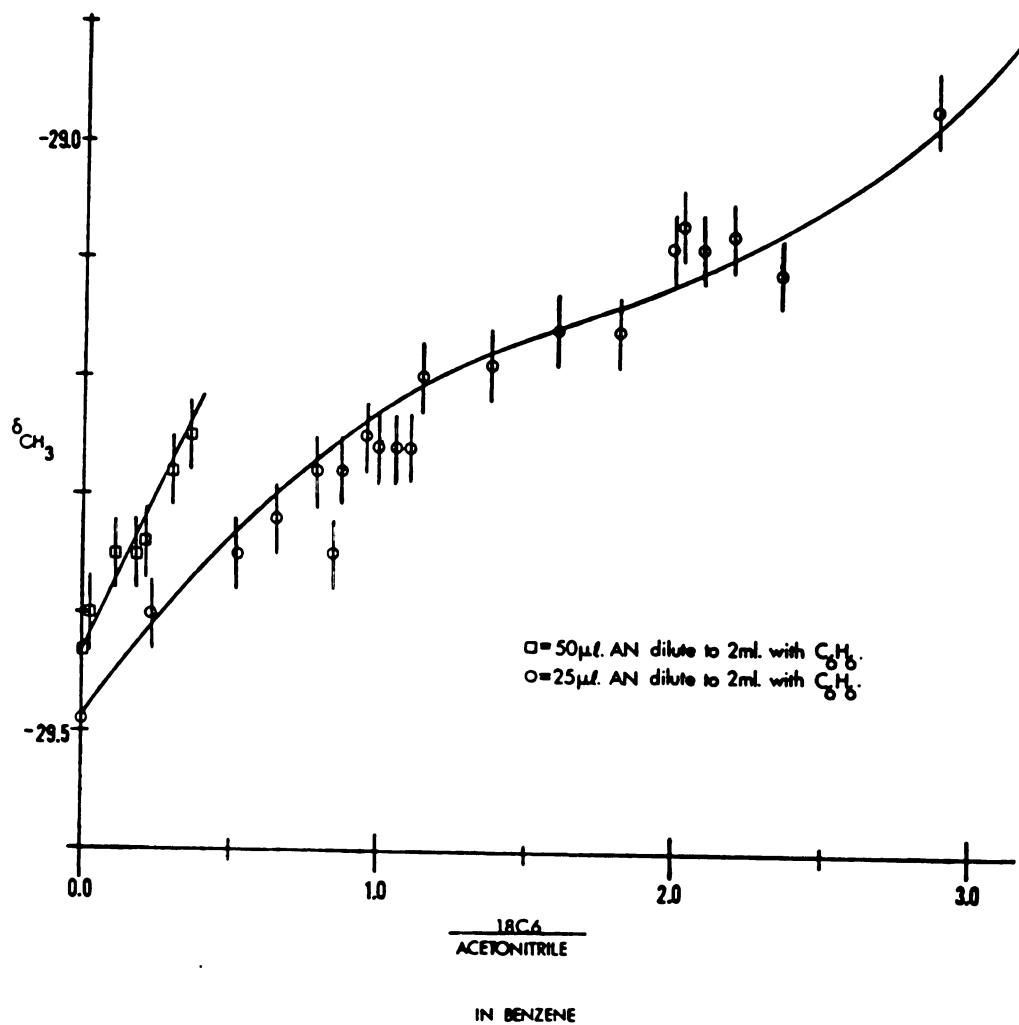


Figure 72 . Plot of the ^{13}C chemical shift of the methyl carbon of MeCN vs. $[^{18}C_6]/[MeCN]$ in benzene.

Table 24. Association Constants of the Complexes of 18-Crown-6 With Several Neutral Guest Molecules at 298°K.

Guest	Background Solvent	Association Constant (m.f. ⁻¹)	Association Constant (l mol ⁻¹)	¹³ C Chemical Shifts, ppm
^a MeCN	C ₆ H ₆	K _{1:1} = 12 ± 2	K _{1:1} = 1.0 ± 0.2	^{CH₃} δ _{1:1} = -28.5 ± 0.1
^b MeCN	AC	K _{1:2} = 2.9 ± 0.5	K _{1:2} = 0.26 ± 0.04	^{CH₃} δ _{1:2} = -25.2 ± 0.7
^a MeCN	CHCl ₃	K _{1:1} = 8 ± 1	K _{1:1} = 0.57 ± 0.07	^{CN} δ _{1:1} = 41.2 ± 0.2
^a MeNO ₂	C ₆ H ₆	K _{1:1} < 4	K _{1:1} < 0.4	
		K _{1:1} = 15 ± 2	K _{1:1} = 1.3 ± 0.2	δ _{1:1} = 34.6 ± 0.3
		K _{1:2} = 16 ± 3	K _{1:2} = 1.4 ± 0.3	δ _{1:2} = 37 ± 1
^a CHCl ₃	C ₆ H ₆	K _{1:1} = 6.8 ± 0.3	K _{1:1} = 0.60 ± 0.03	δ _{1:1} = 50.86 ± 0.08
^b AC	C ₆ H ₆	K _{1:1} < 2.4	K _{1:1} < 0.21	
^a DMF	C ₆ H ₆	K _{1:1} < 2.4	K _{1:1} < 0.21	

^aExternal lock and reference is acetone-d₆.

^bExternal lock and reference is chloroform-d.

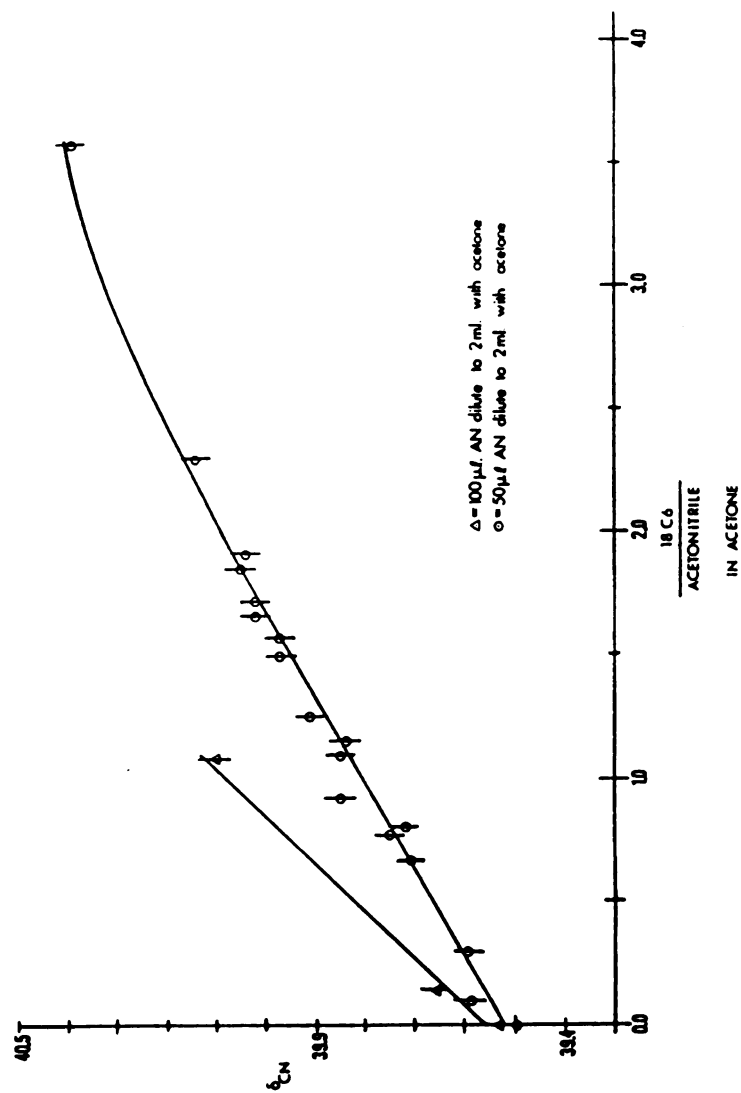
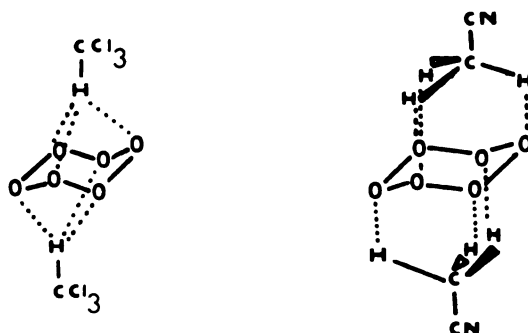


Figure 73. Plots of the carbon-13 chemical shifts of the nitrile carbon of acetonitrile as a function of $[18C6]/[AN]$ mole ratio in acetone.

formed. The carbon-13 chemical shift data were computer analyzed after correction for the chemical shift of the uncomplexed acetonitrile. The results of this analysis are shown in Table 24. Because acetone forms a weak complex with 18C6, K_1 in acetone is smaller than K_1 in benzene.

It is interesting to note that the nitrile group of acetonitrile is affected the most by complexation with 18C6. This is the case for the Raman studies done on the solid complexes as well as the solution studies reported in this thesis. It does not mean, however, that the nitrile group interacts with 18C6. The crystal structure of the 18C6 $2\text{CH}_3\text{CN}$ complex showed that the methyl protons of acetonitrile are hydrogen-bonded to the ether oxygens of 18C6. The mass spectrum of the 18C6-MeCN system indicated that the methyl groups were interacting with the crown in the gas phase. If the methyl group is the site of interaction for both the solid and gas phases, it is logical to expect it to be the interacting site in solution. Furthermore, as discussed previously, the symmetry of 18C6 in chloroform solution has some D_{3d} character. However, in a CCl_4 solution of MeCN-d_3 the crown has D_{3d} symmetry. The D_{3d} symmetry of 18C6 in chloroform results because there is only one hydrogen bonding to three ether oxygens, as shown below. If the methyl group of MeCN-d_3 complexes the crown ether, then

three hydrogens are bonding to three ether oxygens resulting in a rigid conformer with D_{3d} symmetry as shown:



The complexation of 18C6 and nitromethane was also studied in benzene solutions: the results, obtained at 25°C , are shown in Figure 74. The chemical shift plots of the methyl carbon show two breaks indicating the formation of two complexes. The results of the analysis of the data are tabulated in Table 24.

As seen in Table 24, nitromethane forms more stable complexes with 18C6 than does acetonitrile, and that in the former case $K_1 \approx K_2$. Instances of cooperative effects in macrocyclic complexation reactions are well documented by Rebek (208). In these reactions macrocyclic ligands usually undergo conformational changes. It should be noted that, especially in nonaqueous solvents, macrocyclic complexation reactions have negative entropies of complexation largely due to conformational changes (209-211). It seems reasonable, therefore, to assume that in the case of nitromethane the formation of the 1:1 complex predisposes the ligand to accept the second solvent molecule. This effect is not observed with

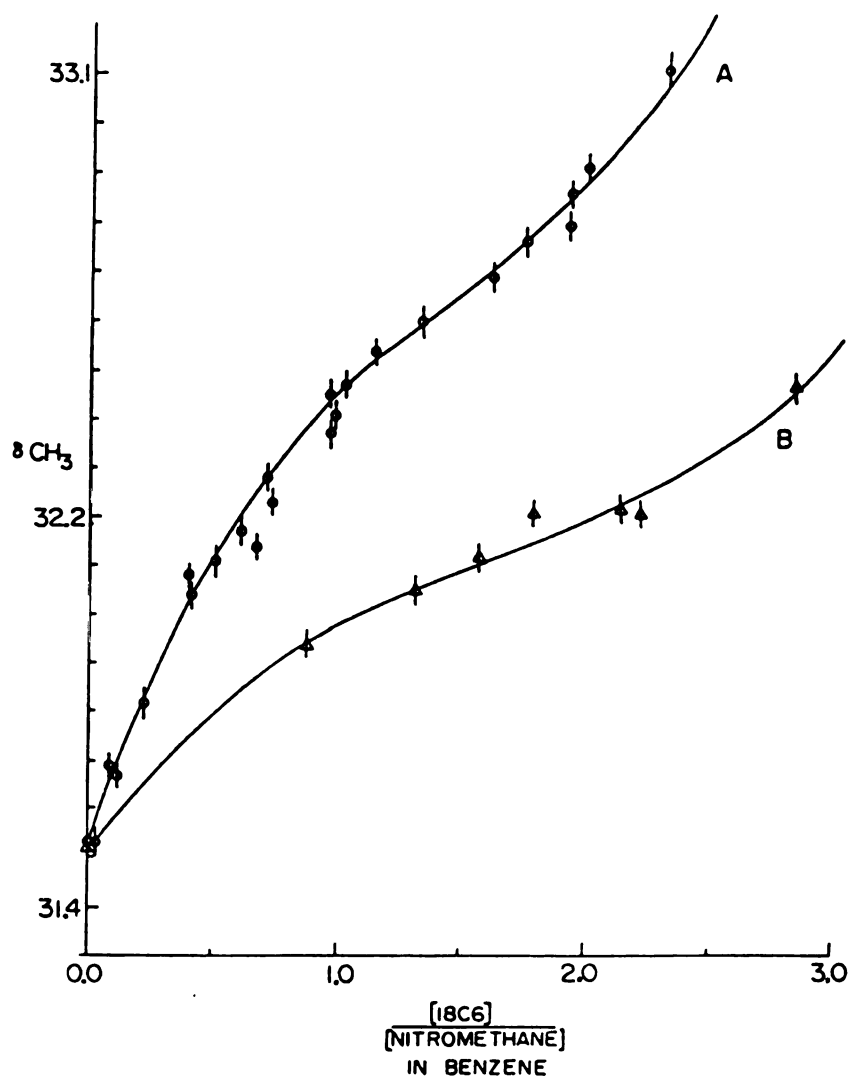


Figure 74 . Plots of the carbon-13 chemical shifts of the methyl carbon of nitromethane as a function of $[18\text{C}_6]/[\text{NM}]$ mole ratio. In the plots (A) refers to solutions prepared using 25 μl of NM and diluting to 2 ml with benzene whereas (B) refers to 25 μl of NM diluted to 5 ml.

acetonitrile, probably because in this case the methyl group is less electropositive than that of nitromethane (212, 58) and a less rigid complex is formed with 18C6.

The results of the complexation of acetonitrile and nitromethane with 18C6 in benzene contrast with those obtained by de Boer et al. (in C_6D_6 at $300^\circ K$, $K_{1:1}^{NM}=1.2\ M^{-1}$ and $K_{1:2}^{NM}=2.5\ M^{-1}$ and $K_{1:1}^{AN}=0.48\ M^{-1}$ (147)). De Boer obtained these results using 1H NMR. Although he corrected the chemical shifts of the "free" complexing solvent molecules, he did not take into account the self-association of these molecules. He also made the assumption that $\delta_{1:1} = \delta_{1:2}$, where $\delta_{1:1}$ and $\delta_{1:2}$ refer to the chemical shifts of the 1:1 and 1:2 18C6:molecule complexes. In his study he used an internal reference and had only ten points. The carbon-13 chemical shift data that were obtained for these systems were analyzed using de Boer's assumptions. The results are tabulated in Table 25. Using his assumptions resulted in $K_2 > K_1$ in one instance for the $MeNO_2$ -18C6 complexation ($\delta_{1:1} \neq \delta_{1:2}$). What was surprising was the effects de Boer's assumptions had on the chemical shifts. The calculated chemical shifts for the 1:1 and 1:2 crown complexes far exceed the carbon-13 chemical shift range. These computer analyses indicate that there is a severe problem with de Boer's model and show the importance of solvent self-associations.

Table 25. Association Constants Obtained for the Complexation of 18C6 With NM and AN Using deBoer's Assumptions.

MODEL	K_{NM} (M^{-1})	$^{13}C \delta_{NM}$ (ppm)	K_{AN} (M^{-1})	$^{13}C \delta_{AN}$ (ppm)
$S+S \xrightleftharpoons{K_d} S_2$ $S+L \xrightleftharpoons{K_{1:1}} SL$ $SL+S \xrightleftharpoons{K_{1:2}} SLS$	$K_d=0.0205 \pm 0.0008$ $K_{1:1}=1.3 \pm 0.2$ $K_{1:2}=1.4 \pm 0.3$	$\delta_S=31.49$ $\delta_{S_2}=37.7 \pm 0.2$ $\delta_{SL}=34.6 \pm 0.3$ $\delta_{SLS}=37 \pm 1$	$K_d=0.0224 \pm 0.0007$ $K_{1:1}=1.0 \pm 0.2$ $K_{1:2}=0.26 \pm 0.04$	$\delta_S=-29.54$ $\delta_{S_2}=-24.1 \pm 0.1$ $\delta_{SL}=-28.5 \pm 0.1$ $\delta_{SLS}=-25.2 \pm 0.7$
deBoer's Model: $S+L \xrightleftharpoons{K_{1:1}} SL$ $SL+S \xrightleftharpoons{K_{1:2}} SLS$ $\delta_{1:1} \neq \delta_{1:2}$	$K_{1:1}=1.0 \pm 0.2$ $K_{1:2}=2.2 \pm 1.3$	$\delta_S=2.24[S]+31.51$ $\delta_{1:1}=430 \pm 70$ $\delta_{1:2}=11000 \pm 4000$	$K_{1:1}=0.63 \pm 0.09$ $K_{1:2}=0.08 \pm 0.02$	$\delta_S=2.34[S]-29.51$ $\delta_{1:1}=-190 \pm 40$ $\delta_{1:2}=-80 \pm 20$
deBoer's Model: $S+L \xrightleftharpoons{K_{1:1}} SL$ $SL+S \xrightleftharpoons{K_{1:2}} SLS$ $\delta_{1:1} = \delta_{1:2}$	$K_{1:1}=1.8 \pm 0.3$ $K_{1:2}=0$	$\delta_S=2.24[S]+31.51$ $\delta_{1:1}=\delta_{1:2}=700 \pm 100$	$K_{1:1}=0.81 \pm 0.09$ $K_{1:2}=0.120 \pm 0.008$	$\delta_S=2.34[S]-29.51$ $\delta_{1:1}=\delta_{1:2}=-270 \pm 40$

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The complexation of 18C6 with CHCl_3 was studied in benzene solutions by ^{13}C NMR spectroscopy. Figure 75 shows the chemical shift plot obtained. The plot indicates formation of the 1:1 complex. The chemical shift data were computer analyzed; the results of the analysis are tabulated in Table 24.

The complexation of AC with 18C6 in benzene was also studied by carbon-13 NMR spectroscopy. The results are plotted in Figure 76. The amount of curvature is very small indicating that the complex is very weak. Attempts to computer analyze the chemical shift data resulted in K_1 approaching zero and $\delta_{1:1}$ approaching infinity. These results simply indicate that the formation constant is too small to be measured by ^{13}C NMR. An upper limit of the formation constant is given in Table 24.

A carbon-13 NMR study was done of the complexation of DMF with 18C6 in benzene. The results of this study are shown in Figure 77. There are three possible sites of complexation for DMF - the two methyl groups and the amide proton. As Figure 77 shows, the chemical shift plots of the carbons of the methyl groups and the amide carbon exhibit a concentration dependence. However no curvature is observed for either of the plots. This implies that both methyl groups and the amide proton interact with 18C6. It also implies that neither site interacts preferentially with 18C6. Consequently, because of the

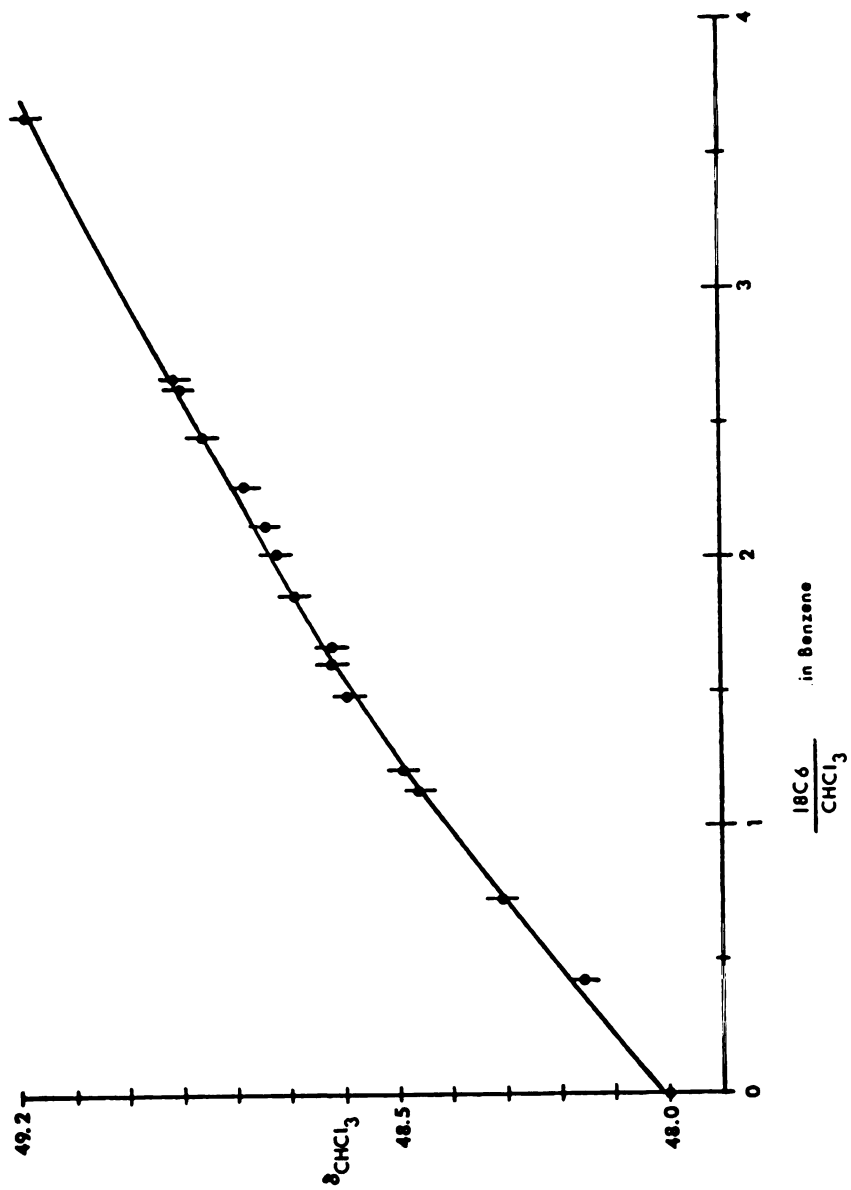


Figure 75. Plot of the carbon-13 chemical shift of chloroform as a function of $[\text{18C}_6]/[\text{CHCl}_3]$ in benzene.

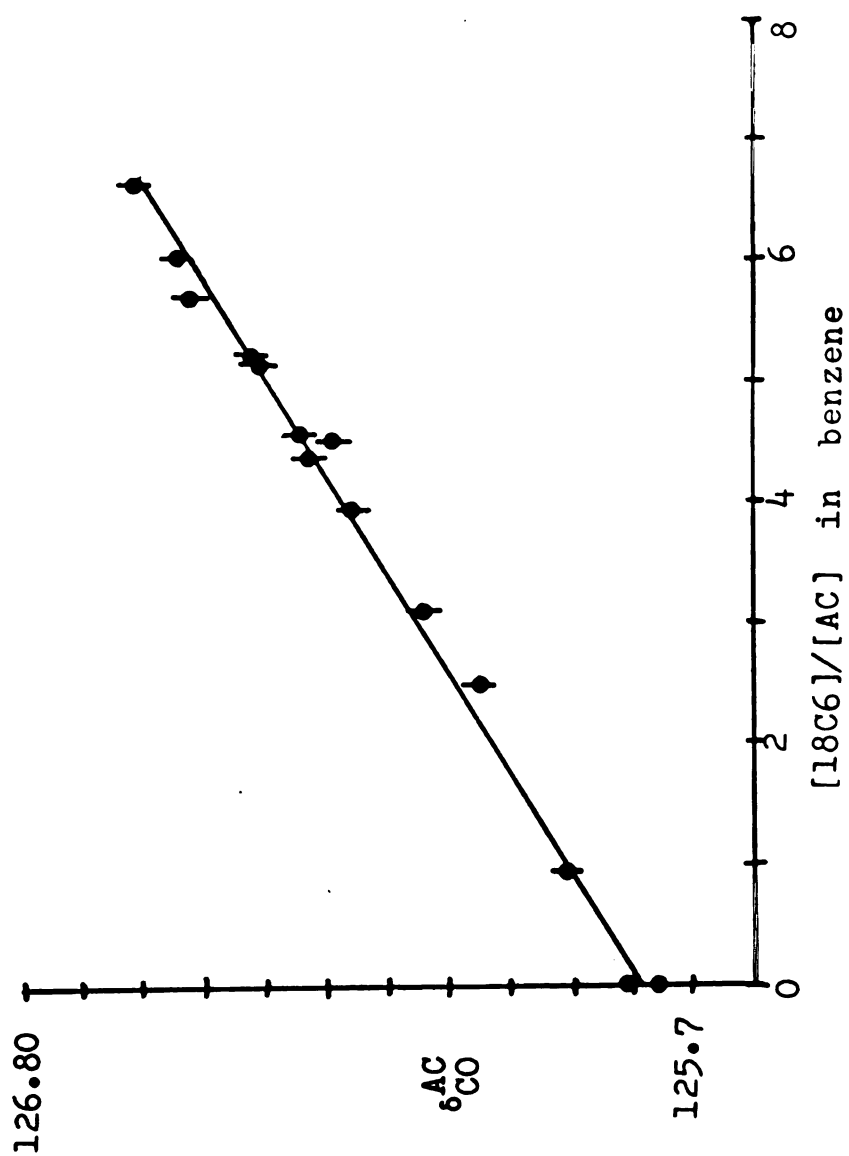


Figure 76. Plot of the carbon-13 chemical shift of acetone as a function of $[\text{18C6}]/[\text{AC}]$ in benzene.

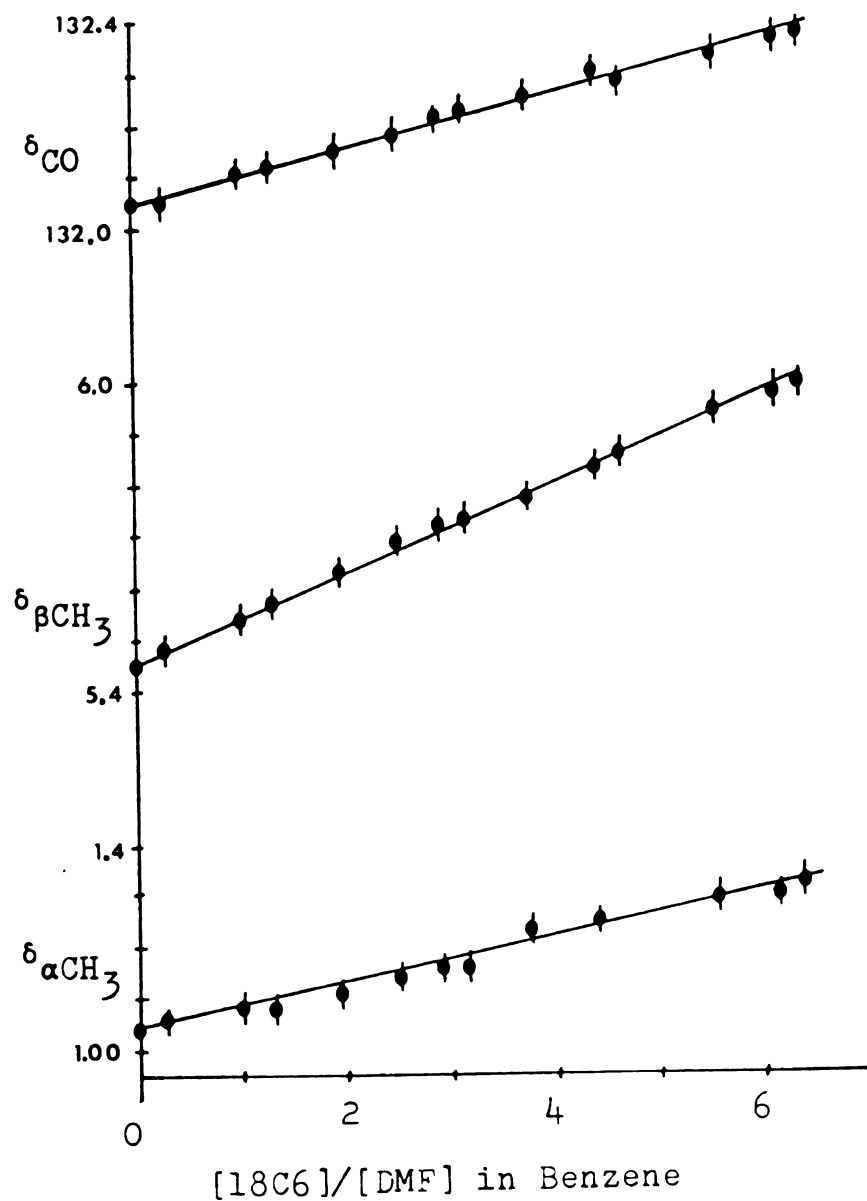


Figure 77 . Plots of the carbon-13 chemical shift of the carbons of DMF as a function of [18C6]/[DMF] in benzene.

multiple sites, the complexation appears to be weak.

The complexation of MeOH with 18C6 in benzene solutions was studied by both ^1H and ^{13}C NMR spectroscopy. The carbon-13 chemical shift data of the methyl carbon (Table 36 of Appendix III) show very little effect due to complexation. The same is not true of the proton chemical shift data. The fact that the methyl carbon shows little effect implies that the interaction between 18C6 and MeOH occurs through the hydroxyl proton. This is further borne out by the proton spectra obtained in benzene and deuterated benzene and shown in Figure 78. Prior to the addition of the 18C6, the hydroxyl proton is not exchanging; i.e., the concentration of methanol is sufficiently low that the methanol is completely solvated. Below an $[\text{18C6}]/[\text{MeOH}]$ mole ratio of 1.00 single resonances are observed for the methyl and hydroxyl groups of MeOH indicating that the hydroxyl proton is in exchange. Beyond mole ratio 1.00, the hydroxyl proton is no longer exchanging. This exchange behavior clearly indicates complexation of 18C6 through the hydroxyl group.

The proton chemical shift plots of the hydroxyl and methyl groups are shown in Figure 79. Both groups show only one break at the same position indicating the formation of a 1:1 complex. The methyl group protons are affected by complexation with 18C6 and this complexation perturbs the methyl group-benzene interaction. The proton

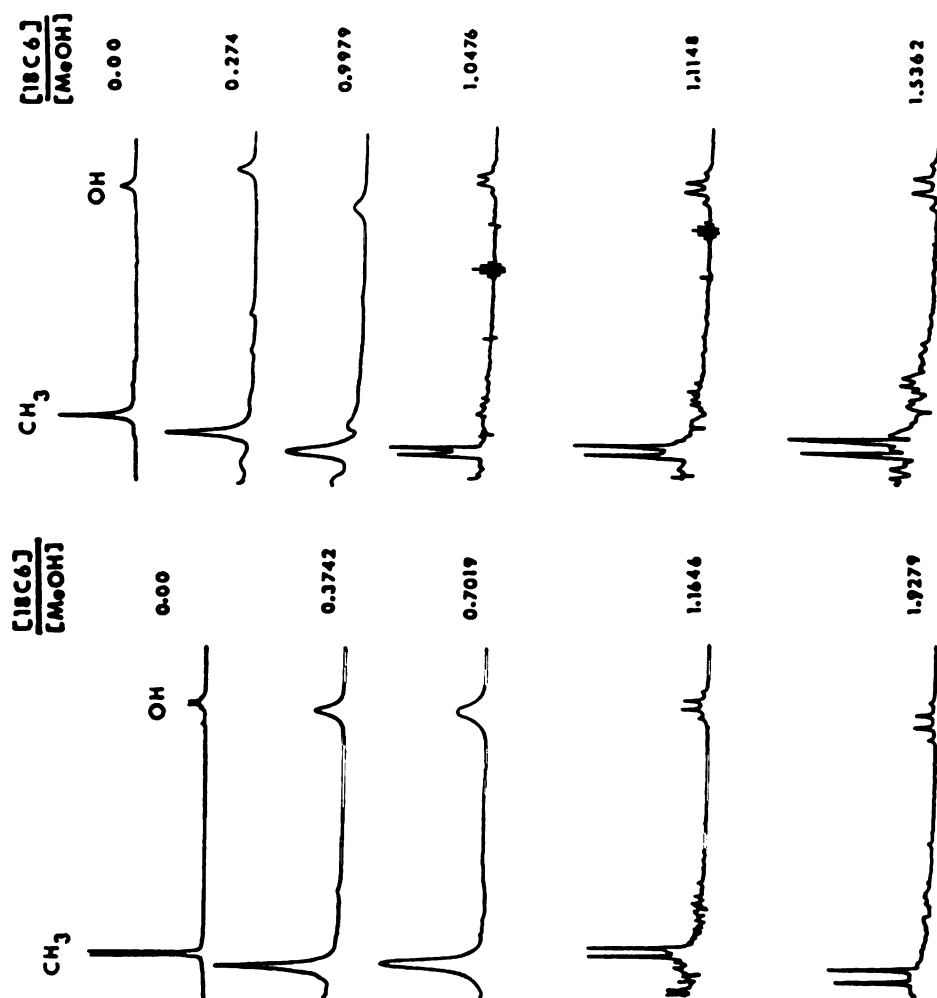


Figure 78. Proton spectra of methanol and 18C6 in benzene and benzene-d₆.

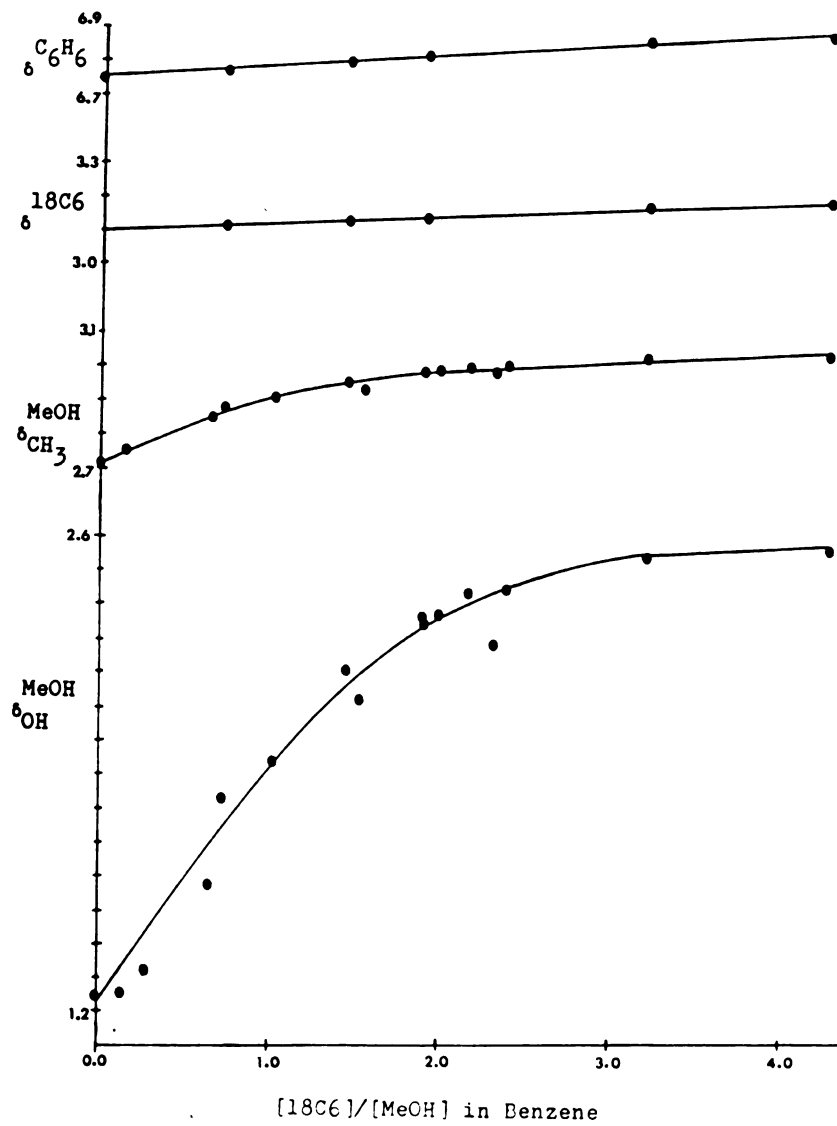


Figure 79. Plots of the proton chemical shifts of C_6H_6 , $18C6$ and MeOH as a function of $[18C6]/[MeOH]$.

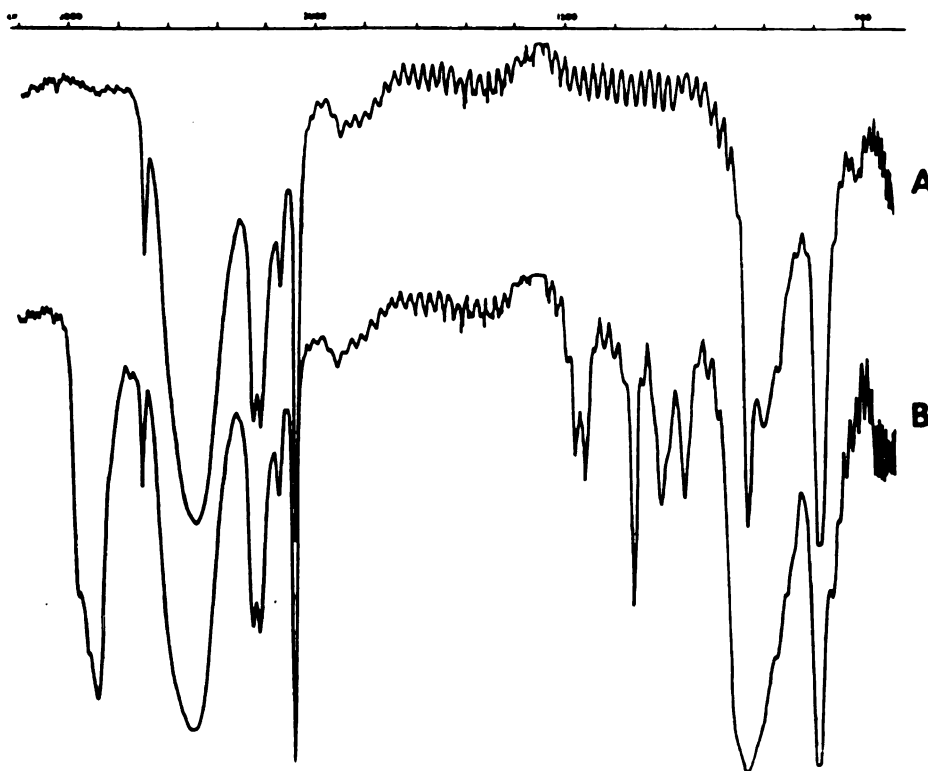
chemical shift data for both the methyl and hydroxyl groups were computer analyzed. The results of this analysis are shown in Table 26. It should be emphasized that this formation constant is a conditional constant since no model was found which would explain the chemical shift behavior of the $\text{MeOH-C}_6\text{H}_6$ system and therefore the "true" formation constant must be larger. In the computer analysis of the $\text{MeOH-18C6-C}_6\text{H}_6$ system, the chemical shift dependence of the "free" methyl and hydroxyl groups were taken into account. The results of the analysis show that methanol forms a fairly stable complex with 18C6.

Infrared spectra of the $\text{MeOH-d}_4\text{-18C6-CCl}_4$ and MeOH-18C6-CCl_4 systems are shown in Figures 80 and 81. These spectra show that no conformational change of 18C6 occurs when either MeOH or MeOH-d_4 are added. This implies interaction through the hydroxyl group similar to that observed for CHCl_3 . Figure 82 shows the OH stretching region of methanol in CCl_4 . As the concentration of 18C6 increases, the monomer peak at 3638 cm^{-1} decreases and a new band due to complexation near 3500 cm^{-1} increases. The size of this new band indicates that the complexation between MeOH and 18C6 is fairly strong. The bands due to methanol aggregates are suppressed with the addition of 18C6. This implies that complexation with 18C6 is sufficiently strong to break up the dimers, trimers, etc. of methanol. This also infers

Table 26. Association Constants of the Complexes of Methanol With Several Polyether Ligands in Benzene at 298°K.

Ligand	Association Constant (m.f. ⁻¹)	Association Constant (l mol ⁻¹)	¹ H Chemical Shift, ppm
^a 18C6	K ₁ :1 = 137 ± 21	K ₁ :1 = 12.2 ± 1.9	δ ^{CH} 3 = 3.05 ± 0.01 δ ^{OH} = 2.70 ± 0.04
^a 15C5	K ₁ :1 = 90 ± 36	K ₁ :1 = 8.0 ± 3.2	δ ^{CH} 3 = 3.07 ± 0.02 δ ^{OH} = 3.1 ± 0.2
^a B15C5	K ₁ :1 = 110 ± 35	K ₁ :1 = 9.8 ± 3.1	δ ^{CH} 3 = 2.84 ± 0.02 δ ^{OH} = 2.34 ± 0.09
^a TG	K ₁ :1 = 55 ± 8	K ₁ :1 = 4.9 ± 0.7	δ ^{CH} 3 = 3.18 ± 0.03 δ ^{OH} = 2.94 ± 0.06

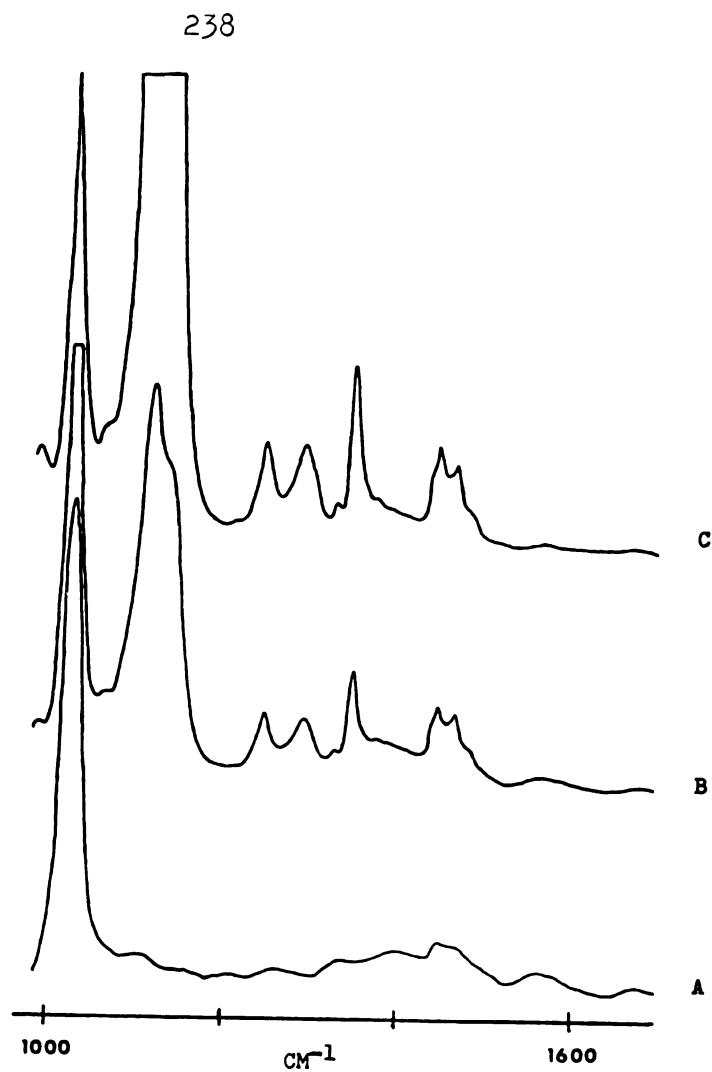
^aChemical shifts are reported relative to TMS in acetone-d₆.



(A) 1.140 M CD_3OD

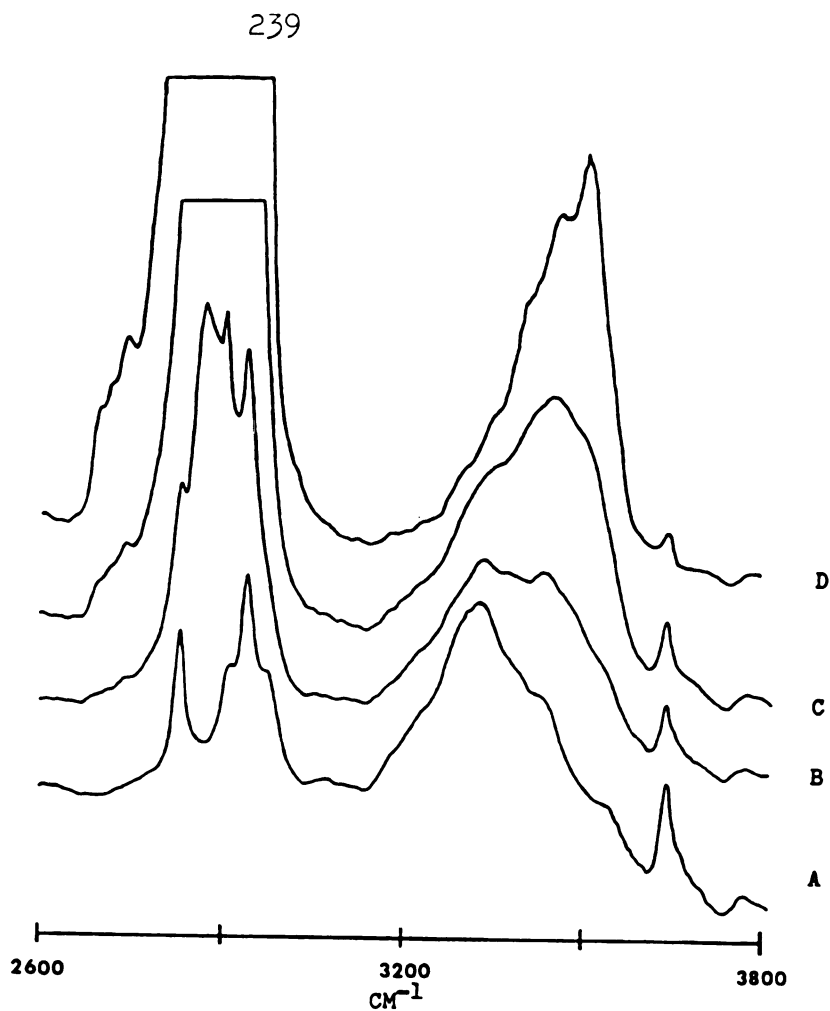
(B) 1.015 M CD_3OD ; $[\text{18C6}]/[\text{CD}_3\text{OD}] = 0.102$

Figure 80. Infrared spectra of solutions of methanol- d_4 and 18C6 in carbon tetrachloride.



- (A) 0.4557 M MeOH
 (B) 0.5368 M MeOH; $[18C6]/[MeOH]=0.2129$
 (C) 0.4806 M MeOH; $[18C6]/[MeOH]=0.5621$

Figure 81. Infrared spectra of the 1000-1600 cm^{-1} region of solutions of methanol and 18C6 in carbon tetrachloride.

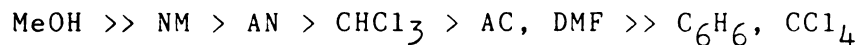


- (A) 0.4557 M MeOH; $[18C6]/[MeOH]=0.00$
 (B) 0.5368 M MeOH; $[18C6]/[MeOH]=0.2129$
 (C) 0.4806 M MeOH; $[18C6]/[MeOH]=0.5621$
 (D) 0.5400 M MeOH; $[18C6]/[MeOH]=1.2615$

Figure 82. Infrared spectra of the CH and OH stretches of methanol ($3020-2780\text{ cm}^{-1}$ and $3800-3200\text{ cm}^{-1}$, respectively) in solutions of methanol and 18C6 in carbon tetrachloride.

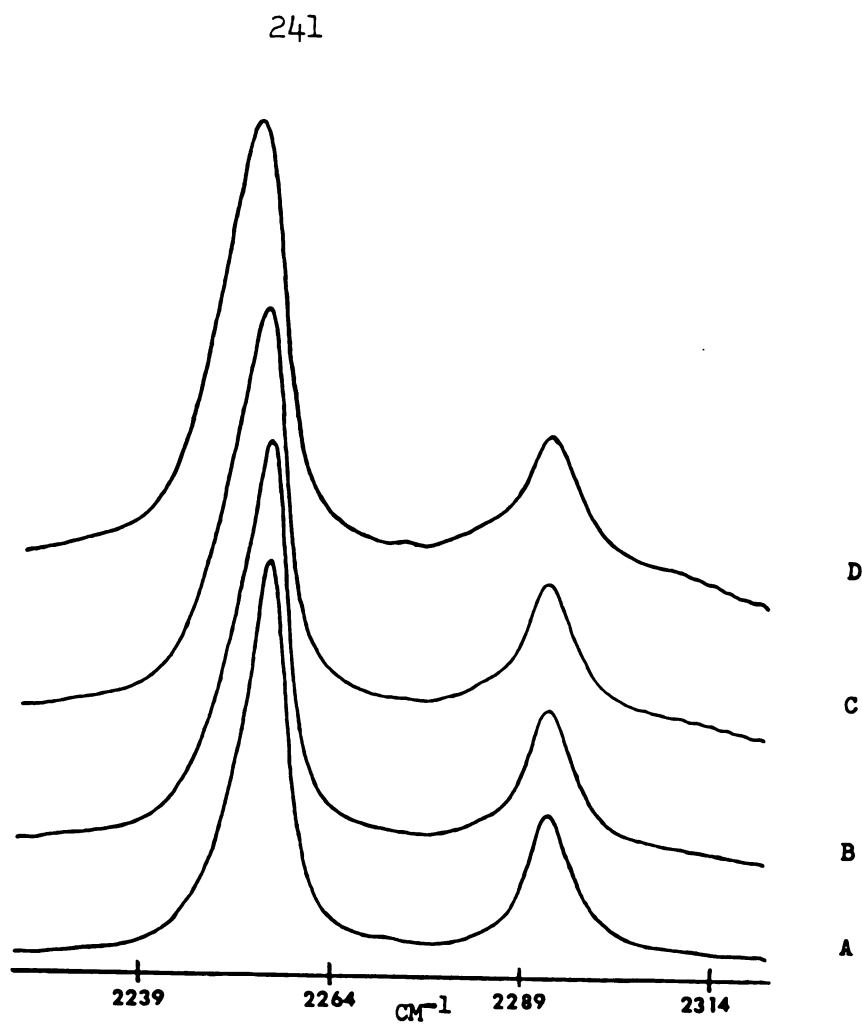
that the site of interaction is the hydroxyl group.

The results shown in Tables 24 and 26 show that the strength of 18C6-solvent interaction varies in the order:



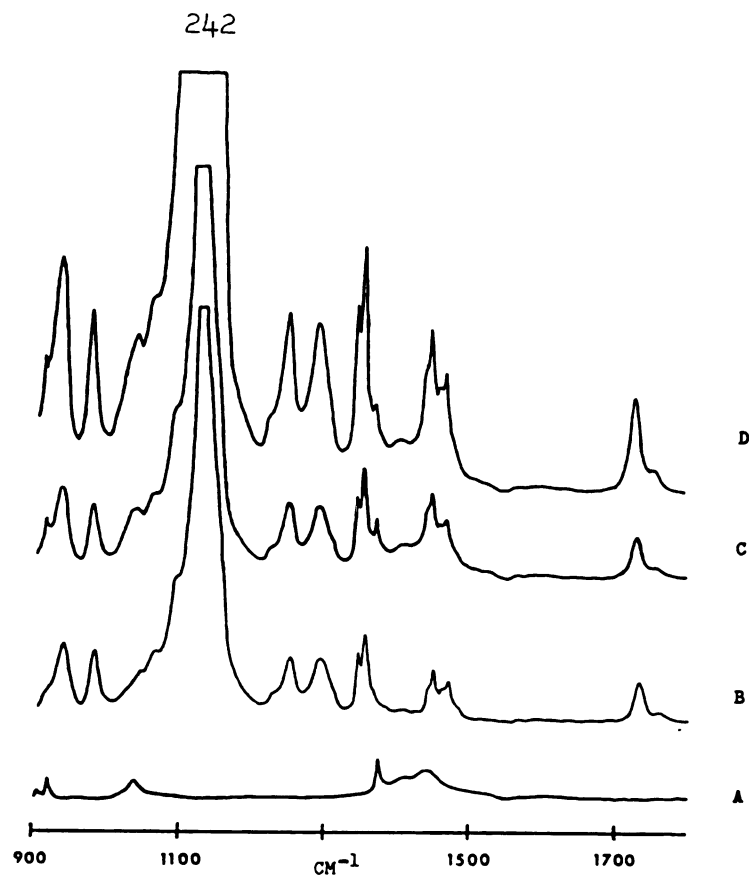
3. 15-CROWN-5 COMPLEXATION WITH NITROMETHANE, ACETONITRILE, CHLOROFORM, ACETONE, DIMETHYLFORMAMIDE AND METHANOL. The complexation of 15C5 with acetonitrile was studied in carbon tetrachloride by infrared spectroscopy. The CN stretch of acetonitrile, ν_2 , occurs at 2255 cm^{-1} . With the addition of 15C5, the ν_2 band due to complexation appears as a shoulder (Figure 83). Furthermore, as shown in Figure 84, no changes were observed in the vibrations of the free and complexed crown indicating that no conformational changes of 15C5 are occurring. These results are in sharp contrast to what was observed for 18C6 and MeCN in CCl_4 solutions. For the MeCN-18C6- CCl_4 system a new band does grow out of ν_2 at 2245 cm^{-1} and a conformational change is observed for 18C6. In CCl_4 , 18C6 exists as a mixture of conformers. With the addition of MeCN, 18C6 assumes D_{3d} symmetry. The infrared spectra clearly indicate that the complexation of MeCN with 15C5 is weaker than with 18C6.

Carbon-13 chemical shifts of acetonitrile carbons were measured in the presence of 15C5 as a function of $[\text{15C5}]/[\text{MeCN}]$ mole ratio at a fixed concentration of MeCN in benzene. The chemical shift plots for the methyl and



- (A) 0.4564 M AN; $[15C5]/[AN]=0.00$
 (B) 0.4653 M AN; $[15C5]/[AN]=0.3688$
 (C) 0.4373 M AN; $[15C5]/[AN]=0.9147$
 (D) 0.4665 M AN; $[15C5]/[AN]=2.0315$

Figure 83. Infrared spectra of the CN stretch of acetonitrile of solutions of 15C5 and acetonitrile in carbon tetrachloride.



- (A) 0.4564 M AN
 (B) 0.1510 M 15C5
 (C) 0.4653 M AN; $[15C5]/[AN]=0.3688$
 (D) 0.4373 M AN; $[15C5]/[AN]=0.9147$

Figure 84. Infrared spectra of the 900-1700 cm^{-1} region of solutions of acetonitrile and 15C5 in carbon tetrachloride.

nitrile carbons of MeCN in benzene (Figure 85) showed one break indicative of the formation of one complex. The carbon-13 chemical shift data were computer analyzed by using KINFIT. The model used to describe the chemical shift data is described in Appendix I. The results of this analysis are tabulated in Table 27.

The complexation of 15C5 and nitromethane was also studied in benzene solution by carbon-13 NMR spectroscopy. Just as for the MeCN-15C5-C₆H₆ system, the chemical shift plot of the MeNO₂-15C5-C₆H₆ system (Figure 86) shows only one break indicative of the formation of a 1:1 complex. The chemical shift data were computer analyzed taking into account the dimerization of MeNO₂. The results of the analysis are tabulated in Table 27.

These results contrast with those obtained for 18C6. With 18C6, MeCN and MeNO₂ form both 1:1 and 1:2 crown:solvent complexes. The formation constants for these complexes with 18C6 are also larger than with 15C5. From space-filling models of 18C6 and 15C5, illustrated in Figure 87, it can be seen that the methyl groups of MeNO₂ and MeCN have the appropriate spacial orientation to hydrogen bond with three of the ether oxygens of 18C6. However, 15C5 is a more rigid molecule and cannot assume a conformation that will allow three of its ether oxygens to hydrogen bond with all three methyl protons. At best only two methyl protons can hydrogen bond to form a complex

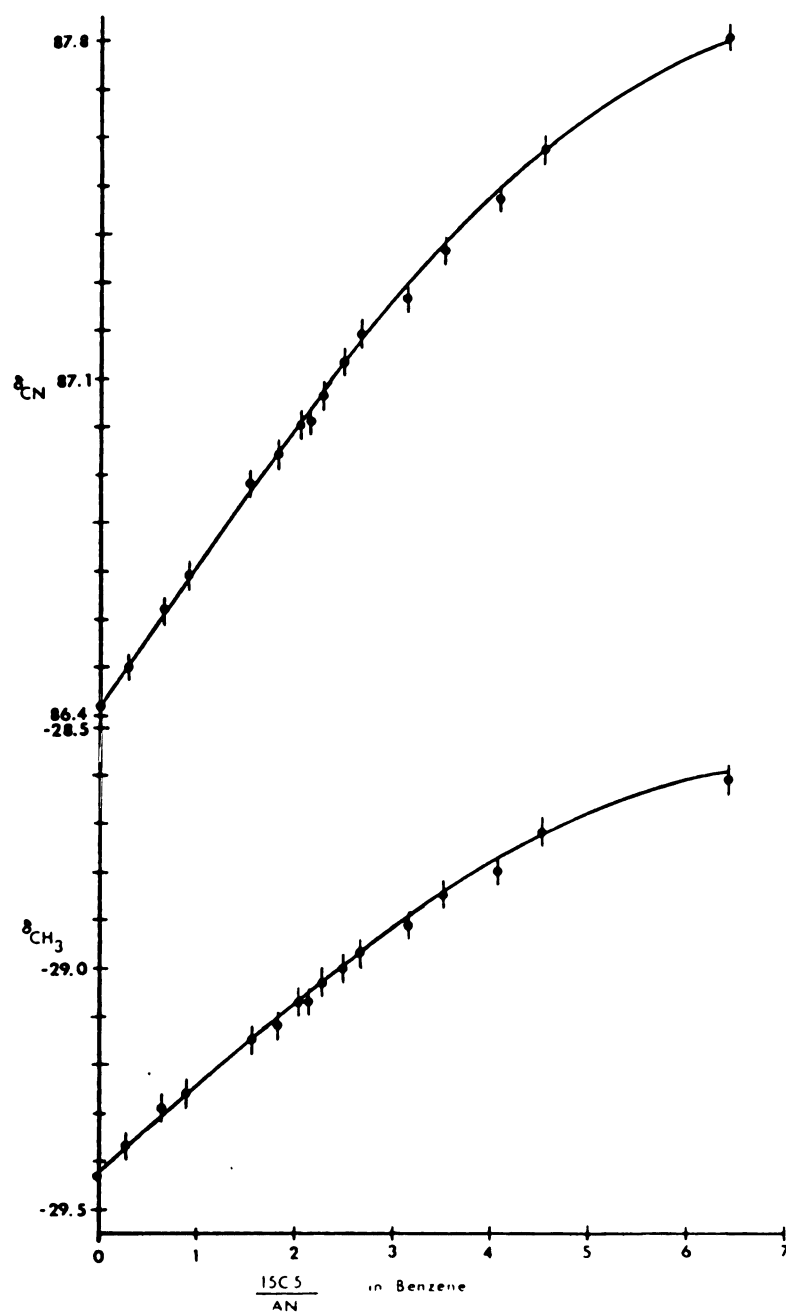


Figure 85. Plots of the carbon-13 chemical shifts of the carbons of AN vs. $[^{15}\text{C}5]/[\text{AN}]$ in benzene.

Table 27. Association Constants for the Complexes of 15-Crown-5 With Several Neutral Guest Molecules in Benzene at 298°K.

Guest	Association Constant (m.f. ⁻¹)	Association Constant (l mol ⁻¹)	¹³ C Chemical Shifts, ppm
^a MeCN	K _{1:1} = 4.5 ± 0.2	K _{1:1} = 0.38 ± 0.02	δ ^{CH₃} = -28.00 ± 0.03 δ ^{CN} = 88.86 ± 0.05
^a MeNO ₂	K _{1:1} = 5.2 ± 0.9	K _{1:1} = 0.46 ± 0.08	δ = 34.3 ± 0.3 ²⁴⁵
^a CHCl ₃	K _{1:1} = 5.4 ± 0.2	K _{1:1} = 0.48 ± 0.02	δ = 50.77 ± 0.07
^b AC	K _{1:1} = 3.2 ± 0.8	K _{1:1} = 0.28 ± 0.07	δ ^{CO} = 127.8 ± 0.3
DMF	K _{1:1} < 2.4	K _{1:1} < 0.21	

^a External lock and reference is acetone-d₆.

^b External lock and reference is chloroform-d.

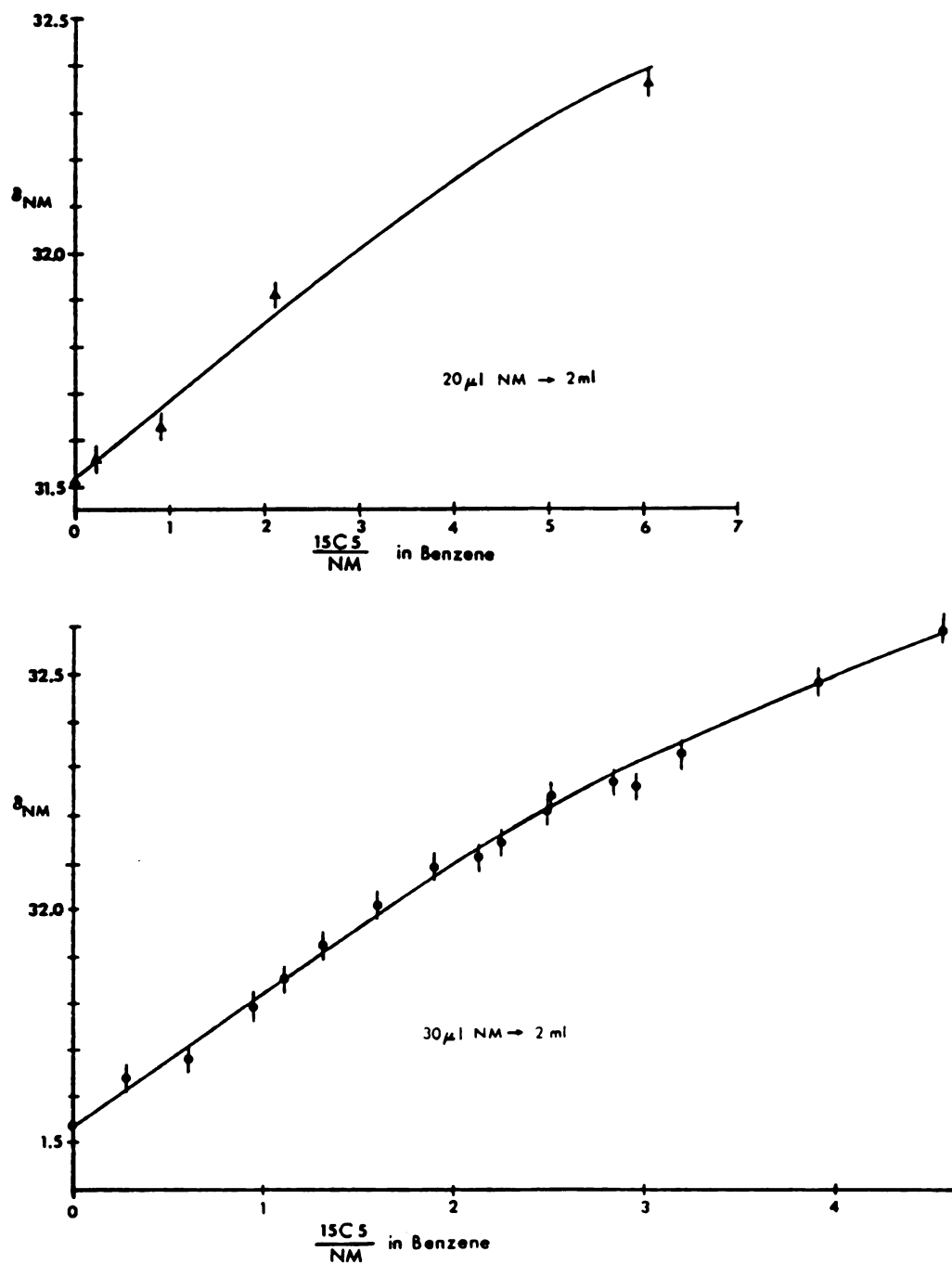


Figure 86. Plot of the carbon-13 chemical shift of NM as a function of $[^{15}C_5]/[NM]$ in benzene.

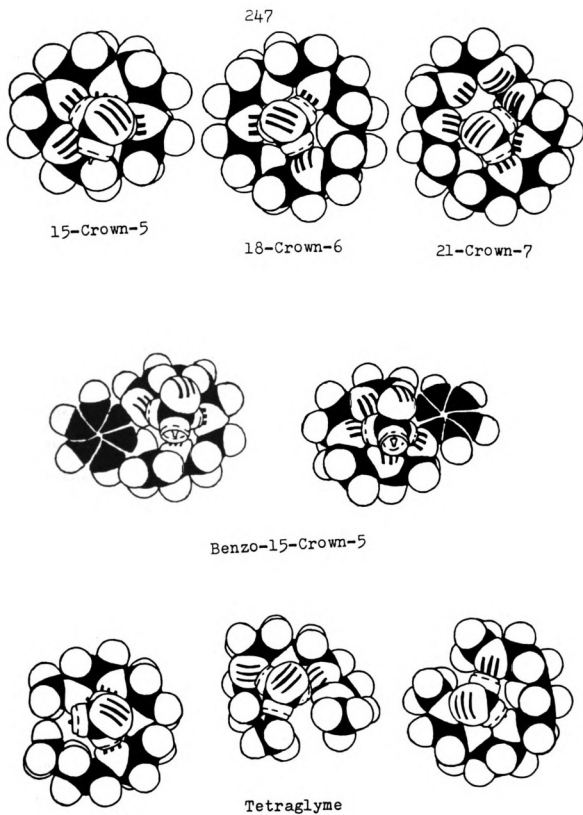


Figure 87. Space-filling models of CH_2 -acid complexes with linear and cyclic polyethers.

with 15C5. As a result of poor orbital overlap, the MeCN and MeNO₂ complexes with 15C5 are weaker than with 18C6. For these same reasons, 18C6 can form both 1:1 and 1:2 crown:solvent complexes whereas 15C5 only forms a 1:1 complex.

A mole ratio study of 15C5 and CHCl₃ in benzene was done by carbon-13 NMR spectroscopy. The plot of chemical shift as a function of mole ratio, shown in Figure 88, shows one break. This indicates that a 1:1 complex forms in solution. The chemical shift data were computer analyzed taking into account the concentration dependence of the chloroform chemical shift. The results of the computer analysis are tabulated in Table 27. It can be seen that the formation constant for the 15C5 complex is the same as that for the MeNO₂-15C5 complex. In addition, a study of the 18C6-CHCl₃-C₆H₆ system showed that, for chloroform, the complexation with 18C6 is only slightly stronger than with 15C5. Both of these observations result because chloroform has only one acidic proton to hydrogen bond to the ether oxygens of 18C6 and 15C5.

The complexation of AC with 15C5 was monitored by using carbon-13 NMR spectroscopy. The results of the study, which are shown in Figure 89, indicate that the complexation is very weak. The data were computer analyzed. The results of the analysis are tabulated in Table 27. It is somewhat surprising that acetone forms a

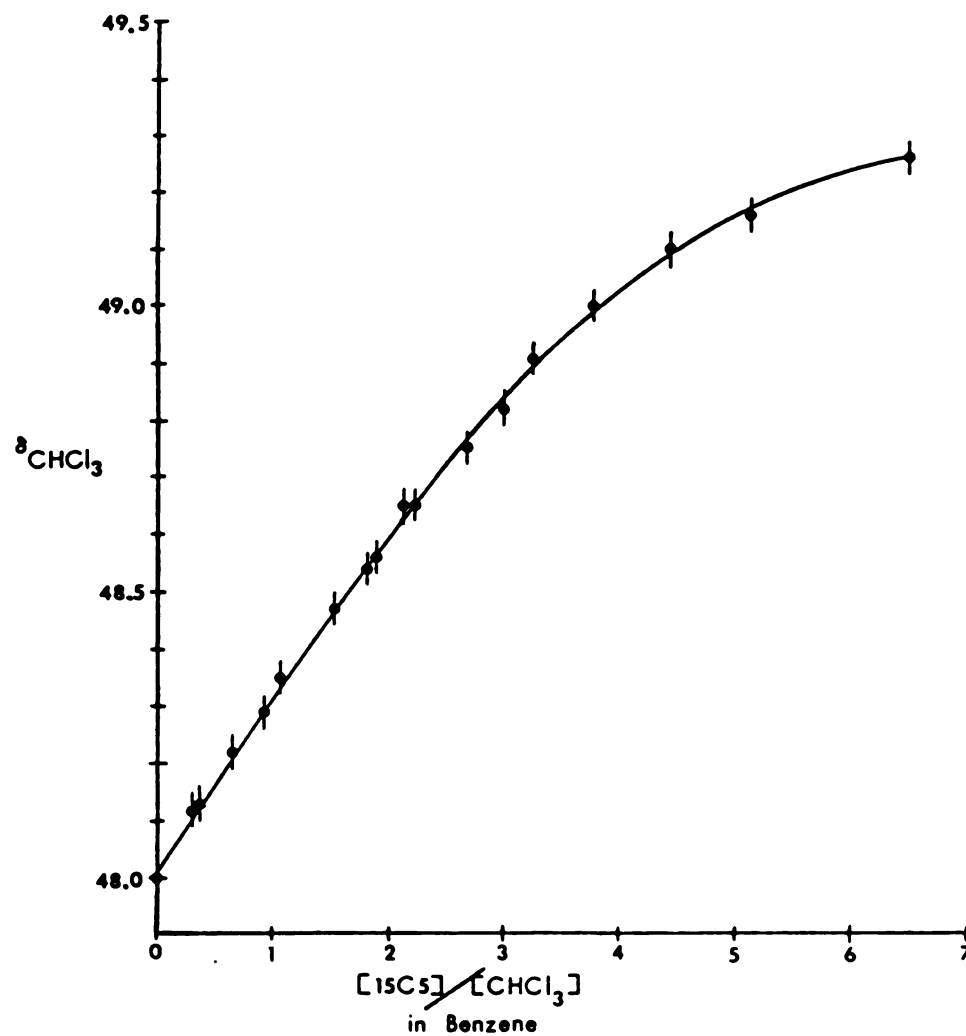


Figure 88. Plot of the carbon-13 chemical shifts of chloroform as a function of $[\text{15C5}]/[\text{CHCl}_3]$ in benzene.

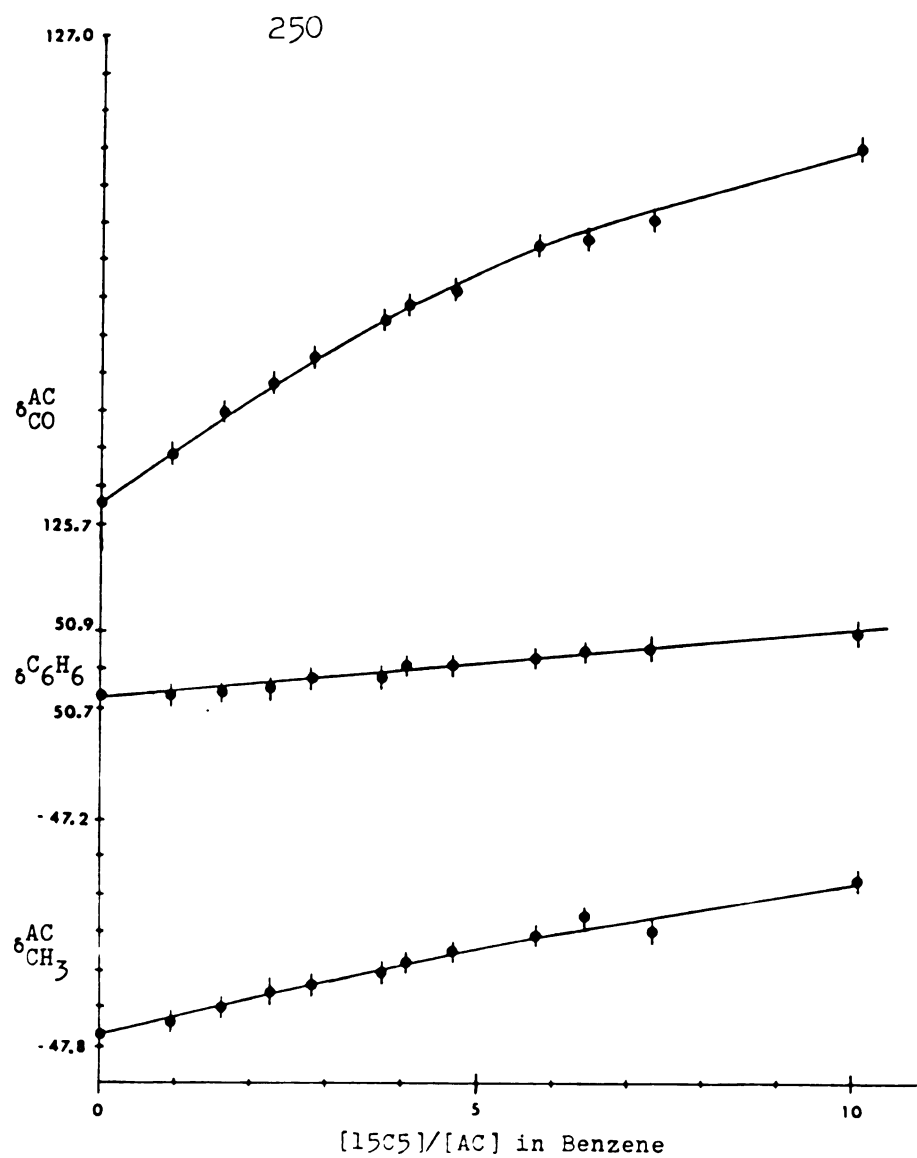
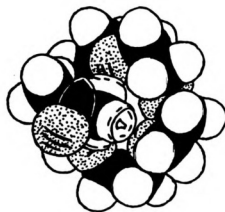


Figure 89. Plots of the carbon-13 chemical shifts of acetone and benzene vs. $[^{15}\text{C}_5]/[\text{AC}]$ in benzene.

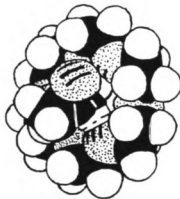
stronger complex with 15C5 than with 18C6. Space-filling models of the two complexes (Figure 90) show that there is appreciable electrostatic repulsion between the carbonyl oxygen of acetone and the ether oxygens of 18C6. With 15C5, these repulsions are minimized. Consequently, AC forms a stronger complex with 15C5 than with 18C6.

The complexation of DMF and 15C5 was also studied by carbon-13 NMR spectroscopy. The results of this study are shown in Figure 91. As with the 18C6-DMF-C₆H₆ system, no curvature is observed for the methyl carbons of DMF in the 15C5-DMF-C₆H₆ system. However, the amide carbon of DMF exhibits slight curvature. As was discussed previously, DMF has three possible sites of complexation. In the case of 18C6, no curvature was observed for the three sites implying that neither site preferentially interacts with 18C6. However, the fact that the chemical shift-mole ratio plot of the amide carbon for the 15C5-DMF-C₆H₆ system shows curvature and those of the methyl carbons do not indicates that, although all three sites interact with 15C5, the proton on the amide carbon interacts preferentially.

The complexation of 15C5 with methanol was studied in benzene solution by proton and carbon-13 NMR spectroscopy. Figure 92 shows a plot of the carbon-13 chemical shift data. Unlike the 18C6-MeOH-C₆H₆ system, the ¹³C chemical shift shows a concentration dependence due to



15-Crown-5



18-Crown-6

Figure 90. Space-filling models of the acetone complex with 15-crown-5 and 18-crown-6.

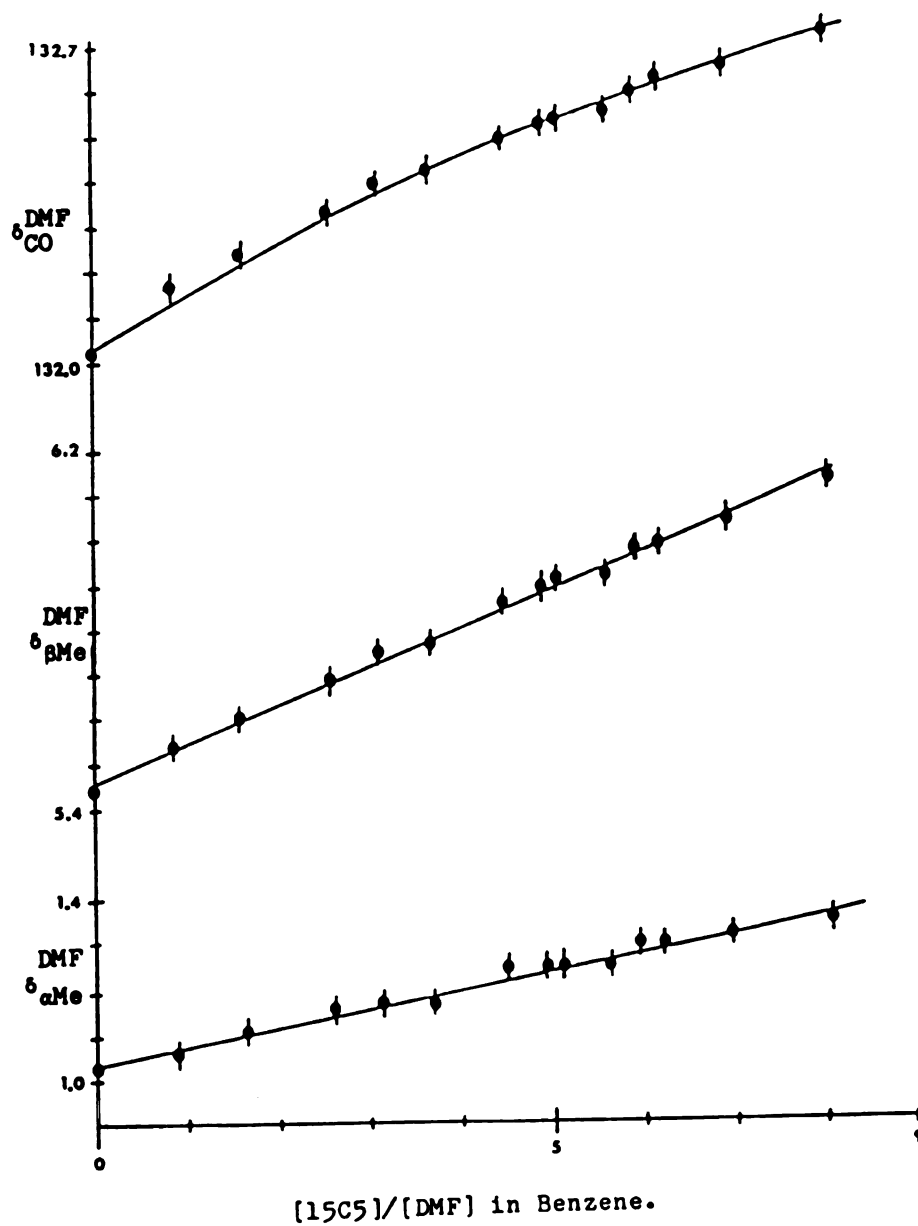


Figure 9¹. Plots of the carbon-13 chemical shifts of N,N-dimethylformamide vs. $[^{15}\text{C}5]/[\text{DMF}]$ in benzene.

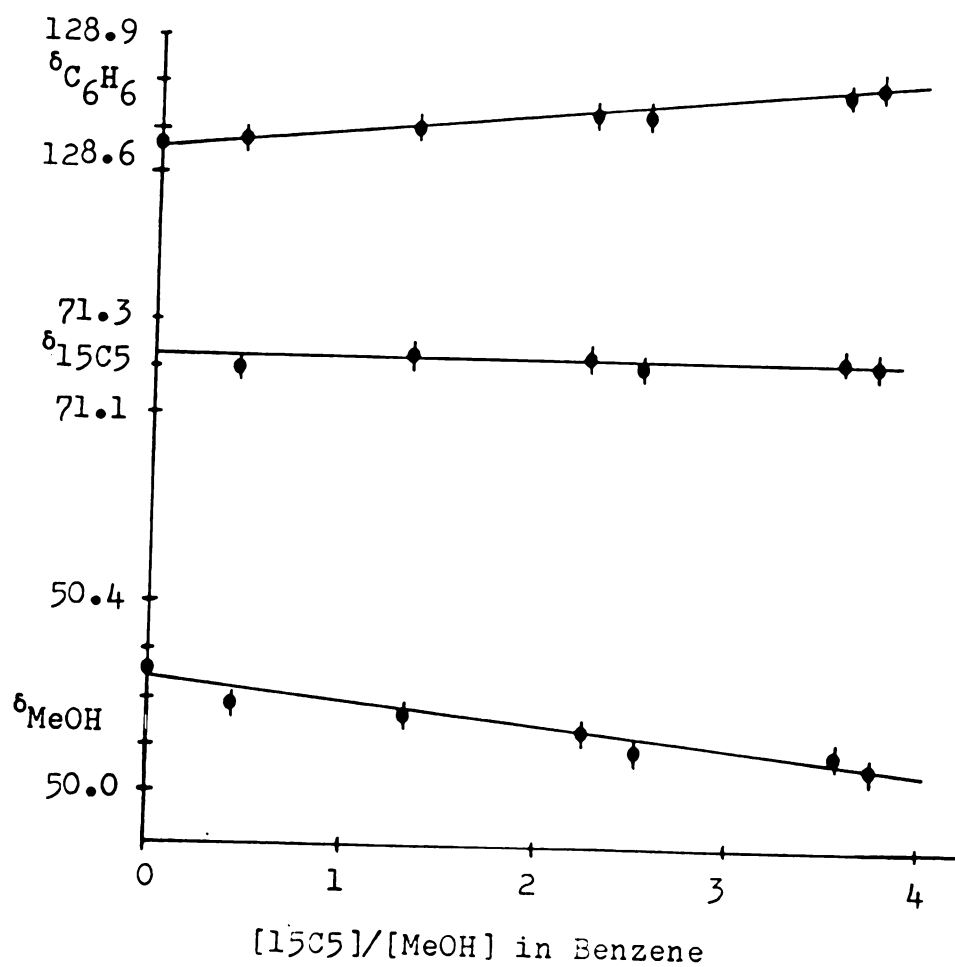


Figure 92. Plots of the carbon-13 chemical shift of methanol, 15-crown-5 and benzene as a function of $[15C5]/[MeOH]$ in benzene.

complexation. However the lack of curvature suggests that the site of complexation is through the OH group. This is borne out by the proton spectra shown in Figure 93. At mole ratio 0.00, the methyl group is a doublet and the hydroxyl group is a quartet indicating that the hydroxyl group is completely solvated. As 15C5 is added, single resonances are observed for both the methyl and hydroxyl groups indicating that the hydroxyl proton is exchanging. As the concentration of 15C5 increases the hydroxyl group resonance broadens and decreases in intensity. At $[15C5]/[MeOH]$ mole ratio of 2.00, the hydroxyl resonance has disappeared into the baseline. This behavior is obviously due to exchange broadening. The proton chemical shifts and line widths of methanol as a function of temperature were obtained for $[15C5]/[MeOH]$ mole ratios of 0.36 and 1.06. The results, tabulated in Tables 28 and 29 show that the proton chemical shifts and line widths are greatly influenced by temperature.

The proton chemical shift-mole ratio plots are shown in Figure 94. The chemical shift data were computer analyzed taking into account the concentration dependence of the chemical shift of "free" methanol. The uncertainty in the formation constant is fairly large. This uncertainty results from the large line widths of the methanol resonances which lead to large uncertainties in the chemical shift data. However, within the

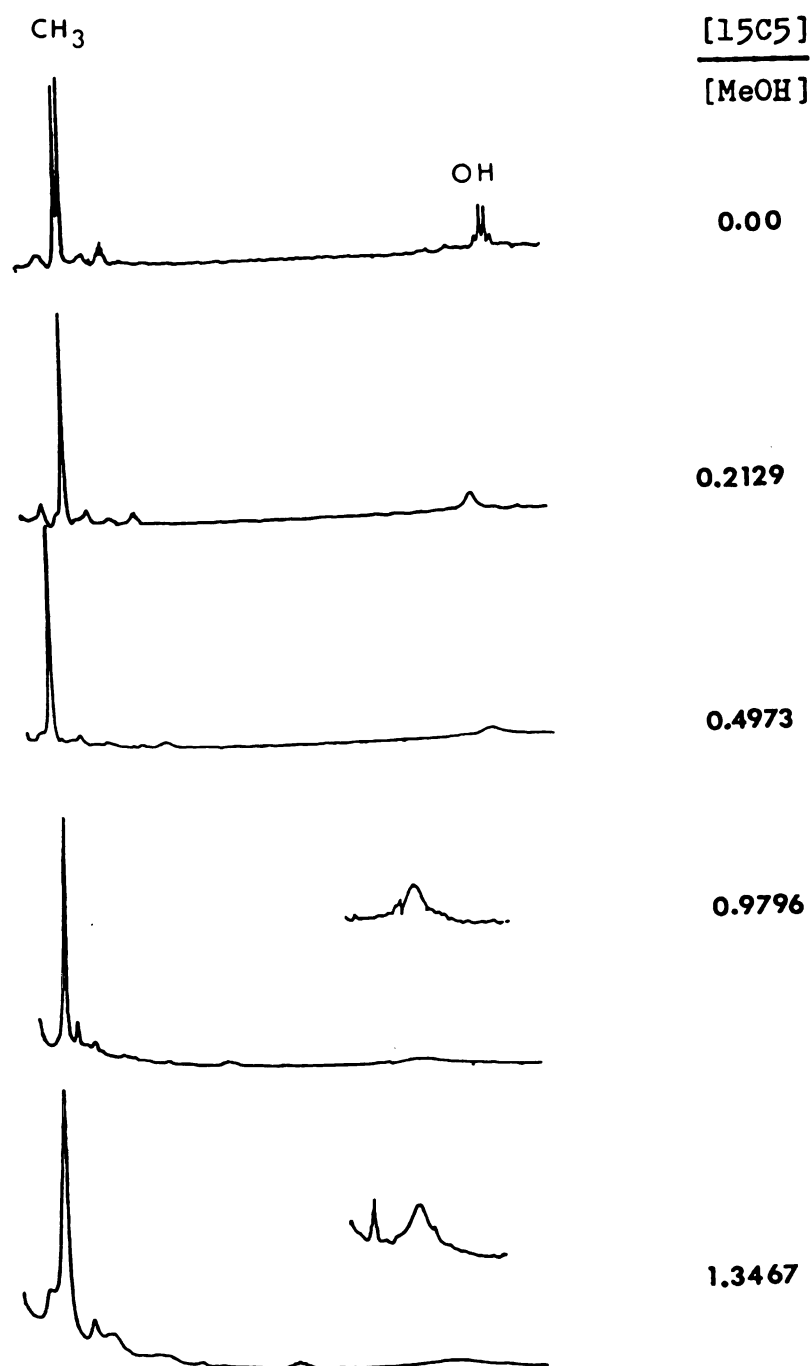


Figure 93. Proton spectra obtained for solutions of methanol and 15-crown-5 in benzene.

Table 28. Proton Chemical Shift Data for a Solution of [15C5]/[MeOH]=0.3649 in Benzene as a Function of Temperature.

TEMPERATURE (°C)	MeOH ^a δ_{OH} (ppm)	OH $\Delta\nu_{\frac{1}{2}}$ (Hz)	MeOH δ_{CH_3} (ppm)	CH ₃ $\Delta\nu_{\frac{1}{2}}$ (Hz)	15C5 δ (ppm)	C ₆ H ₆ δ (ppm)
52	1.77	35.62	3.80	1.28	4.16	7.82
46	1.98	40.50	3.81	1.58	4.15	7.81
39	2.25	33.32	3.81	1.58	4.13	7.80
32	2.47	29.67	3.82	1.13	4.11	7.79
25	2.70	29.52	3.82	1.43	4.09	7.77
25	2.71	31.49	3.82	1.88	4.09	7.77
20	2.86	29.04	3.82	1.90	4.08	7.77
15	3.01	33.92	3.83	1.88	4.07	7.76
10	3.18	26.76	3.83	2.03	4.06	7.75

^aChemical shifts are reported relative to TMS in acetone-d₆. Uncertainty in the chemical shifts is ± 0.01 ppm.

Table 29. Proton Chemical Shift Data for a Solution of [15C5]/[MeOH]=1.0589 in Benzene as a Function of Temperature.

TEMPERATURE (°C)	MeOH ^a δ _{OH} (ppm)	Δν _{1/2} OH (Hz)	MeOH δ _{CH₃} (ppm)	Δν _{1/2} CH ₃ (Hz)	δ ^{15C5} (ppm)	δ ^{C₆H₆} (ppm)
40	2.89	40.50	3.91	1.28	4.15	7.82
32	3.13	38.37	3.92	1.13	4.13	7.81
25	3.35	34.99	3.93	1.43	4.11	7.79
20	3.49	37.15	3.93	1.60	4.10	7.79
15	3.62	31.22	3.94	1.60	4.09	7.78

^aChemical shifts are reported relative to TMS in acetone-d₆. Uncertainty in the chemical shifts is ±0.01 pp.

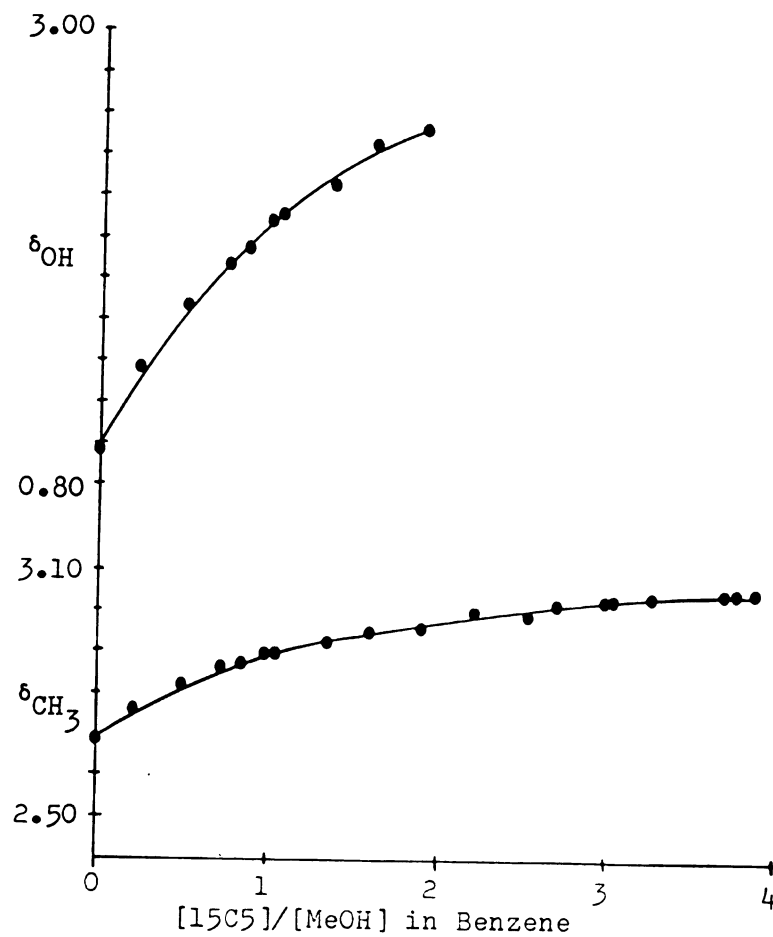
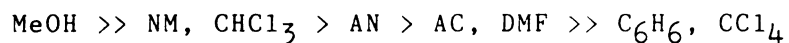


Figure 94. Plots of the proton chemical shift of the methyl and hydroxyl groups of methanol as a function of $[15C5]/[MeOH]$ in benzene.

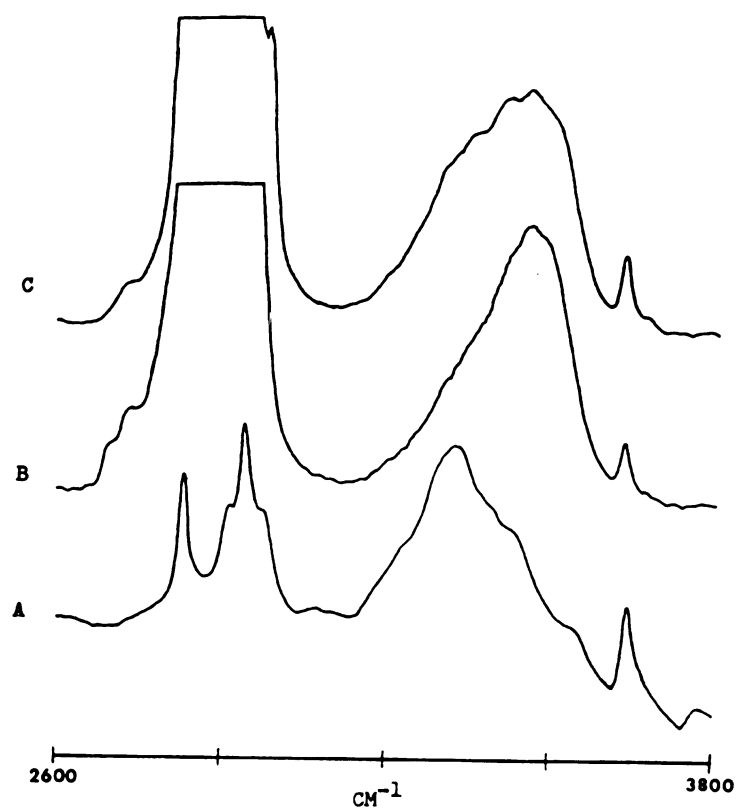
uncertainties, the 15C5 complex with methanol is weaker than the 18C6 complex.

Figure 95 shows the OH-stretching region of methanol in CCl_4 . The spectrum of the "free" methanol shows the existence of many species. A monomer band occurs at 3638 cm^{-1} . The band at 3350 cm^{-1} is a composite of the aggregated forms of methanol. With the addition of 15C5, a strong band due to the complex is observed at $\sim 3500 \text{ cm}^{-1}$. The composite band is suppressed indicating that 15C5 is strong enough to break up the dimers, trimers, etc. of methanol. Figure 96 shows the infrared spectrum of 15C5 in the $1600\text{--}900 \text{ cm}^{-1}$ region. This spectrum shows that 15C5 does not undergo a conformational change upon complexation.

The results shown in Tables 26 and 27 indicate that the strength of the 15C5-solvent interaction varies in the order:

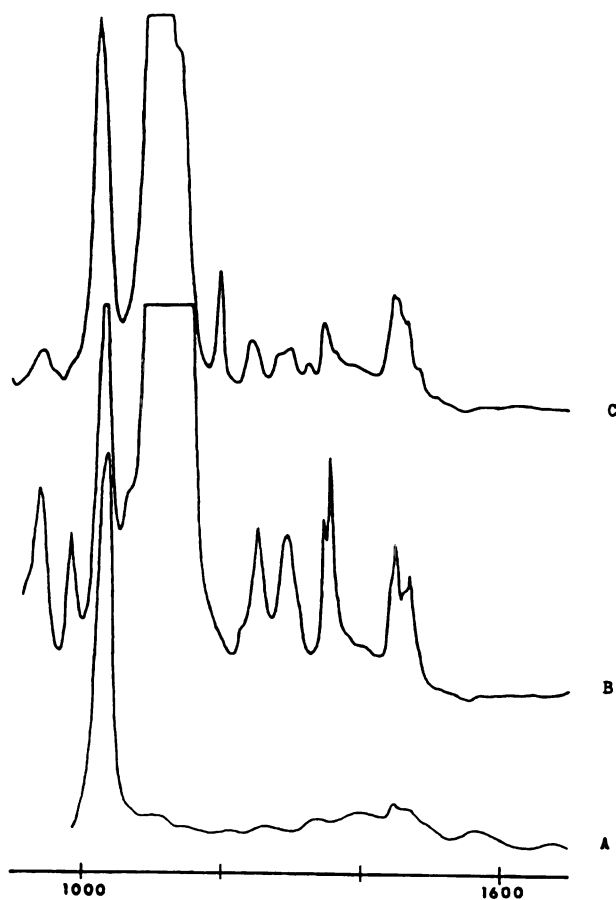


4. TETRAGLYME COMPLEXATION WITH ACETONITRILE, NITROMETHANE, CHLOROFORM AND METHANOL. Tetraglyme, TG, is the five-oxygen linear polyether analogue of 15C5. The complexation of TG with MeCN, MeNO_2 and CHCl_3 in benzene was studied by carbon-13 NMR spectroscopy. For each system, only one break was observed in the chemical shift-concentration plots (Figures 97-99) implying that the TG only forms 1:1 complexes with MeCN, MeNO_2 and



- (A) 0.4557 M MeOH
(B) 0.4900 M MeOH; $[\text{15C5}]/[\text{MeOH}]=0.7996$
(C) 0.5602 M MeOH; $[\text{TG}]/[\text{MeOH}]=0.3822$

Figure 95. Infrared spectra of the CH and OH stretches of methanol ($3020\text{--}2780\text{ cm}^{-1}$ and $3800\text{--}3200\text{ cm}^{-1}$, respectively) in solutions of methanol-15C5 and methanol-TG in carbon tetrachloride.



- (A) 0.4564 M MeOH
(B) 0.4900 M MeOH; $[15C5]/[MeOH]=0.7996$
(C) 0.5602 M MeOH; $[TG]/[MeOH]=0.3822$

Figure 96. Infrared spectra of the 1000-1600 cm^{-1} region of methanol-15C5 and methanol-tetraglyme solutions in carbon tetrachloride.

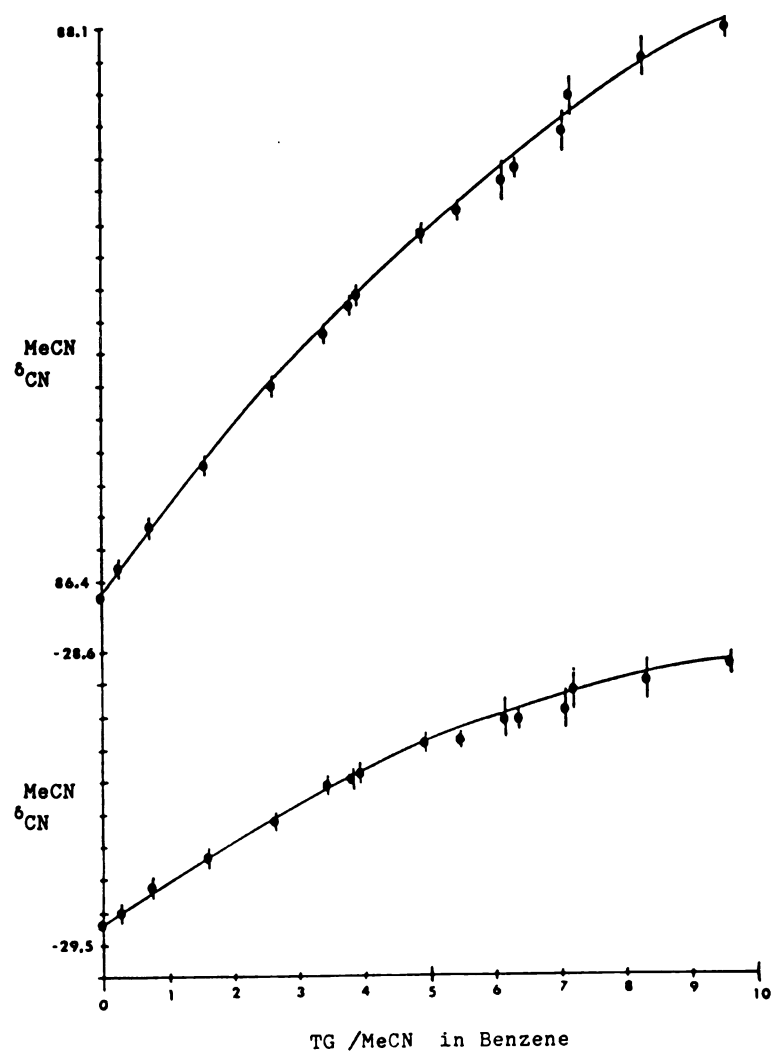


Figure 97. Plots of the carbon-13 chemical shifts of Acetonitrile vs. $\text{[TG]}/\text{[MeCN]}$ in benzene.

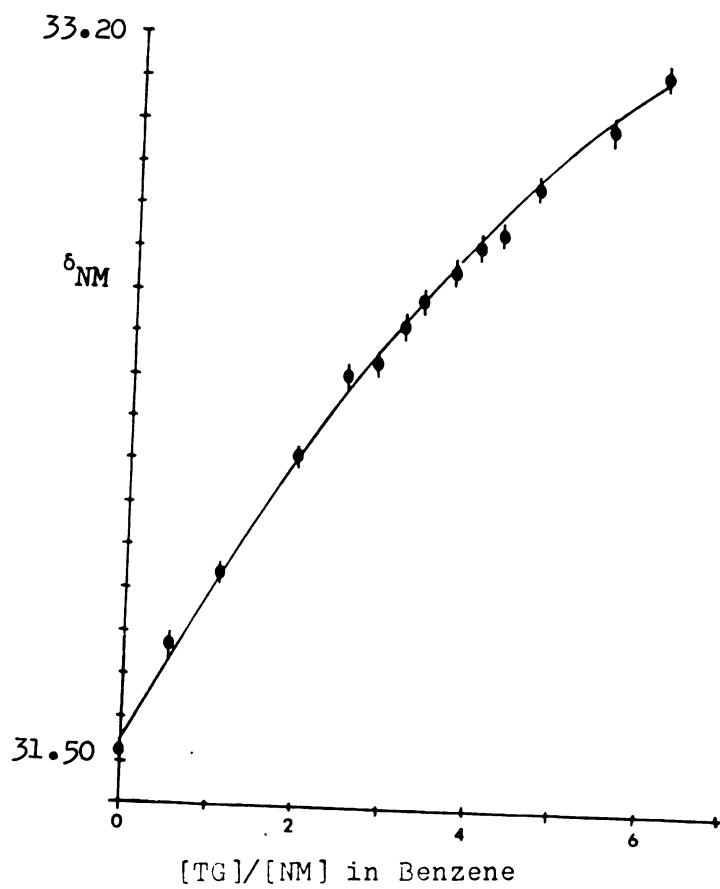


Figure 98. Plot of the carbon-13 chemical shift of nitromethane as a function of $[TG]/[NM]$ in benzene.

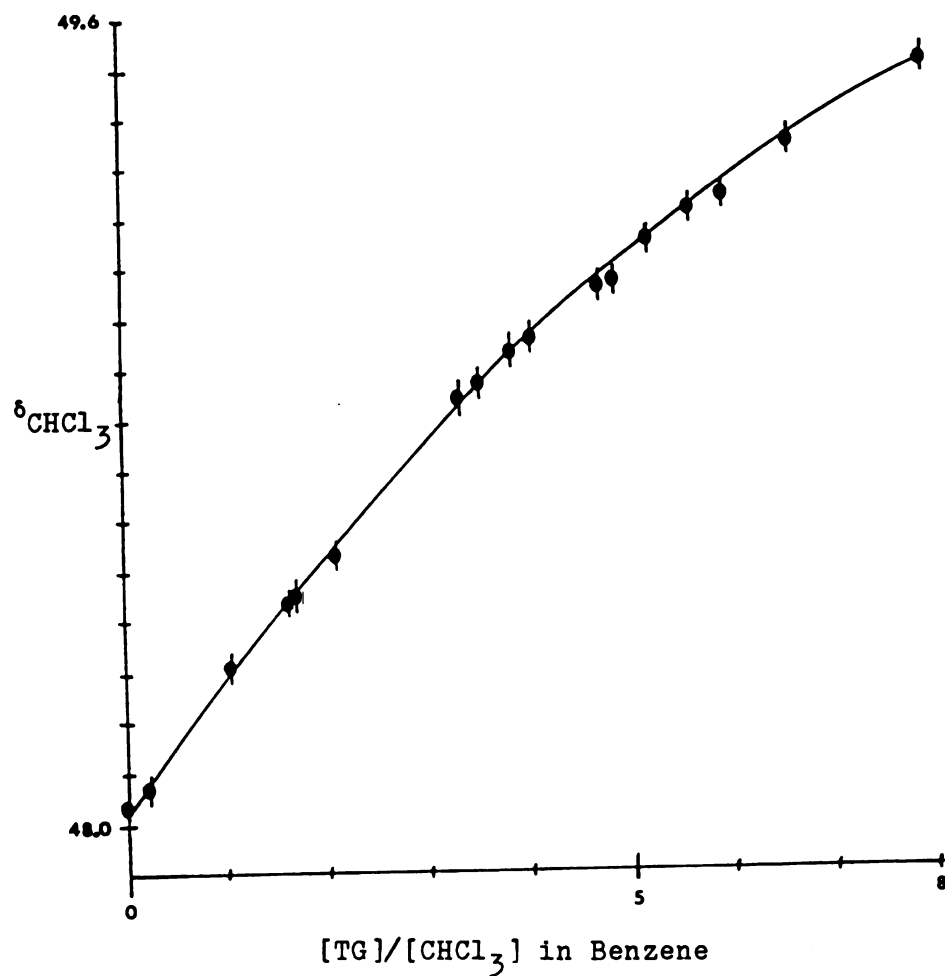


Figure 99 . Plot of the carbon-13 chemical shifts of chloroform vs. $[\text{TG}]/[\text{CHCl}_3]$.

CHCl_3 . The chemical shift data were computer analyzed. As the results in Table 30 indicate, no difference is observed between the formation constants obtained for 15C5 and TG. The solvation studies of TG in deuterated benzene (Chapter IV) indicated that in benzene- d_6 TG has a cyclic conformation. This is not surprising since the ether oxygens are hydrophilic and the ethylene linkages are hydrophobic. Since "like dissolves like", TG orients the ether oxygens away from the benzene resulting in a cyclic conformation.

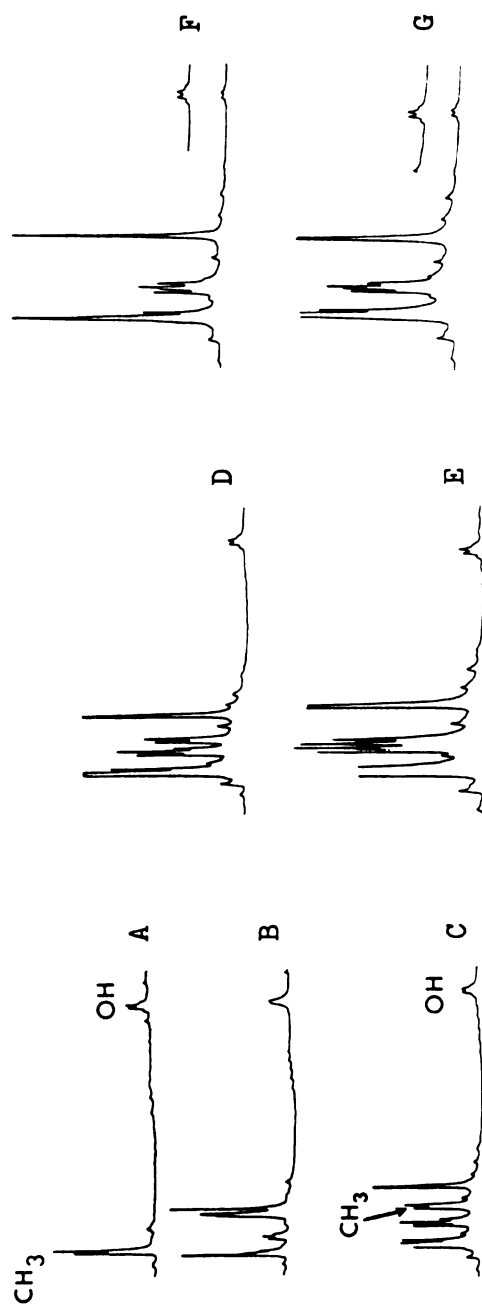
The complexation of TG with MeOH was studied in CCl_4 by IR spectroscopy. Figure 95 shows the OH stretching region of MeOH. With the addition of TG, a new band due to the complex appears at 3500 cm^{-1} . However, the monomer band and composite band due to the methanol aggregates are still very intense, which contrasts with what was observed for the MeOH-15C5- CCl_4 and MeOH-18C6- CCl_4 systems, and implies that MeOH forms a weaker complex with TG than with either 18C6 or 15C5.

The complexation of TG and MeOH in benzene was monitored with proton NMR spectroscopy. Figure 100 shows the proton spectra obtained. At all mole ratios studied, the resonance due to the methyl group is a doublet and the hydroxyl group is a quartet. These observations indicate that the hydroxyl proton is not exchanging which implies that the TG complexation with MeOH is fairly weak. A

Table 30. Association Constants of the Complexes of Tetraglyme With Several Neutral Guest Molecules in benzene at 298 K.

Guest	Association Constant (m.f. ⁻¹)	Association Constant (l mol ⁻¹)	¹³ C Chemical Shifts, ppm
MeCN ^a	K _{1:1} = 4.3 ± 0.2	K _{1:1} = 0.39 ± 0.02	δ ^{CH₃} = -28.20 ± 0.02 δ ^{CN} = 88.91 ± 0.04
^a MeNO ₂	K _{1:1} = 5.0 ± 0.5	K _{1:1} = 0.44 ± 0.04	δ = 34.4 ± 0.2
^a CHCl ₃	K _{1:1} = 6.5 ± 0.2	K _{1:1} = 0.57 ± 0.02	δ = 50.62 ± 0.05

^aExternal lock and reference is acetone-d₆.



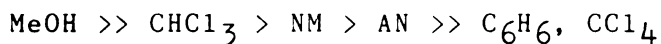
268

<u>SPECTRUM</u>	<u>[TG l / [MeOH]</u>	<u>SPECTRUM</u>	<u>[TG l / [MeOH]</u>
A	0.00	E	1.2262
B	0.1964	F	1.8538
C	0.5786	G	2.1471
D	0.9792		

Figure 10Q. Proton spectra of solutions of methanol and tetraglyme in benzene.

proton chemical shift-[TG]/[MeOH] mole ratio plot (Figure 101) shows only one break indicating the formation of a 1:1 complex. The results of the computer analysis of the chemical shift data are tabulated in Table 26.

Figure 87 shows space-filling models of the tetraglyme complexes with a molecule containing an acidic methyl group. These models show that the glyme is able to wrap itself around the CH_3 group. The results in Tables 26 and 30 show that the strength of the TG-solvent interaction varies in the order:



Comparison of these results with those obtained for 15C5 seem to indicate that differences in the solvation of cyclic and linear polyethers is not a major contributor to the "macrocyclic effect" as was suggested by Margerum and Hinz (112, 113) more than a decade ago for the polyaza ligands.

5. BENZO-15-CROWN-5 COMPLEXATION WITH ACETONITRILE, NITROMETHANE, CHLOROFORM AND METHANOL. Figure 102 shows a proton spectrum of B15C5 in deuterated benzene. With the addition of MeCN, CHCl_3 , MeNO_2 and MeOH the resonance due to protons 1 and 2 (assignments are discussed in Chapter IV) shift upfield and the extent of proton-proton coupling is noticeably diminished. No changes were observed for the benzene ring of B15C5. These results indicate that complexation is through the ether oxygens - particularly

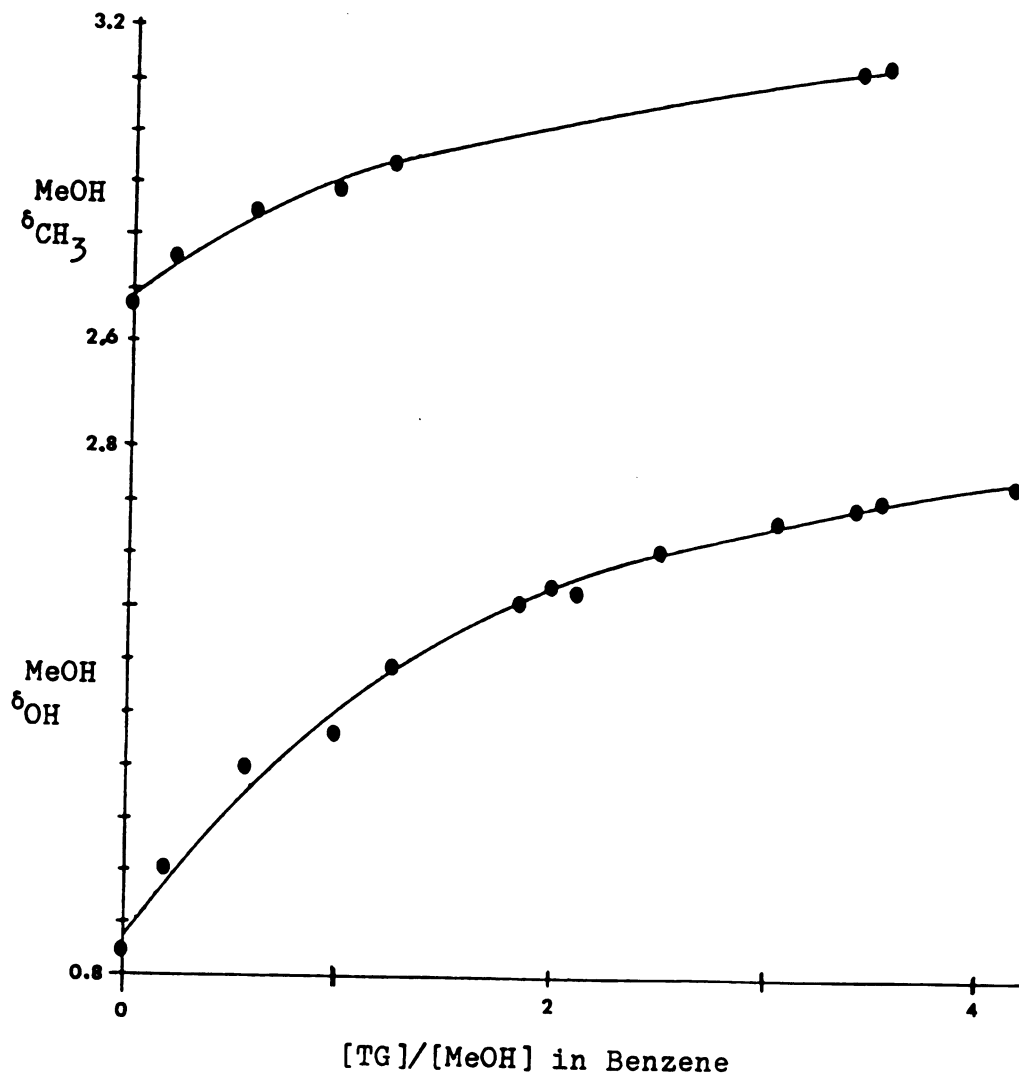
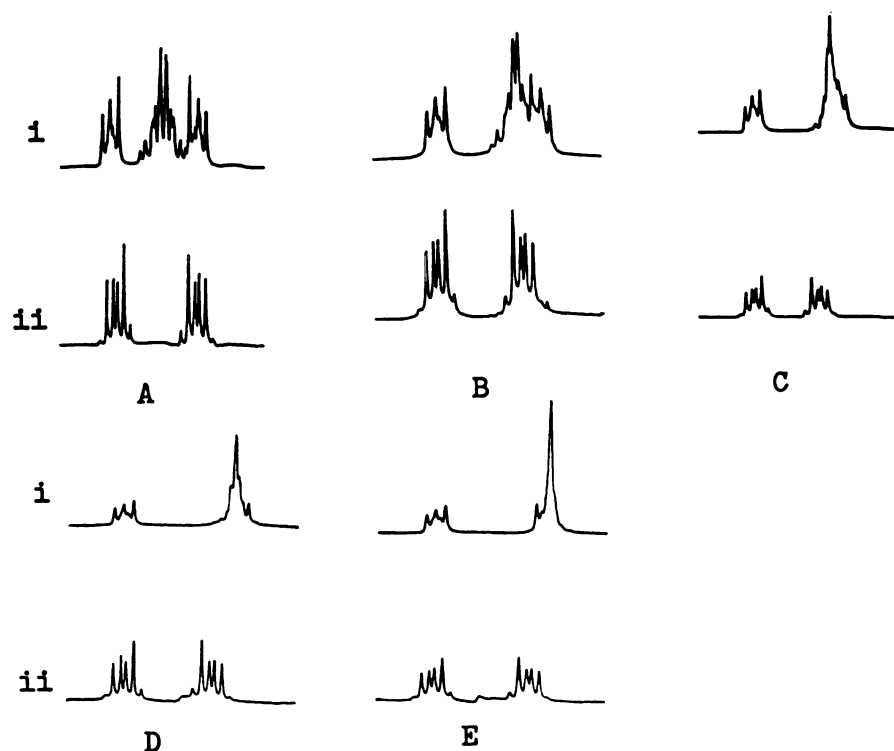


Figure 101. Plots of the proton chemical shifts of methanol vs. [TG]/[MeOH] in benzene.



(A) B15C5 in C_6D_6

(B) $[Chloroform-d]/[B15C5]=11.48$

(C) $[Acetonitrile-d_3]/[B15C5]=55.87$

(D) $[Nitromethane-d_3]/[B15C5]=40.11$

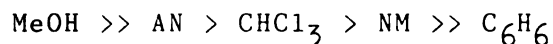
(E) $[Methanol-d_4]/[B15C5]=31.02$

Figure¹⁰². Proton spectra of solutions of B15C5 (where i refers to the ether protons and ii to the aromatic protons) in deuterated benzene.

the oxygens furthest from the aromatic ring.

Carbon-13 NMR studies of the complexation of B15C5 with MeCN, MeNO₂ and CHCl₃ were conducted in benzene solution. As with TG and 15C5, only one break was observed in the chemical shift-concentration plots shown in Figures 103-105. This, in turn, implies that a 1:1 complex forms in solution. The chemical shift data were computer analyzed and the results are tabulated in Table 31. The MeOH-B15C5-C₆H₆ system was studied by proton and carbon-13 NMR spectroscopy. The carbon-13 chemical shift data are shown in Table ⁵² of Appendix III. Just as for the MeOH-18C6-C₆H₆ and MeOH-15C5-C₆H₆ systems, the carbon-13 chemical shift of MeOH shows little effect due to complexation. The exchange behavior of MeOH in these solutions is similar to that observed for the TG-MeOH-C₆H₆ system discussed previously. The proton chemical shift-mole ratio plots are shown in Figure 106. Only one break is observed in the plots. Computer analysis showed that the chemical shift data were adequately described by the formation of a 1:1 complex. The results of the analysis are tabulated in Table 26.

The results in Tables 26 and 31 show that the ligand-solvent interactions can be arranged in the following series:



The reactivity series for B15C5 sharply contrasts with

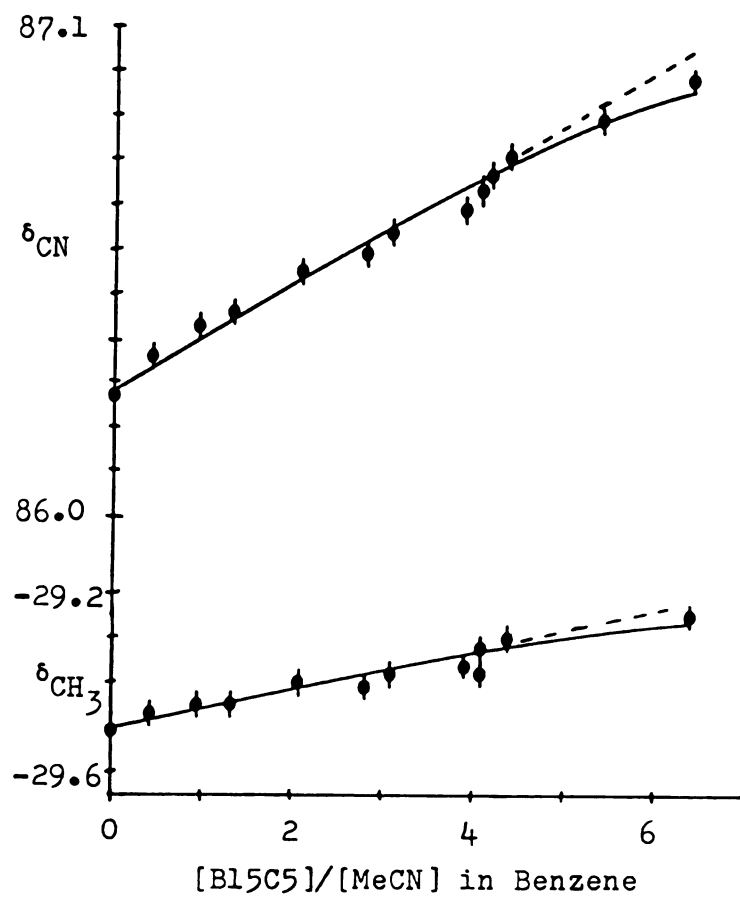


Figure 103. Plots of the carbon-13 chemical shifts of acetonitrile as a function of [B15C5]/[MeCN] mole ratio.

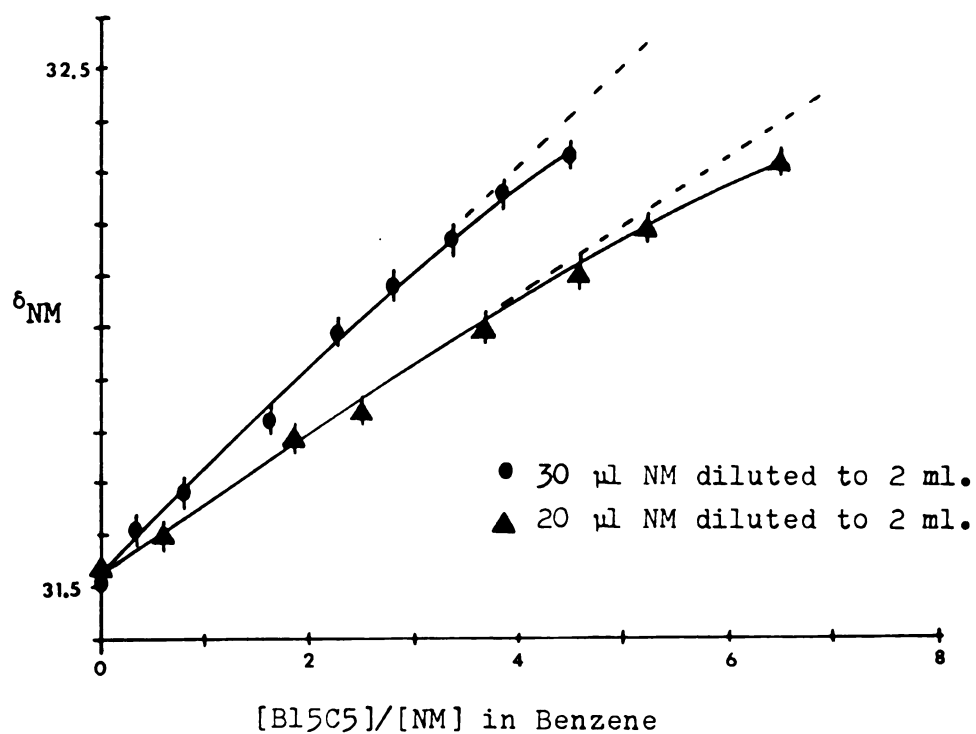


Figure 104. Plot of the carbon-13 chemical shift of nitromethane as a function of $[B15C5]/[NM]$ in benzene.

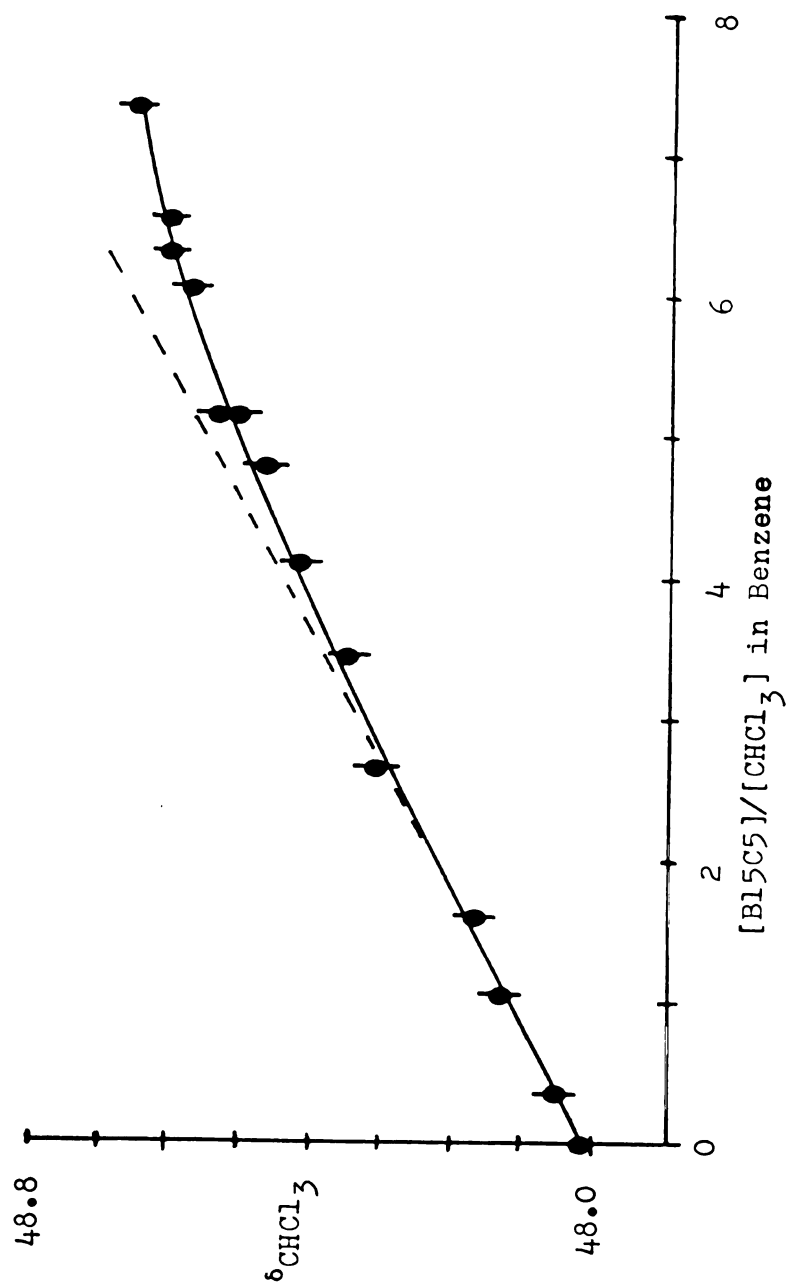


Figure 105. Plot of the carbon-13 chemical shift of chloroform as a function of $[\text{B15C5}]/[\text{CHCl}_3]$ in benzene.

Table 31 • Association Constants of the Complexes of Benzo-15-Crown-5 With Several Neutral Molecules in Benzene at 298°K.

Guest	Association Constant (m.f. ⁻¹)	Association Constant (l mol ⁻¹)	¹³ C Chemical Shift, ppm
MeCN ^a	K _{1:1} = 5.1 ± 0.6	K _{1:1} = 0.43 ± 0.05	δ ^{CN} = 88.3 ± 0.2
MeNO ₂ ^a	K _{1:1} = 2.5 ± 0.6	K _{1:1} = 0.22 ± 0.05	δ = 35.2 ± 0.7
CHCl ₃ ^a	K _{1:1} = 3.5 ± 0.5	K _{1:1} = 0.31 ± 0.04	δ = 50.3 ± 0.2

^aExternal lock and reference is acetone-d₆.

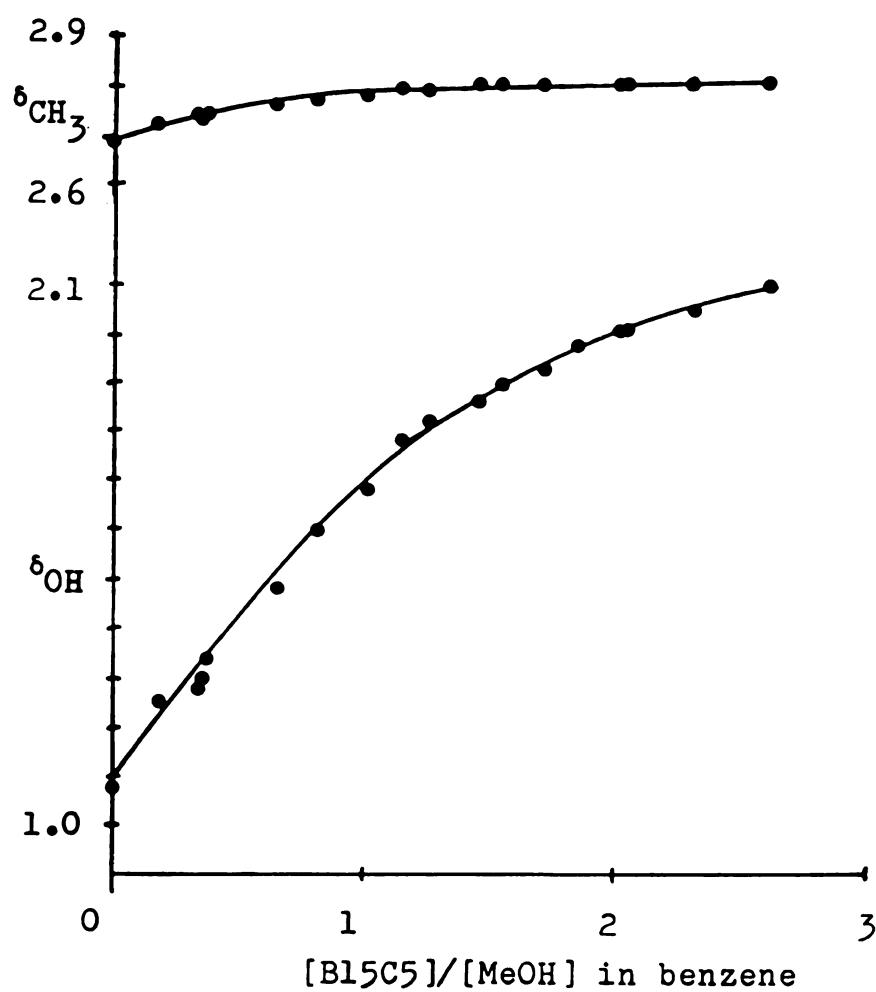
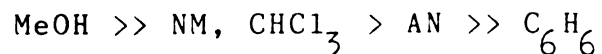


Figure 106 Plots of the proton chemical shifts of methanol as a function of $[B15C5]/[MeOH]$ in benzene.

that observed for 15C5:

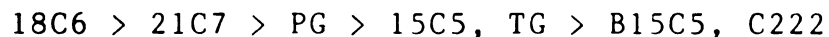


Furthermore, MeOH and AN form stronger complexes with B15C5 than with 15C5. This was a puzzling result. Since the aromatic ring makes B15C5 less flexible than 15C5, it was assumed that B15C5 would be less able to accommodate a guest molecule resulting in the formation of weaker complexes. This seems to be the case for NM and CHCl_3 but not MeOH and AN. This apparent discrepancy may be due to complexation between B15C5 and benzene. As was discussed in the previous chapter, benzene forms a π -complex with the aromatic ring of B15C5. Formation of this π -complex blocks the aromatic ring and makes it unable to participate in any interactions with either AN, NM, CHCl_3 or MeOH. Consequently, the only available site for interaction for AN, NM, CHCl_3 and MeOH is the ether oxygens. However, formation of the B15C5- C_6H_6 π -complex partially blocks the cavity and may make it difficult for a guest molecule to complex the ether oxygens. The fact that the B15C5 protons furthest away from the aromatic ring are affected the most by complexation with either NM, AN, CHCl_3 or MeOH suggests that this may be the case (Figure 87 shows a space-filling model for the B15C5 complex with a CH_3 -acid). The $-\text{NO}_2$ and $-\text{CCl}_3$ groups are bulkier groups than $-\text{CN}$ and $-\text{CH}_3$. Consequently, NM and CHCl_3 form weaker complexes with B15C5 than do AN and

MeOH.

The B15C5-C₆H₆ interaction explains the observed reactivity series for B15C5. However, it does not explain why AN and MeOH form stronger complexes with B15C5 than with 15C5. This apparent discrepancy may be due to the inductive effects of the aromatic ring. The aromatic ring of B15C5 is electron rich. The ether oxygens directly bonded to the aromatic ring withdraw electron density from the aromatic ring. This, in turn, results in the cyclic polyether portion of the molecule becoming a stronger electron donor. Any guest molecules which can overcome the steric hindrance due to the B15C5-C₆H₆ π -complex could form a stronger complex with B15C5 than with 15C5 because the ether oxygens of B15C5 are better electron donors than those of 15C5.

6. NITROMETHANE COMPLEXATION WITH PENTAGLYME, 21-CROWN-7 AND CRYPTAND 222. The complexation reactions of nitromethane with PG, 21C7 and C222 in benzene were monitored by carbon-13 NMR spectroscopy. The results are plotted in Figures 107-109. In each of the plots, one break is observed indicating that, in solution, only a 1:1 complex is formed. The chemical shift data were computer analyzed. The results of this analysis are tabulated in Table 32. The results of these studies indicate the following reactivity series for NM in benzene:



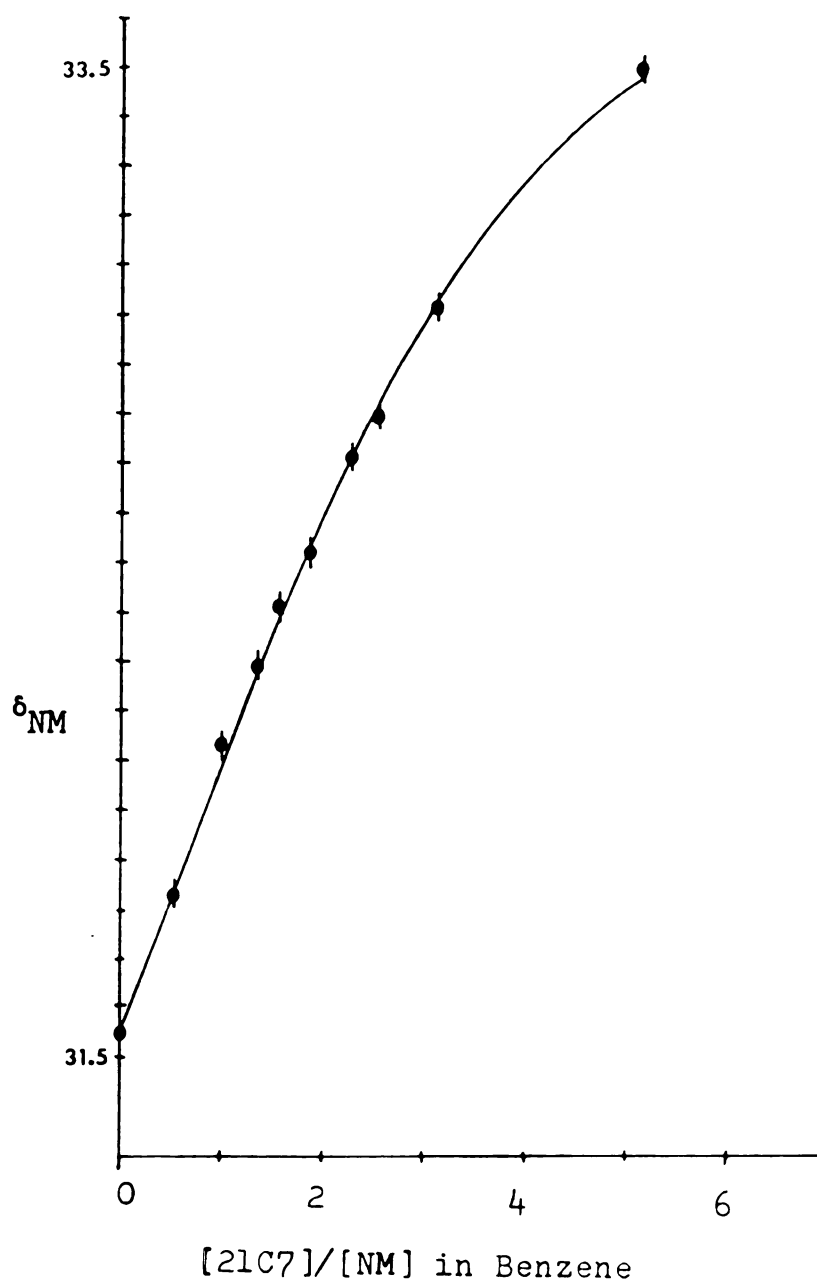


Figure 107. Plot of the carbon-13 chemical shift of nitromethane as a function of $[21C7]/[NM]$ in benzene.

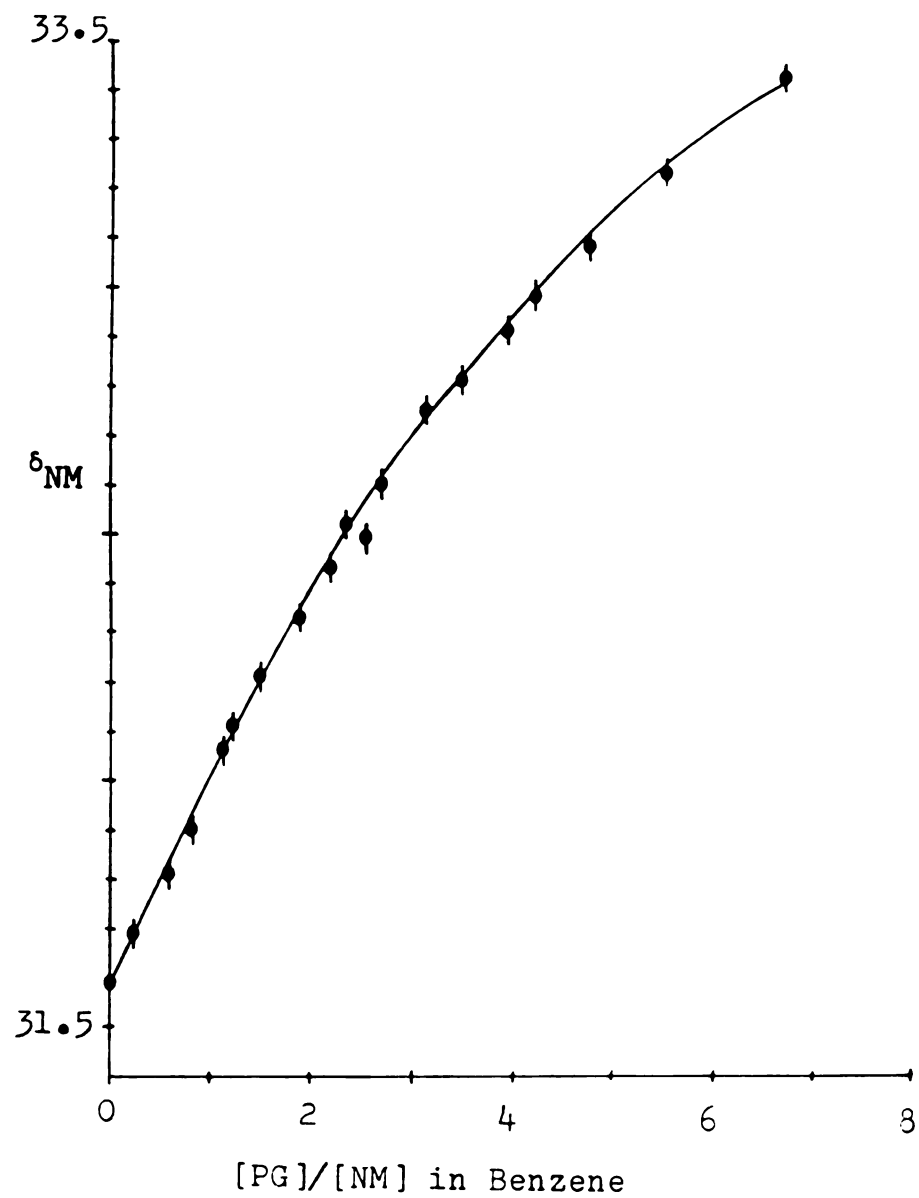


Figure 108. Plot of the carbon-13 chemical shift of nitromethane as a function of $[\text{PG}]/[\text{NM}]$ in benzene.

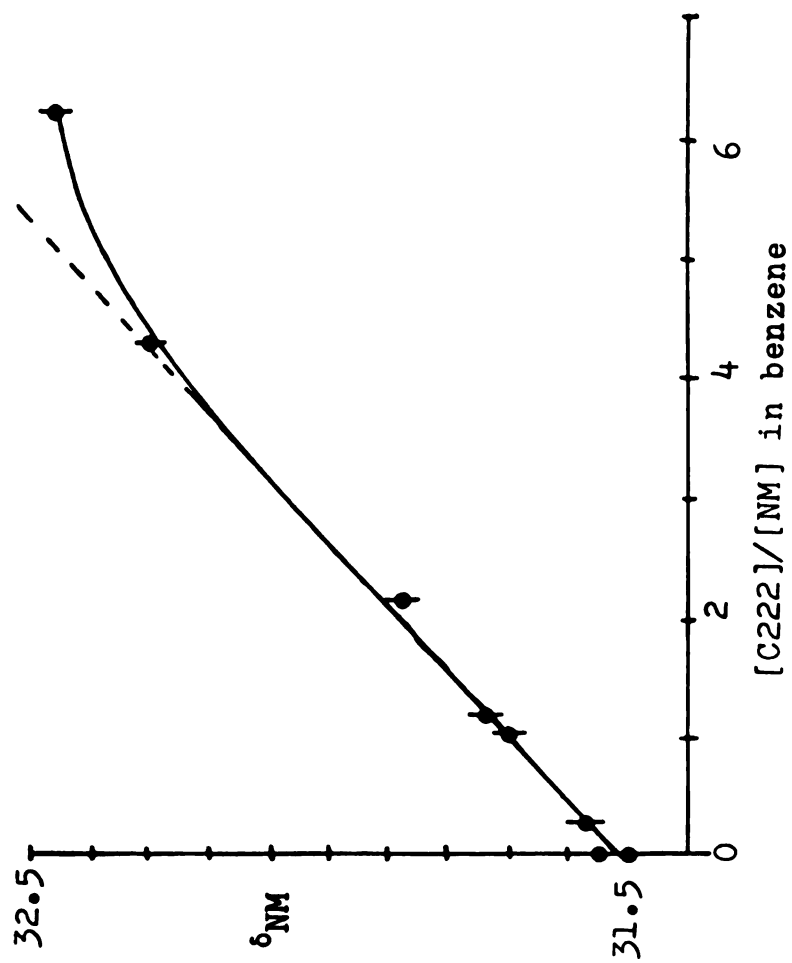


Figure 109. Plot of the carbon-13 chemical shift of nitromethane as a function of $[\text{C222}]/[\text{NM}]$ in benzene.

Table 32. Association Constants of the Complexes of Nitromethane With Several Macrocylic Ligands in Benzene at 298°K.

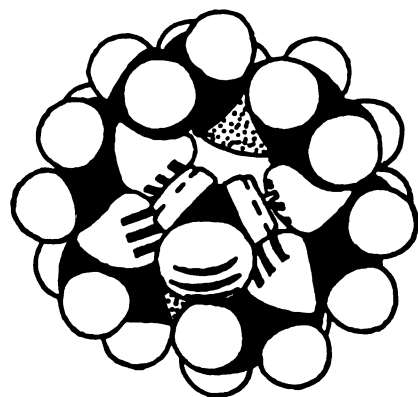
Ligand	Association Constant (m.f. ⁻¹)	Association Constant (l mol ⁻¹)	¹³ C Chemical Shift, ppm
^a 21C7	K _{1:1} = 13 ± 1	K _{1:1} = 1.15 ± 0.09	δ = 34.9 ± 0.1
^a PG	K _{1:1} = 7.1 ± 0.2	K _{1:1} = 0.63 ± 0.02	δ = 34.25 ± 0.04
^a C222	K _{1:1} = 2.4 ± 0.9	K _{1:1} = 0.21 ± 0.08	δ = 35 ± 1

^aChemical shifts are reported relative to acetone-d₆.

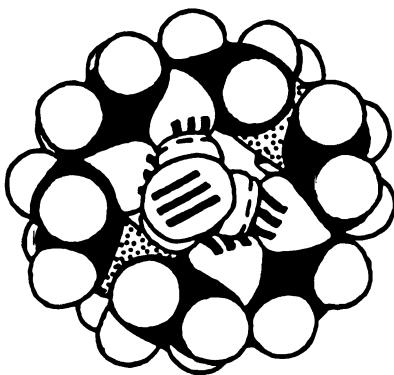
It should be emphasized that, in solution, 21C7, PG, etc. only form a 1:1 complex. The addition of NM to 18C6 results in the immediate formation of a crystalline complex which can, with care, be recrystallized. When NM is added to 21C7, small crystals of the complex slowly form. These crystals are extremely unstable. Once they are removed from the mother liquor they decompose. This implies that the 2:1 NM:21C7 complex is unstable. Figure 87 shows a space-filling model of the 1:1 complex of 21C7 with a CH_3 -acid. The crown is very flexible, compared to 18C6, and can easily assume a conformation to complex one CH_3 -acid. However, the remaining ether oxygens cannot, without some difficulty, orient themselves in order to accommodate a second CH_3 -acid.

Nitromethane forms a very weak complex with C222. Space-filling models (Figure 110) indicate that CH_3 -acids form a "crown-like" complex with one of the faces of the cryptand; i.e., the CH_3 group does not penetrate the cavity of the cryptand. A "crown-like" complex implies a "planar" complex. Space-filling models indicate that in its most symmetrical conformation, C222 does not have a planar face. In order to complex NM, the cryptand must undergo a conformational change. Conformational changes expend energy resulting in the formation of weaker complexes.

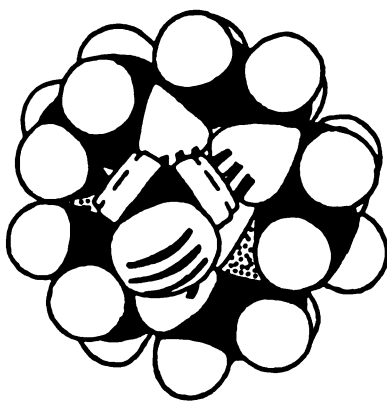
7. DIAZA-18-CROWN-6 COMPLEXATION WITH ACETONITRILE



CRYPTAND 222



CRYPTAND 221



CRYPTAND 211

Figure 10. Space-filling models of CH_3 -acid complexes with cryptands 222, 221, and 211.

AND MALONONITRILE. The malonitrile complex with 18C6 was prepared by using the procedure described by Knochel (148). The complex consisted of fine, white needles. In deuterated chloroform, the complex shows two proton resonances -- one at 3.62 ppm vs. TMS due to 18C6 and one at 4.01 ppm vs. TMS due to malononitrile (the literature value of the chemical shift of malononitrile in the complex is 4.00 ppm (152)). The deuterated chloroform solution is clear and colorless. "Free" malononitrile resonates at 3.58 relative to TMS (literature value 3.58 ppm (152)). The 0.42 ppm change in the malononitrile chemical shift indicates that complexation occurs. The intensities of the 18C6 and malononitrile resonances were 16.88 and 2.81, respectively. For a 2:1 complex of malononitrile, $C_3H_2N_2$, and 18C6, $C_{12}H_{24}O_6$, one would expect a ratio of intensities, $I_{18C6} / I_{CH_2(CN)_2}$, of 6.00. Experimentally, we find a ratio of 6.01. Therefore, we can conclude that the stoichiometry of the complex is indeed two malononitriles to one 18C6. Table 33 tabulates the proton and carbon-13 chemical shift data for malononitrile and the complex in deuterated chloroform.

An attempt was made to prepare the malononitrile complex with DA18C6. The procedure used was the same as that used to prepare the malononitrile complex with 18C6. Instead of forming a crystalline solid, a red-orange oil formed. Proton and carbon-13 spectra of the oil and

Table 33. Proton and Carbon-13 Chemical Shift Data for Solutions of Malononitrile and the $18\text{C}6 \cdot (\text{CH}_2(\text{CN})_2)_2$ Complex in Chloroform-d.

COMPOUND	^{a, b}	
	CARBON-13 CHEMICAL SHIFT (ppm)	PROTON CHEMICAL SHIFT (ppm)
Malononitrile	$\delta_{\text{CH}_2} = 8.61$ $\delta_{\text{CN}} = 109.02$	$\delta_{\text{CH}_2} = 3.58$
1:2 18C6 Complex with Malononitrile	$\delta_{\text{CH}_2} = 8.10$ $\delta_{\text{CN}} = 111.49$ $\delta_{18\text{C}6} = 70.03$	$\delta_{18\text{C}6} = 3.62$ $\delta_{\text{CH}_2} = 4.01$

^aChemical shifts are reported relative to TMS in acetone-d₆.

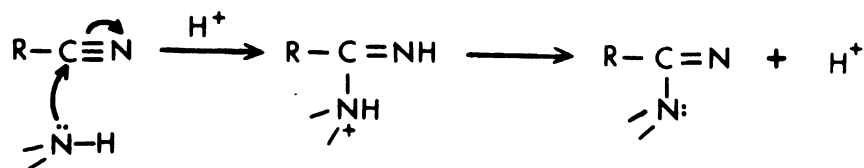
^bUncertainty in the carbon-13 chemical shifts is ± 0.06 ppm.

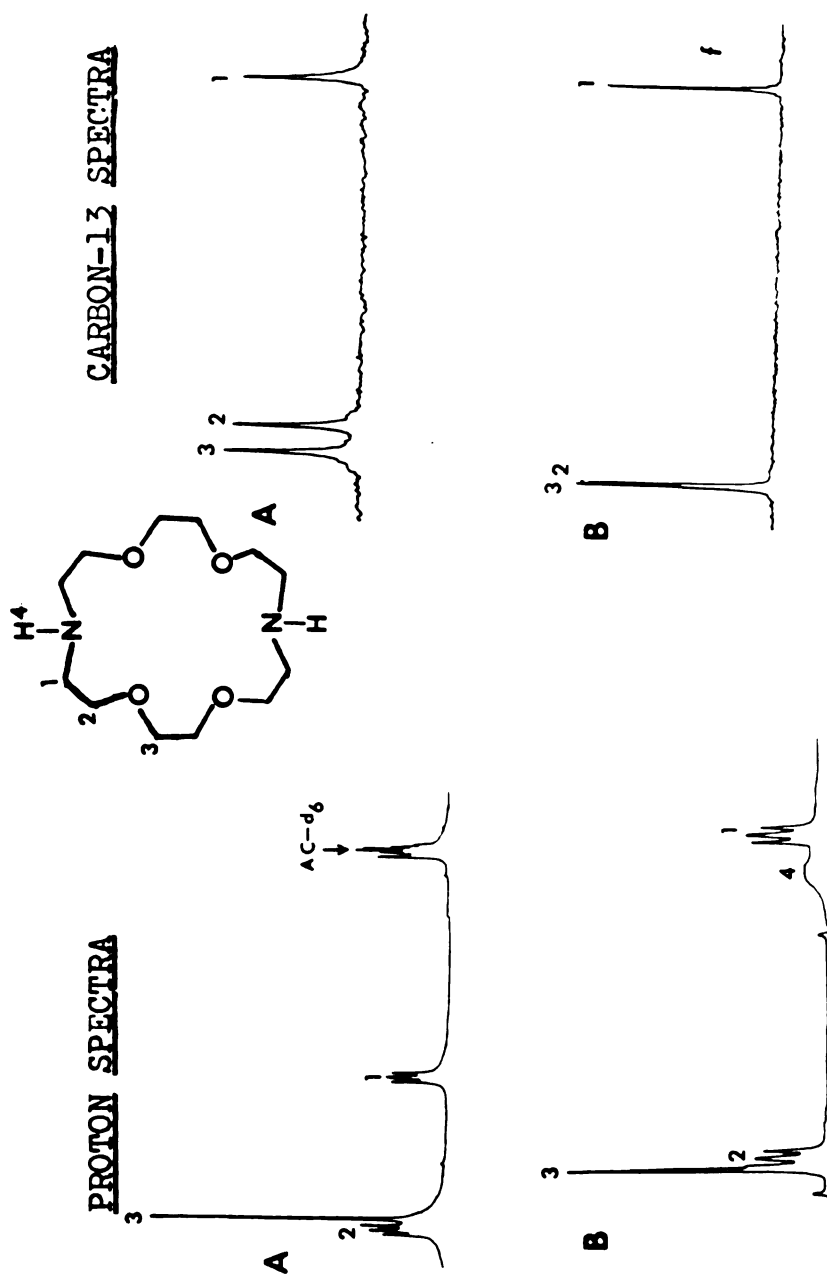
^cUncertainty in the proton chemical shifts is ± 0.01 ppm.

DA18C6 in acetone- d_6 were obtained. These spectra are shown in Figure 111. The NMR spectra and the color change indicate that something other than guest-host complexation was occurring between malononitrile and DA18C6.

To better understand what is occurring between DA18C6 and malononitrile, solutions of malononitrile, DA18C6, and 2:1 malononitrile:DA18C6 were prepared in chloroform- d . The solutions of DA18C6 and malononitrile were clear and colorless. However, the solution containing DA18C6 and malononitrile was red-orange in color and contained a suspension of oil droplets. Proton and carbon-13 NMR spectra were obtained for these solutions. These spectra are shown in Figures 112 and 113. The physical appearance of the solutions and the NMR spectra indicate that a chemical reaction is occurring between DA18C6 and malononitrile. Since such a reaction does not occur between 18C6 and malononitrile, this implies that the reaction involves the amine protons of DA18C6.

A search of the literature revealed that primary and secondary amines react with nitriles to give substituted amidines but only if the nitrile contains electron-withdrawing groups; e.g., Cl_3CCN (213). Ordinary nitriles do not give this reaction. The mechanism used to describe this reaction is shown below (214):



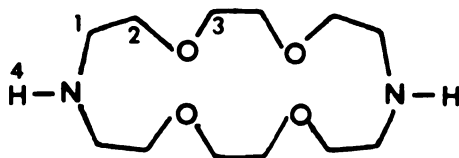


Figure¹¹¹. Proton and carbon-13 spectra of the oil obtained in the attempt to synthesize the 2:1 malononitrile:DAL8C6 complex where:

(A) Oil in acetone-d₆.

(B) DAL8C6 in acetone-d₆.

Table³⁴ . Proton and Carbon-13 Chemical Shift Data
 Obtained for the Oil Prepared When Attempting to
 Synthesize the 2:1 Malononitrile:DA18C6 Complex.

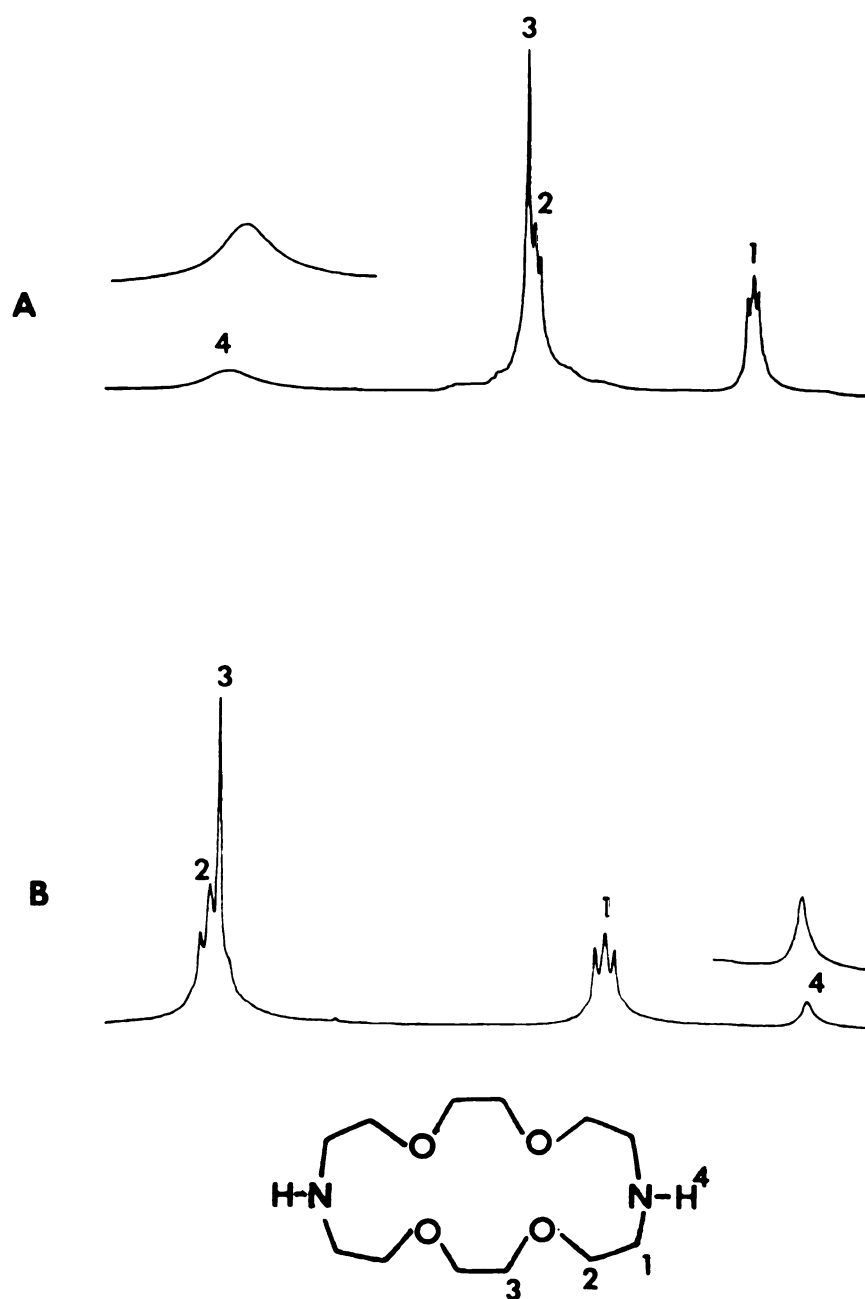


SOLUTION	PROTON ^{a, b} CHEMICAL SHIFT (ppm)	CARBON-13 ^{a, c} CHEMICAL SHIFT (ppm)
DA18C6 in acetone-d ₆	$\delta_4 = 2.88$ $\delta_1 = 2.77$ $\delta_2 = 3.60$ $\delta_3 = 3.63$	$\delta_1 = 50.34$ $\delta_2 = 71.14$ $\delta_3 = 71.20$
Oil in acetone-d ₆	$\delta_1 = 3.05$ $\delta_2 = 3.69$ $\delta_3 = 3.65$ $\delta_2 = 2.07$	$\delta_1 = 49.49$ $\delta_2 = 69.20$ $\delta_3 = 70.64$

^aChemical shifts are reported relative to TMS in acetone-d₆.

^bUncertainty in the chemical shifts is ± 0.01 ppm.

^cUncertainty in the chemical shifts is ± 0.06 ppm.



Figure¹¹². Proton spectra of solutions of DA18C6 and malononitrile in chloroform-d where:

(A) DA18C6 and malononitrile in CDCl_3 .

(B) DA18C6 in CDCl_3 .

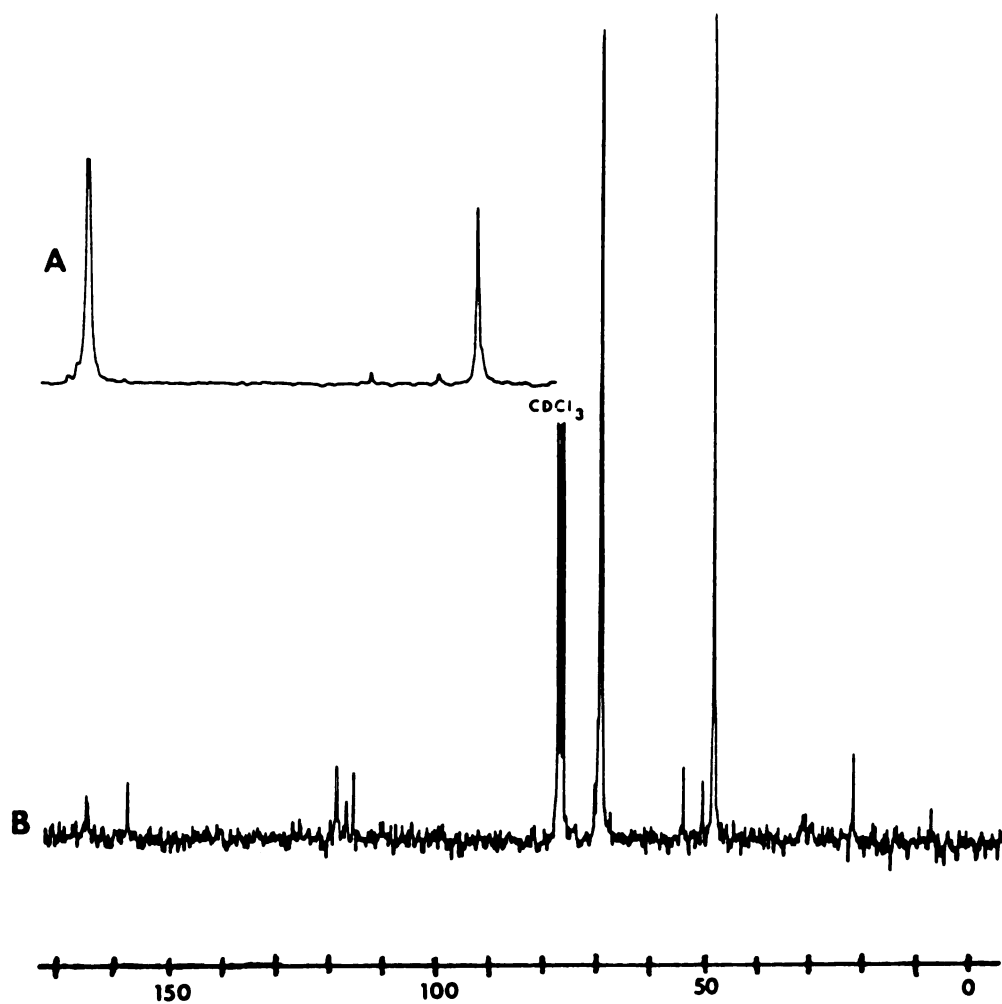
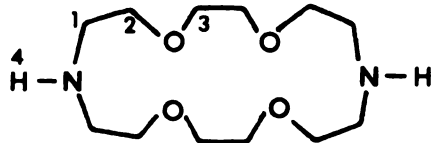


Figure 13. Carbon-13 spectra of a solution of DA18C6 and malononitrile in chloroform-d where (A) is a reduction of the region between 71-45 ppm of spectrum B.

Table 35. Carbon-13 and Proton Chemical Shift Data
Obtained for Solutions of Malononitrile and
DA18C6 in Chloroform-d.



SOLUTION	PROTON CHEMICAL SHIFT (ppm) ^{c, d}	CARBON-13 CHEMICAL SHIFT (ppm) ^{c, e}
Malononitrile ^a	$\delta_{\text{CH}_2} = 3.58$	$\delta_{\text{CH}_2} = 8.61$ $\delta_{\text{CN}} = 109.02$
DA18C6 ^a	$\delta_4 = 2.34$ $\delta_1 = 2.75$ $\delta_2 = 3.55$ $\delta_3 = 3.54$	$\delta_1 = 49.30$ $\delta_2 = 70.24$ $\delta_3 = 70.32$
2:1 Malononitrile ^a and 18C6	$\delta_{\text{CH}_2} = 4.01$ $\delta_{18\text{C6}} = 3.62$	$\delta_{\text{CH}_2} = 8.10$ $\delta_{\text{CN}} = 111.49$ $\delta_{18\text{C6}} = 70.03$
2:1 Malononitrile ^b and DA18C6	$\delta_{\text{C=NH}} = 4.58$ $\delta_1 = 2.77$ $\delta_2 = 3.51$ $\delta_3 = 3.54$	$\delta_{\text{CH}_2} = 8.54$ $\delta_{\text{CN}} = 114.37,$ $115.67, \&$ 117.43 $\delta_{\text{CNH}} = 155.83 \&$ 163.16 $\delta_1(\text{soln.}) = 49.03$ $\delta_2(\text{soln.}) = 69.76$ $\delta_3(\text{soln.}) = 69.88$ $\delta_1(\text{oil}) = 22.83$ $\delta_2(\text{oil}) = 51.09$ $\delta_3(\text{oil}) = 54.65$

Table 35. Continue.

^aSolution is clear and colorless.

^bSolution is red-orange in color and contains suspended oil droplets.

^cChemical shifts are reported relative to TMS in acetone- d_6 .

^dUncertainty in the chemical shifts is ± 0.01 ppm.

^eUncertainty in the chemical shifts is ± 0.03 ppm.

Amides with C=NH tend to be especially unstable if the amidine contains an acidic hydrogen (the amidine system itself is basic) (215). Carbon-13 NMR spectra of aliphatic amidines show that the amidine carbon resonates between 150-155 ppm vs. TMS.

The NMR spectra obtained in CDCl_3 indicate that DA18C6 and malononitrile do indeed react to give an amidine, or a mixture of amidines. In the carbon-13 spectrum two resonances are observed at 163 and 156 ppm relative to TMS and are due to the amidine carbon, $-\text{C}=\text{NH}$. The resonances from 114-118 ppm are due to CN and those at 69.9, 69.8 and 49.1 ppm are due to DA18C6. The small peaks at 54.7, 51.1 and 22.9 ppm are probably the DA18C6 resonances of the suspended oil droplets. The appearances of these resonances are the same as those observed for the oil obtained in the synthesis attempts. The proton spectrum of free DA18C6 in CDCl_3 shows the N-H resonance upfield from the macrocyclic protons. With the addition of malonitrile, this proton is shifted downfield by more than 2 ppm and is broadened. The broadening could be due to exchange between the amidine(s) and any unreacted DA18C6. The downfield shift is indicative of amidine formation since, in the amidine functional group, the proton is adjacent to a double bond. Protons of double bonds are typically found 4 to 6 ppm downfield from TMS.

Although the attempt to prepare the

malononitrile-DA18C6 complex was unsuccessful, the results were not totally negative. These results help explain the data obtained for the interaction between DA18C6 and acetonitrile. The complexation of DA18C6 and MeCN was studied in chloroform and benzene solutions by carbon-13 NMR spectroscopy. The results are shown in Figure 114. The solubility of DA18C6 is low in benzene. However, the carbon-13 chemical shifts of MeCN shift downfield with increasing $[DA18C6]/[MeCN]$ mole ratio showing that complexation does occur. Greater solubilities were achieved in chloroform. Plots of the carbon-13 chemical shift data for the DA18C6-MeCN-CHCl₃ system are shown in Figure 114. The carbon-13 chemical shifts of MeCN show a slight downfield shift with the addition of DA18C6 indicating that complexation occurs. However, in chloroform, this complex appears to be very weak. The carbon-13 chemical shift of chloroform changes considerably with the addition of DA18C6 to the MeCN-CHCl₃ system. This suggests that DA18C6 forms a complex with CHCl₃. Formation of a DA18C6•CHCl₃ complex and CHCl₃•MeCN complexes (discussed in Chapter III) weakens the DA18C6•MeCN complexation in chloroform.

Infrared spectra of DA18C6 and MeCN and MeCN-d₃ were obtained in carbon tetrachloride. The IR spectra of the CD stretch and CN stretch are shown in Figures 115 and 116, respectively. The CH₂-rocking region of DA18C6 is

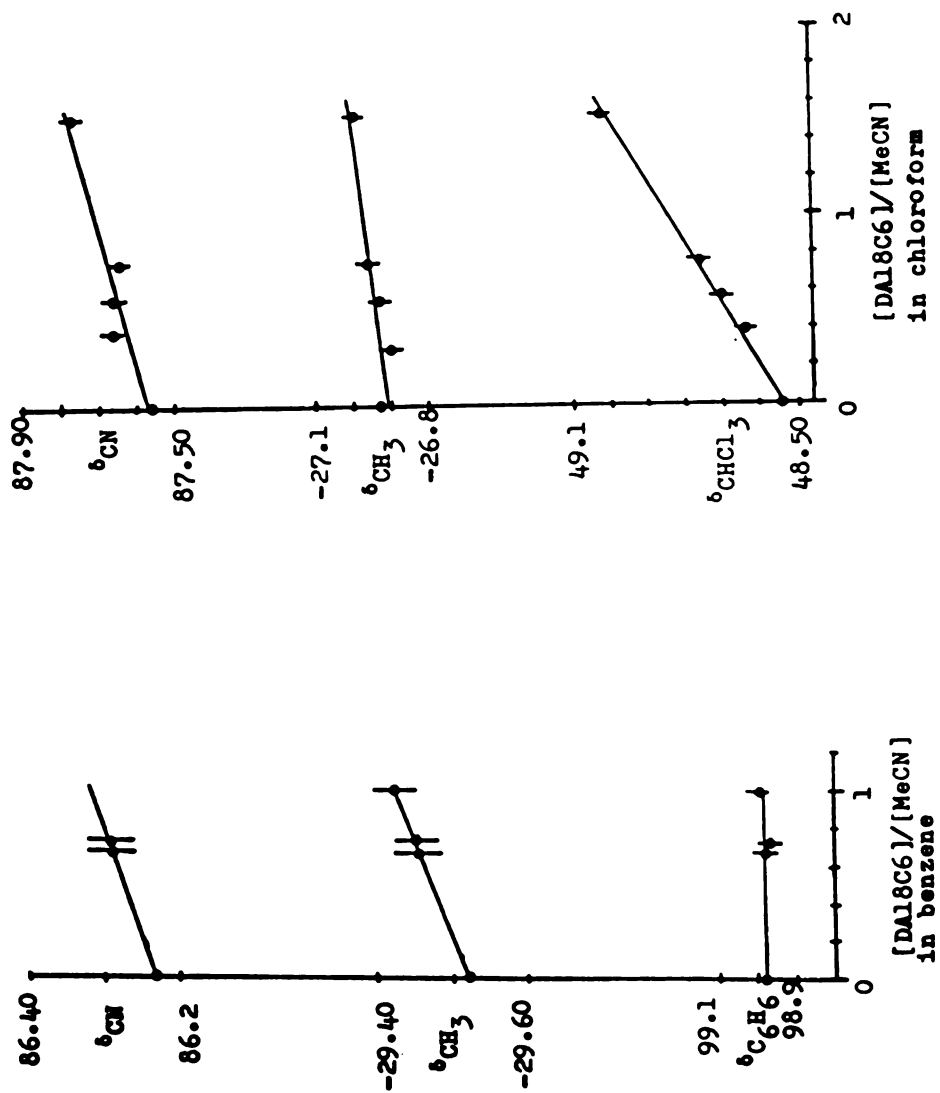
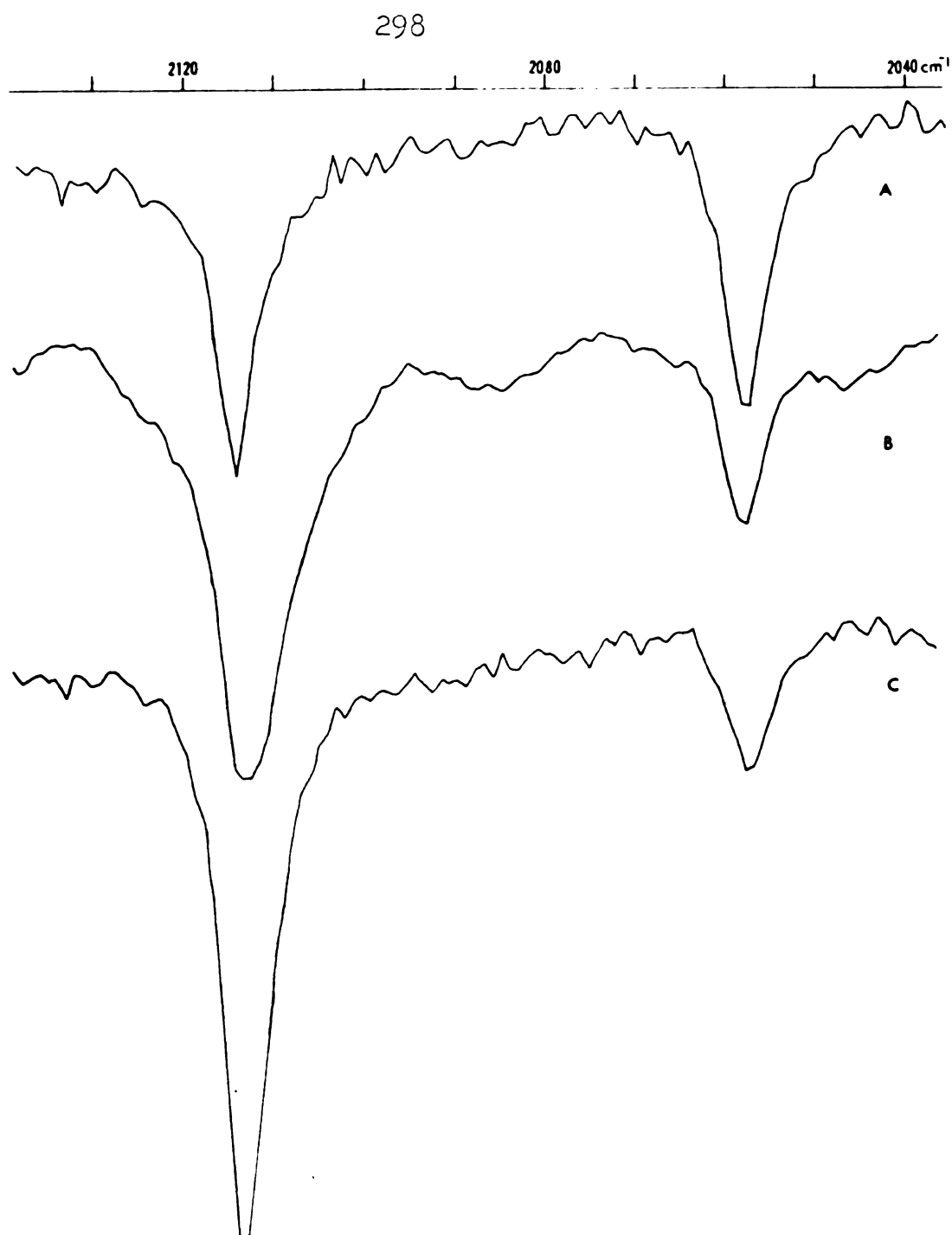
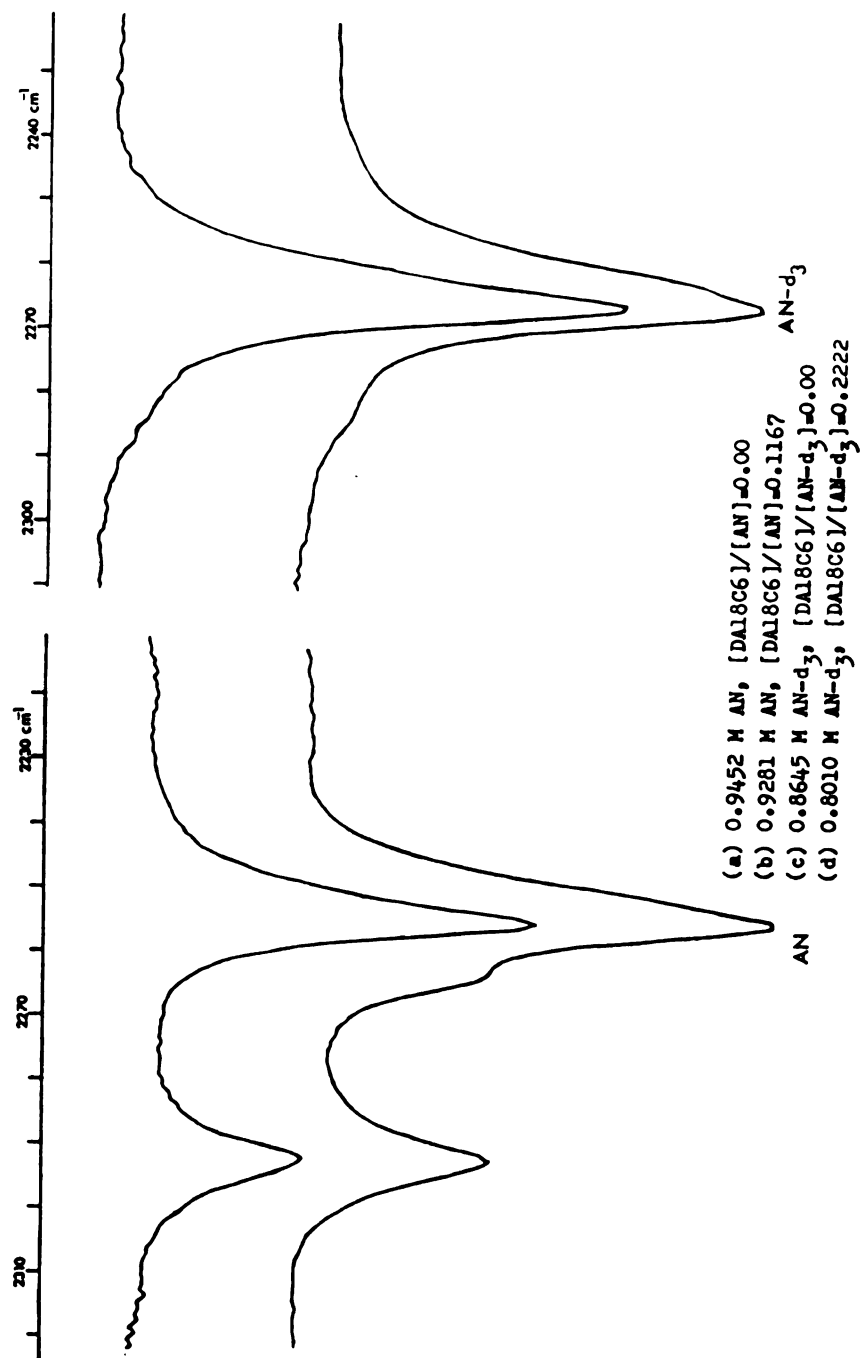


Figure 114. Plots of the carbon-13 chemical shifts of acetonitrile and the background solvent as a function of [DAL8C6]/[AN] in benzene and chloroform.



- (A) 0.4243 M AN-d₃
 (B) 0.8010 M AN-d₃; [DA18C6]/[AN-d₃]=0.2222
 (C) 0.4232 M AN-d₃; [18C6]/[AN-d₃]=0.2012

Figure 115 Infrared spectra of the C-D stretch of AN-d₃ in solutions of AN-d₃ and either DA18C6 or 18C6 in carbon tetrachloride.



Figurell6. Infrared spectra of the C≡N stretch of AN and AN-d₃ for solutions of MeCN and DAL8C6 in carbon tetrachloride.

shown in Figure 117. The changes observed in the IR spectra can be summarized as follows:

(1) a new ν_2 band due to complexation appears at high frequency.

(2) with the addition of DA18C6, ν_1 increases in intensity and broadens.

(3) no changes were observed for the skeletal vibrations of DA18C6 upon the addition of either MeCN or MeCN-d₃. This indicates that the conformation of the crown is not changing.

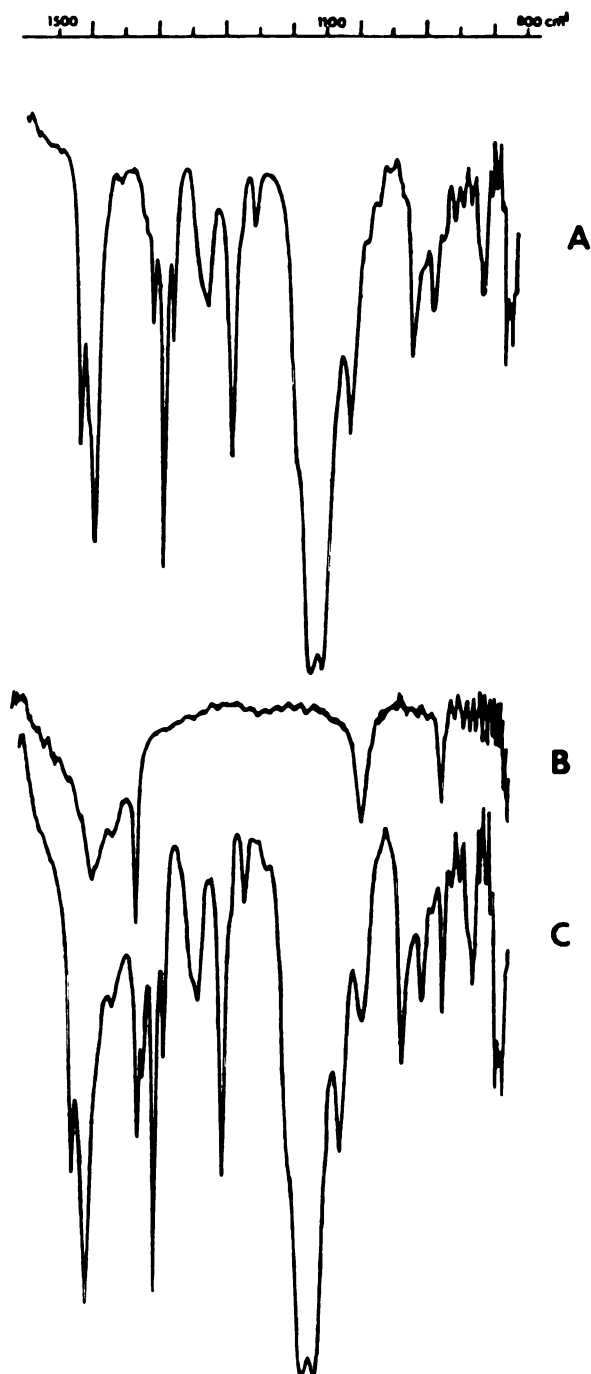
These results are vastly different from those obtained for the 18C6-MeCN-CCl₄ system. For 18C6 and MeCN in CCl₄, the following changes were observed in the IR spectra:

(1) A new ν_2 band due to complexation appears at low frequency.

(2) ν_1 of MeCN-d₃ increases in intensity with the addition of 18C6.

(3) The skeletal vibrations of the crown indicate that 18C6 changes conformation upon the addition of either MeCN or of MeCN-d₃. In CCl₄, 18C6 has a random conformation; upon the addition of either MeCN or MeCN-d₃, the crown assumes D_{3d} symmetry.

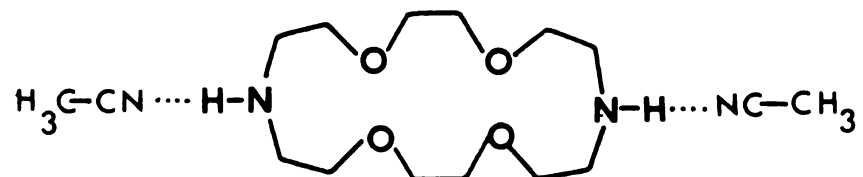
The results obtained for the malononitrile-DA18C6 system explain the contradictory IR results. The results



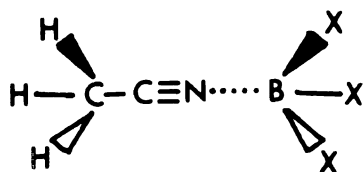
- (A) 0.22 M DAL8C6
(B) 0.9452 M AN; [DAL8C6]/[AN]=0.00
(C) 0.3472 M AN; [DAL8C6]/[AN]=0.1167

Figure¹¹⁷. Infrared spectra, in the 1500-800 cm⁻¹ region, of solutions of DAL8C6 and AN in CCl₄.

obtained for DA18C6 and malononitrile indicate that the nitrile group has an affinity for amine protons. It is quite possible, therefore, that acetonitrile complexes DA18C6 not through the methyl group but through the nitrile group as shown below:



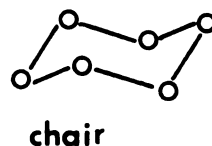
Such hydrogen-bonded complexes have been observed in the gas phase for MeCN and HF as well as for MeCN and HCl (19, 20). These complexes have been shown to be linear, i.e., R-N-H-X. Furthermore, for molecular complexes of MeCN with BF_3 , BCl_3 , and BBr_3 , ν_2 of MeCN is shifted to higher frequencies (16). X-ray measurements have shown that these complexes have the following structure (195):



For these complexes, it has been established that the ν_2 stretching frequency of the nitrile group increases upon complex formation with electron acceptors. The reason for this frequency rise has been attributed to an increase in the force constant on complex formation. In fact, X-ray measurements of the BF_3 and BCl_3 complexes of MeCN have shown that the CN bond length decreases upon

complex formation.

8. ACETONITRILE COMPLEXATION WITH DITHIA-18-CROWN-6 AND CRYPTAND 222. Infrared spectra were obtained for solutions of DT18C6, DT18C6 and MeCN-d₃, and DT18C6 and MeCN in CCl₄. No changes in ν_1 or ν_2 of AN or AN-d₃ with the addition of DT18C6 were observed. Also, as shown in Figure 118, no changes were observed in the vibrational bands of the crown. These data indicate that if there is any complexation between DT18C6 and MeCN it is extremely weak. This is not surprising since DT18C6, as shown below, has its heteroatoms spatially arranged in a boat conformation instead of a chair:



If complexation occurs through the methyl group, the chair conformation would be favored over the boat conformation.

Infrared spectra were obtained for solutions of MeCN and C222 in CCl₄. The infrared spectrum of the C222-MeCN solution in CCl₄ is additive. This indicates that, if any complexation was occurring, it is very weak. Proton and carbon-13 spectra were obtained for solutions of C222 in CCl₄ and MeCN. The chemical shift data are tabulated in Table 36. The data indicate that the environment of C222 is different in these two solvents. This, in turn,

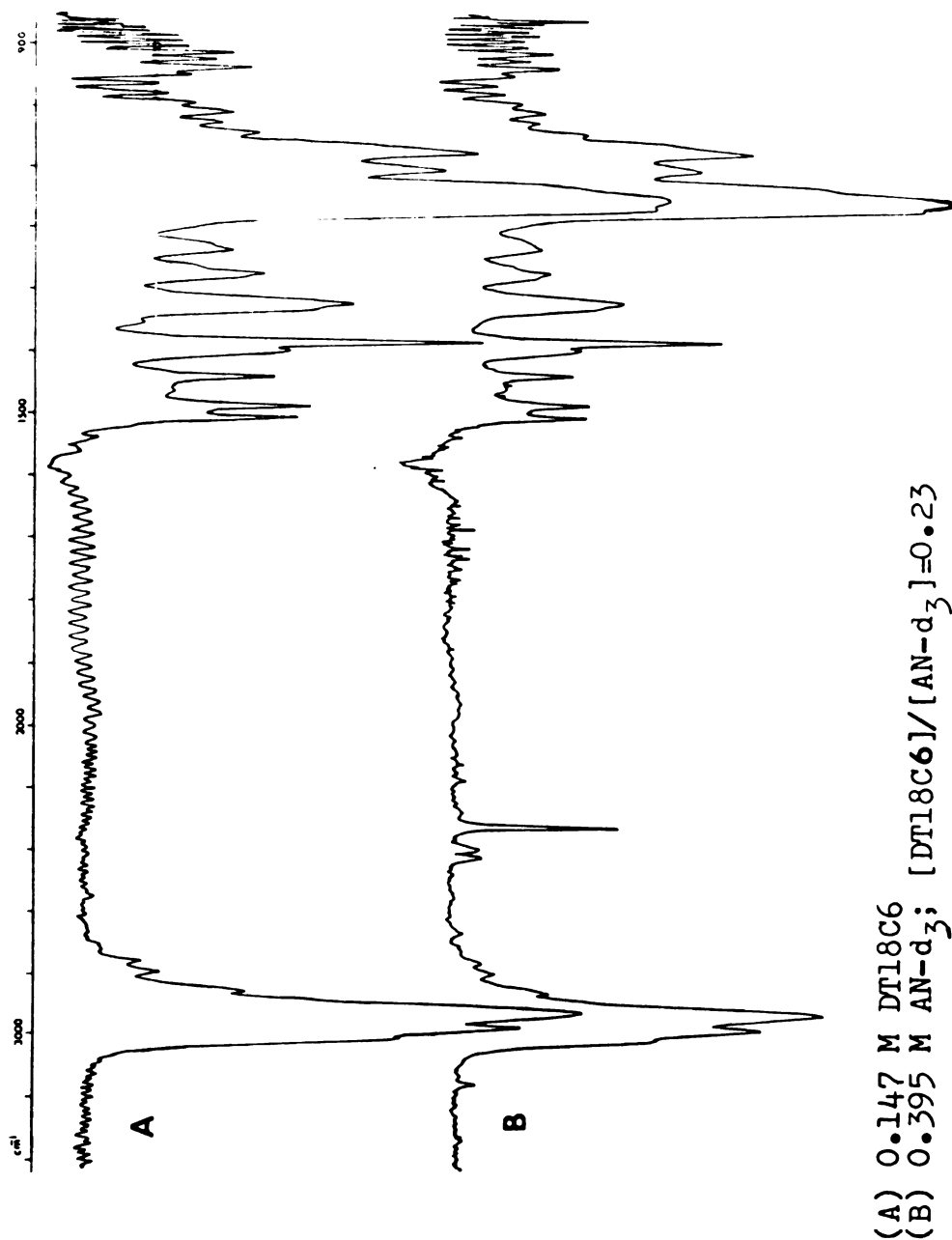


Figure 118. Infrared spectra of solutions of AN-d₃ and DT18C6 in carbon tetrachloride.

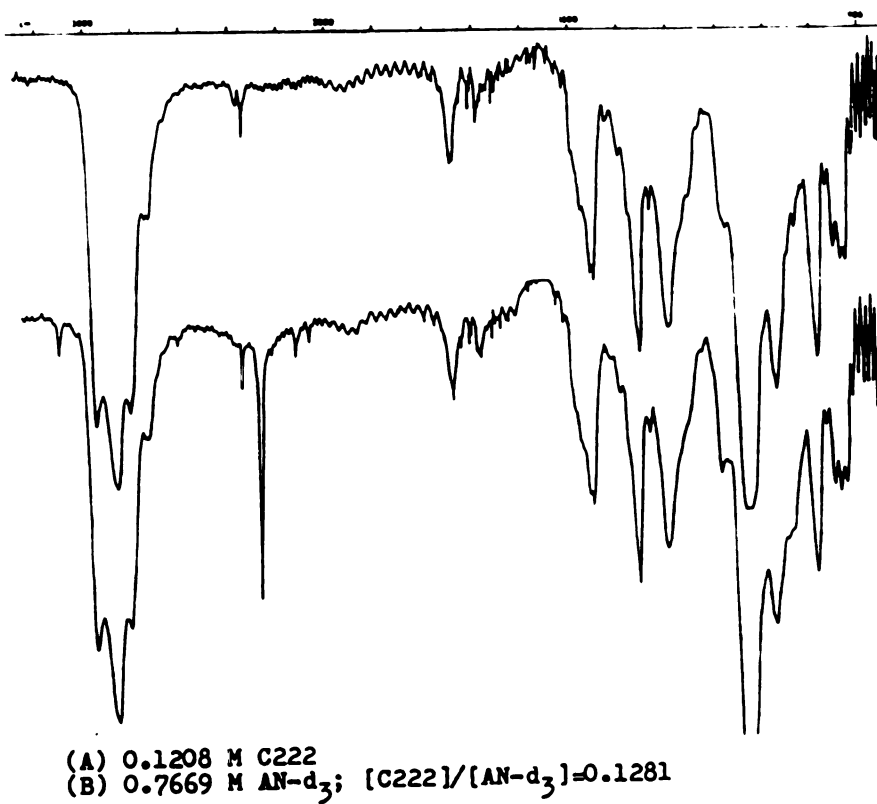
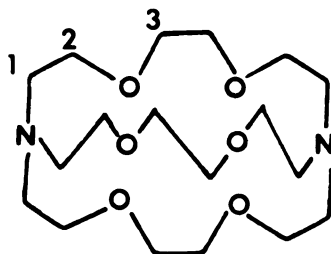


Figure 19. Infrared spectra of solutions of C222 and AN-d₃ in carbon tetrachloride.

Table 36. Carbon-13 Chemical Shift Data for Solutions of C222 in Acetonitrile and Carbon Tetrachloride.^a

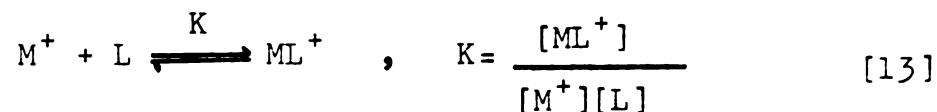


	C222 in MeCN	C222 in CCl ₄
δ_1^{C222}	27.26	28.01
δ_2^{C222}	40.89	41.18
δ_3^{C222}	41.65	42.10

^aChemical shifts are reported relative to acetone-d₆ in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

indicates that the solvation of C222 in CCl_4 is different from that in MeCN. However, it says nothing conclusive about the complexation of MeCN and C222.

9. THE EFFECT OF LIGAND SOLVATION ON THE THERMODYNAMICS OF METAL CATION COMPLEXATION. The equilibrium constant for metal cation-crown complexation is given by the following expression:



where M^+ refers to the metal cation, L to the crown and ML^+ to the complex. Since we have an ion-molecule reaction, the effect of activity coefficients can be ignored in dilute solutions. Experimentally, however, in solvents which also complex the crown, a conditional equilibrium constant, K' , is measured. This conditional equilibrium constant can be defined by the following expression:

$$\text{K}' = \frac{[\text{ML}^+]}{[\text{M}^+][\text{L}']} \quad [14]$$

where $[\text{L}']$ refers to the concentration of crown uncomplexed by M^+ . This concentration $[\text{L}']$ includes the concentration of crown in all its solvated forms as shown:

$$[L'] = [L] + [SL] + [SLS] \quad [15]$$

where $[L]$ is the concentration of crown not complexed by the solvent and $[SL]$ and $[SLS]$ are the concentrations of the 1:1 and 1:2 crown:solvent complexes respectively. The thermodynamic and conditional equilibrium constants are related to one another by the following expression:

$$K' = \alpha_L K \quad [16]$$

where:

$$\alpha_L = \frac{1}{1 + K_1[S] + K_1K_2[S]^2} \quad [17]$$

In equation [17], $[S]$ is the concentration of monomeric solvent and K_1 and K_2 are the formation constants for the 1:1 and 1:2 crown:solvent complexes, respectively.

Using the above equation and the values of the formation constants for the crown-solvent interactions in benzene, α_L was calculated to see the effect of ligand-solvent interactions on the stabilities of the ligand-metal ion complexes. In these calculations the assumption was made that the concentration of "free" solvent is greater than that of solvent bound by the ligand and metal ion. For a solution of crown or cryptand and metal cation in a solvent this is a valid assumption since the analytical concentration of solvent is much greater than the analytical concentrations of

either the ligand or metal ion. Using this assumption, α_L for the solvents and ligands were calculated. The values obtained are tabulated in Table 37. These results clearly show how great an effect solvent-ligand interactions can have on the complexation of metal cations.

For the NM complexes with 18C6 and PG, α_L for 18C6 is twenty times larger than α_L for PG. There is no difference in the α_L 's for TG and 15C5. These results show that differences in the solvation of the cyclic and noncyclic polyether ligands does not account for the "macrocyclic effect".

C. CONCLUSIONS

The purpose of this investigation was to determine the effect ligand solvation had on metal ion complexation. The calculations of α_L clearly show that the solvation of crowns and cryptands can have a profound effect on metal ion complexation. Boss (216) aptly demonstrated that the complexation differences of DA18C6 and 18C6 with Li^+ , Na^+ , K^+ , Cs^+ , Tl^+ and Ba^{2+} could be explained by taking ligand solvation into account.

A decade ago, Margerum and Hinz (112, 113) postulated that differences in the solvation of cyclic and noncyclic ligands accounted for the "macrocyclic effect". This work indicates that ligand solvation does

Table 37. Values of α_L Calculated for the Solvent-Ligand Interactions.

SOLVENT	LIGAND	α_L	K^a (M^{-1})
NM	18C6	3.39×10^{-3}	294.65 K'
NM	15C5	0.1495	6.69 K'
NM	21C7	6.57×10^{-2}	15.22 K'
NM	PG	0.114	8.79 K'
NM	TG	0.155	6.44 K'
NM	C222	0.278	3.60 K'
NM	B15C5	0.269	3.72 K'
AN	18C6	1.89×10^{-2}	52.85 K'
AN	15C5	0.1759	5.69 K'
AN	TG	0.1722	5.81 K'
AN	B15C5	0.1587	6.30 K'
MeOH	18C6	3.31×10^{-3}	302.3 K'
MeOH	15C5	5.04×10^{-3}	198.6 K'
MeOH	TG	8.26×10^{-3}	121.0 K'
MeOH	B15C5	4.13×10^{-3}	242.1 K'
CHCl ₃	18C6	0.1183	8.46 K'
CHCl ₃	15C5	0.1436	6.96 K'
CHCl ₃	TG	0.1237	8.08 K'
CHCl ₃	B15C5	0.2061	4.85 K'
AC	18C6	>0.363	$<2.75 K'$
AC	15C5	0.300	3.33 K'

^aK and K' refer to the thermodynamic and conditional formation constants, respectively, for M^+-L complexation.

not account for the differences in the complexing abilities of cyclic and linear polyether ligands.

Other workers have studied solvent-ligand complexations using an "inert" background solvent. The major difference between this study and the work of other investigators is that solvent self-associations were taken into account. Although the dimerization constants were very small, they did profoundly effect the values of the solvent-ligand complexation constants as was shown when the chemical shift data of the $18\text{C}6\text{-MeCN-C}_6\text{H}_6$ and $18\text{C}6\text{-MeNO}_2\text{-C}_6\text{H}_6$ systems were analyzed without taking into account the dimerization constant.

CHAPTER VI

MISCELLANEOUS PART

A. SILVER NITRATE IN ACETONITRILE

Proton and carbon-13 NMR spectra were obtained for solutions of silver nitrate, AgNO_3 , in acetonitrile, in which it is soluble to the extent of 0.1905 mole fraction AgNO_3 . Plots of chemical shifts as a function of the mole fraction of AgNO_3 are shown in Figures 120 and 121.

Raman studies by Janz et. al. (217) have shown that silver nitrate interacts with the nitrile group of acetonitrile. It has been speculated that the nitrogen of MeCN donates its electron pair to the cation through a sigma bond. However, it is possible for the Ag^+ ion to back-donate this electron density to the nitrogen by forming a π -bond between a d-orbital of the cation and the π^* orbital of the nitrile group. The following relative strengths of pi-acceptors have been proposed on the basis of infrared data (212):

$\text{NO} > \text{CO} \approx \text{RNC} \approx \text{PF}_3 > \text{PCl}_3 > \text{PCl}_2\text{OR} > \text{PCl}_2\text{R} > \text{PBr}_2\text{R} > \text{PCl(OR)}_2$
 $> \text{PClR}_2 > \text{P(OR)}_3 > \text{PR}_3 \approx \text{SR}_2 > \text{RCN} > \text{o-phenanthroline} >$
alkyl amines, ethers and alcohols

From this series it can be seen that acetonitrile should not be a very strong π -acceptor and that the interaction between Ag^+ and MeCN is predominantly through the sigma bond. The π -accepting tendency of CN^- is also much lower than that of CO, NO or RNC and that this is due to its negative charge. Furthermore CN^- is a strong sigma donor.

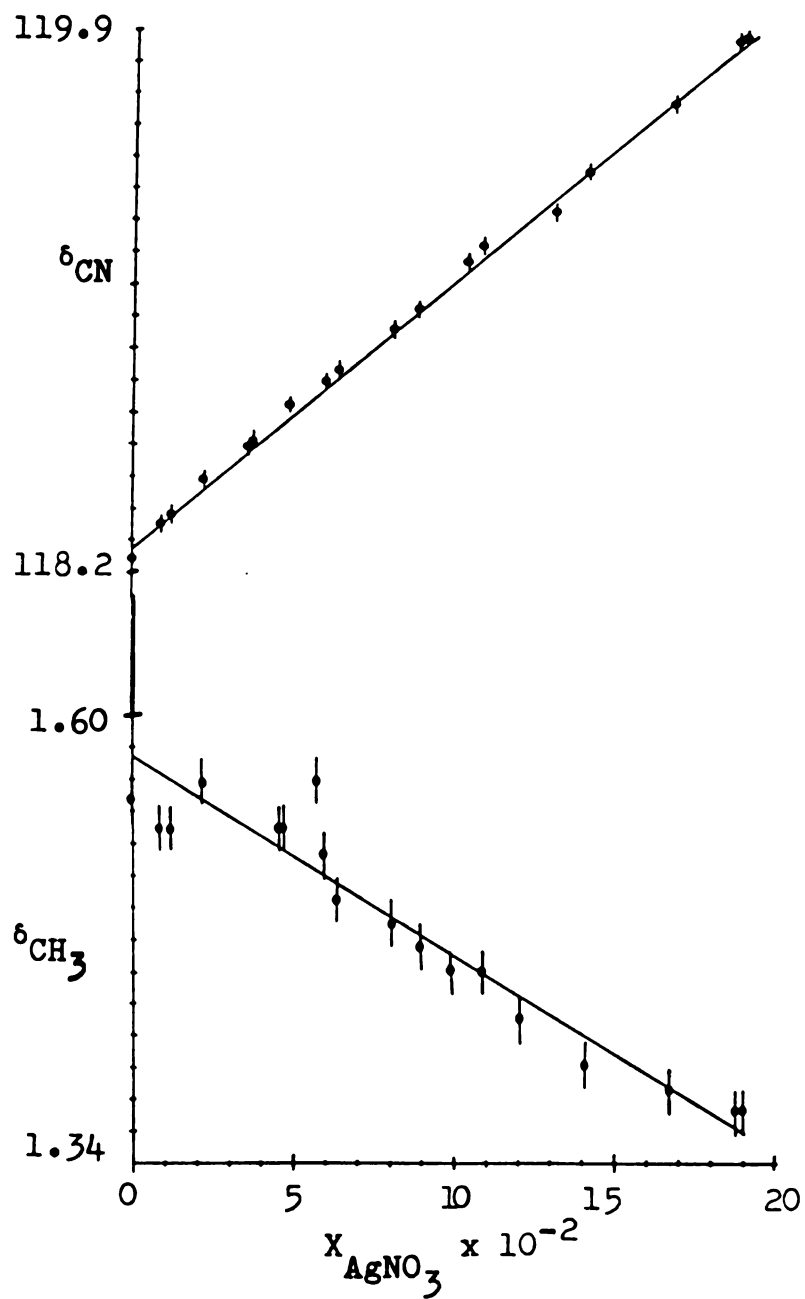


Figure 120. Plots of the carbon-13 chemical shift of the methyl and nitrile carbons of acetonitrile as a function of mole fraction of silver nitrate.

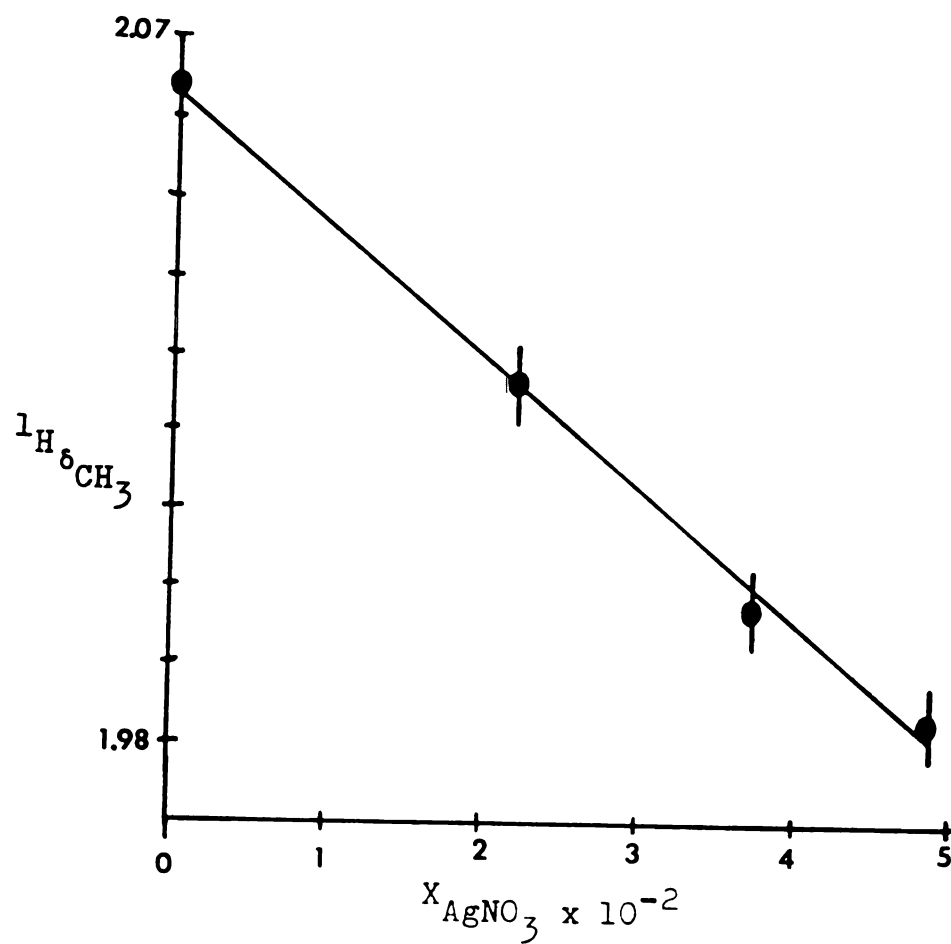


Figure 121. Plot of the proton chemical shift of acetonitrile as a function of mole fraction of silver nitrate.

Consequently back-bonding is not necessary to explain the stability of its complexes with metals in normal oxidation states (218).

The chemical shift- X_{AgNO_3} plots, shown in Figures 120 and 121, indicate that complexation with Ag^+ is through a sigma bond with minimal, if any, back-bonding. The chemical shift of the carbon-13 nucleus, like the proton nucleus, has a large diamagnetic contribution. Therefore, upfield shifts are indicative of an increase in electron density and downfield shifts are indicative of a decrease in electron density. With the addition of $AgNO_3$ to MeCN, a downfield chemical shift is observed for the nitrile carbon. When the MeCN complexes Ag^+ , the cation withdraws electron density from the nitrogen, and consequently, from the triple bond of the nitrile group, which would result in the nitrile group taking on more cyanide-like character. It should be noted that 50 ppm downfield shifts are observed as one goes from a nitrile, $R-C\equiv N:$, to a cyanide anion, $:C\equiv N:^-$ (219). Upfield shifts are observed for both the methyl carbon and methyl protons indicative of increased electron density which is probably due to the solvation of the nitrate anion.

The chemical shift data for the silver nitrate-acetonitrile system show that the nitrile and methyl groups of acetonitrile act independently of one another. This was also found to be the case for the

acetonitrile-carbon tetrachloride and acetonitrile-chloroform systems discussed in chapter III.

**B. SOLID STATE NMR OF NaSCN·C221
AND KSCN·C221**

Figure 122 shows the crystal structures of the NaSCN and KSCN complexes of C221. In the solid state, the conformation of the cryptand in these complexes is different. From these crystal structures it is obvious that the sodium ion occupies a central position whereas the potassium ion lies in the cavity of the 18-membered ring rather than in the cavity of the bicyclic ligand. The coordination shell of the potassium ion is completed by a thiocyanate ion. However, for sodium the solvation shell is completely replaced by the ligand.

Solid complexes of NaSCN and KSCN with C221 were prepared in the same manner as described by Mathieu, Moras and Weiss (220). Carbon-13 and proton NMR spectra of these complexes as well as the uncomplexed ligand were obtained in chloroform-d. These spectra are shown in Figures 123-126. The spectra of the free and complexed cryptand are different. This in turn implies that the conformation of the free and complexed cryptands is different. The $\text{Na}^+\cdot\text{C221}$ resonances are all upfield from those of the $\text{K}^+\cdot\text{C221}$ cryptate and in the latter case carbons 4 and 5 become separated by about 4.2 ppm. This

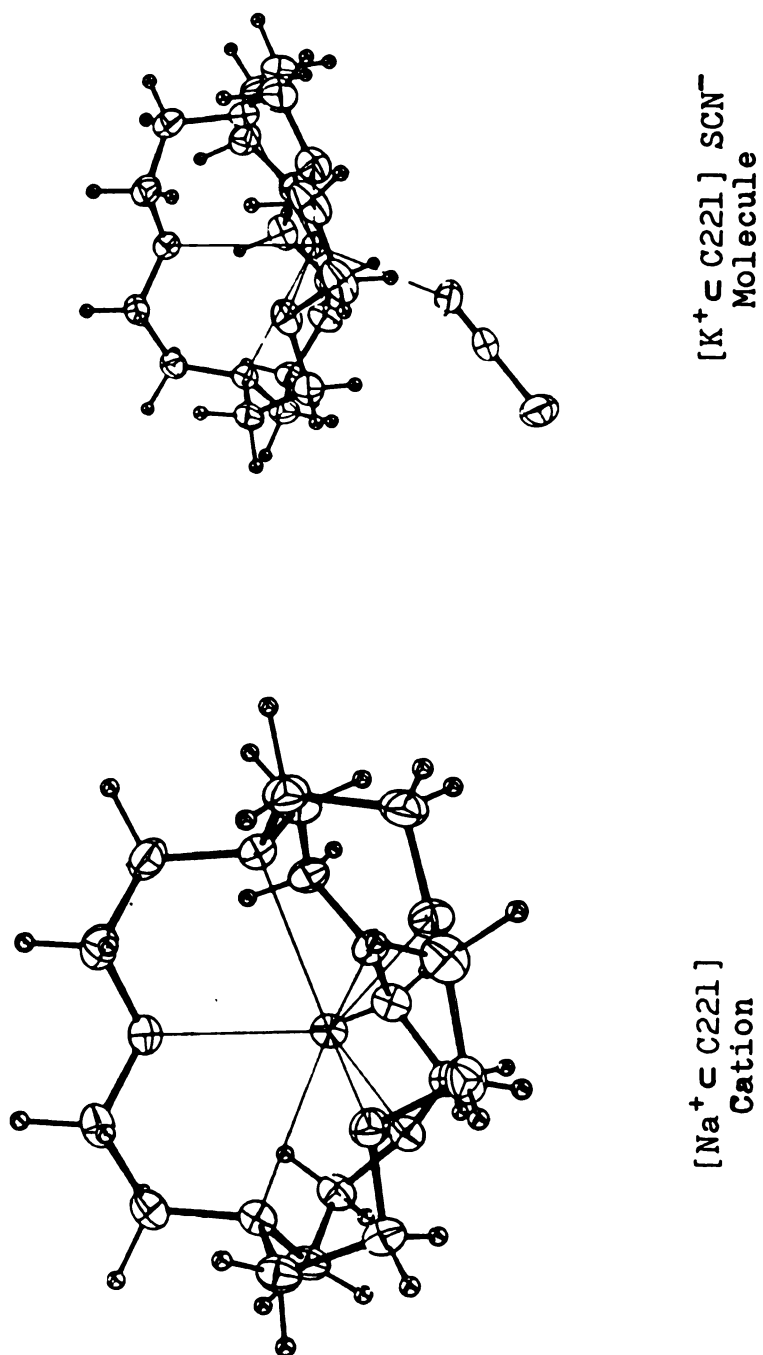


Figure 122. Crystal structures of the NaSCN and KSCN complexes with C221 (220).

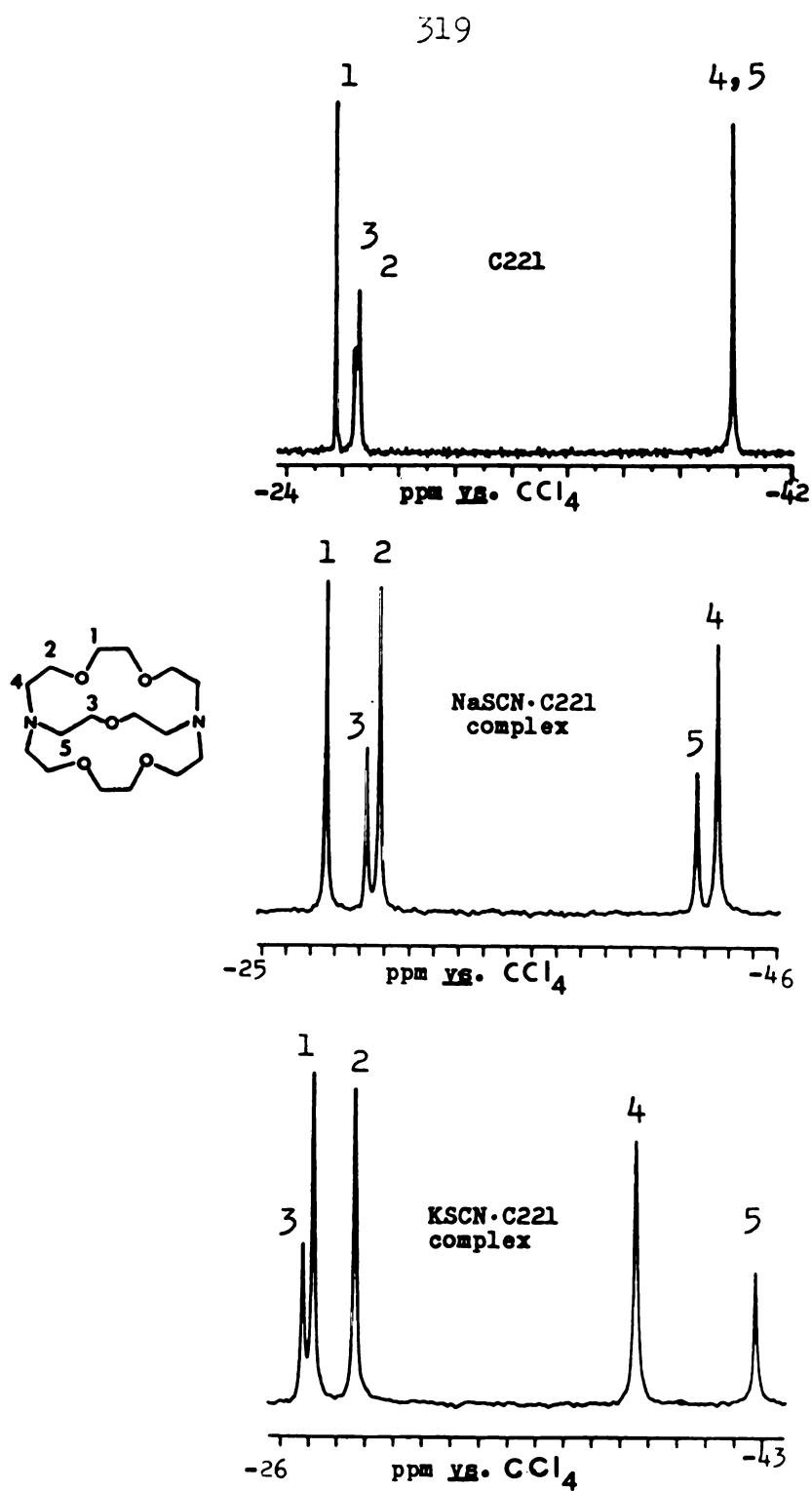


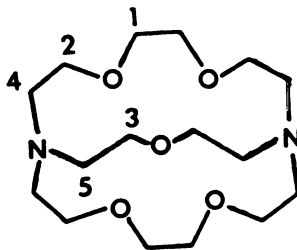
Figure 123. Carbon-13 spectra of C221, NaSCN·C221, and KSCN·C221 in chloroform-d.

Table 38. Carbon-13 Chemical Shifts of Free and Complexed Cryptand 221 in Chloroform-d.^{a, b}

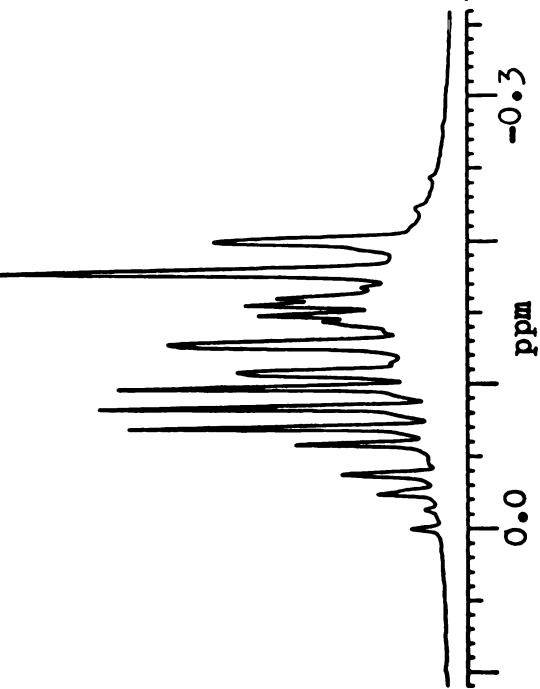
CHEMICAL SHIFT	C221	NaSCN•C221	KSCN•C221
δ_1	-25.76	-27.64	-26.77
δ_2	-26.46	-29.28	-27.15
δ_3	-26.46	-29.80	-28.67
δ_4	-39.83	-43.50	-38.56
δ_5	-39.83	-42.69	-42.77

^aChemical shifts are reported relative to CCl_4 in ppm.
Uncertainty in the chemical shifts is ± 0.03 ppm.

^bChemical shift assignment is shown below:



Expansion of the ether protons:



Expansion of the amine protons:

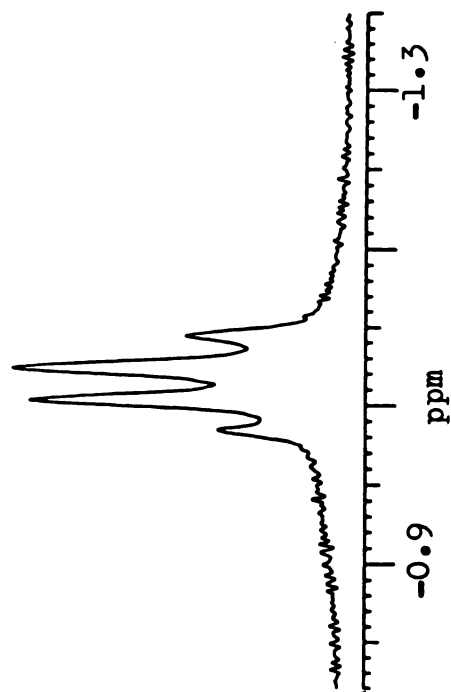


Figure 124. Proton spectrum of C22I in chloroform-d.

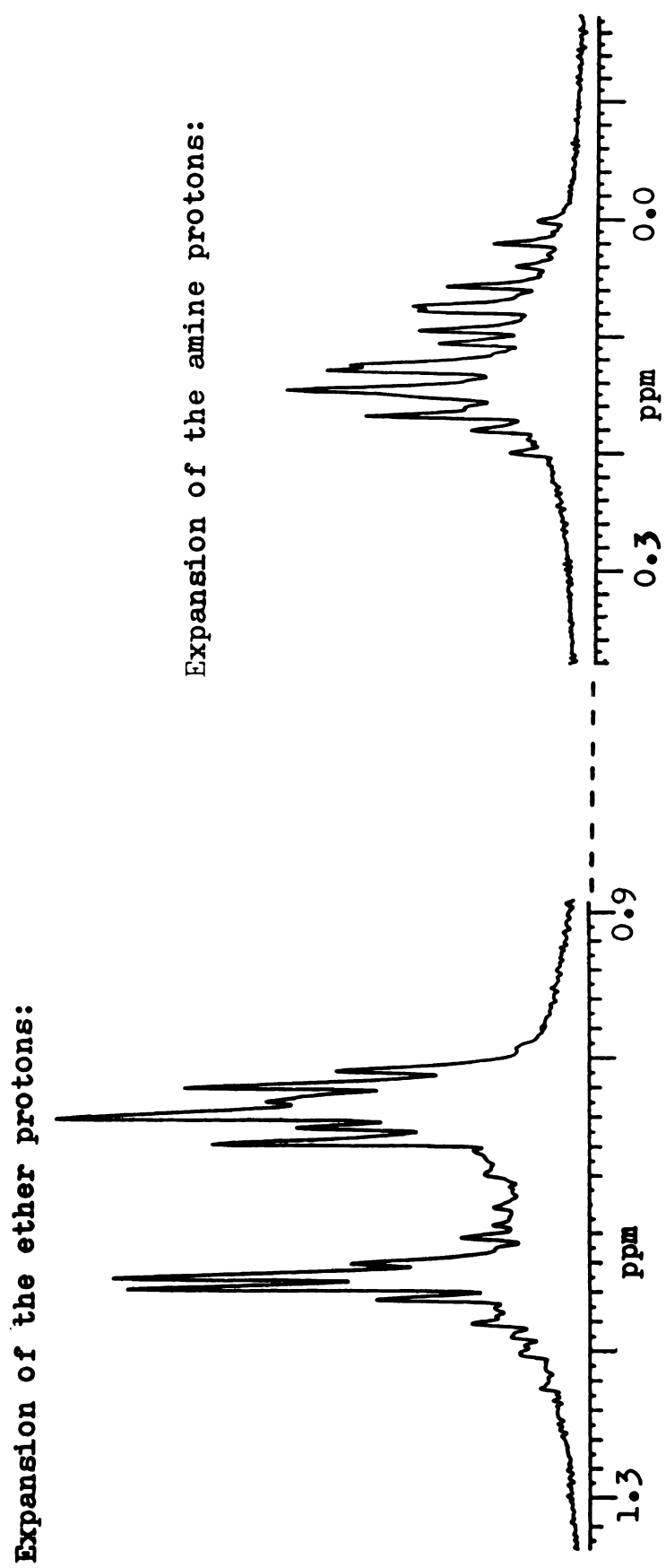
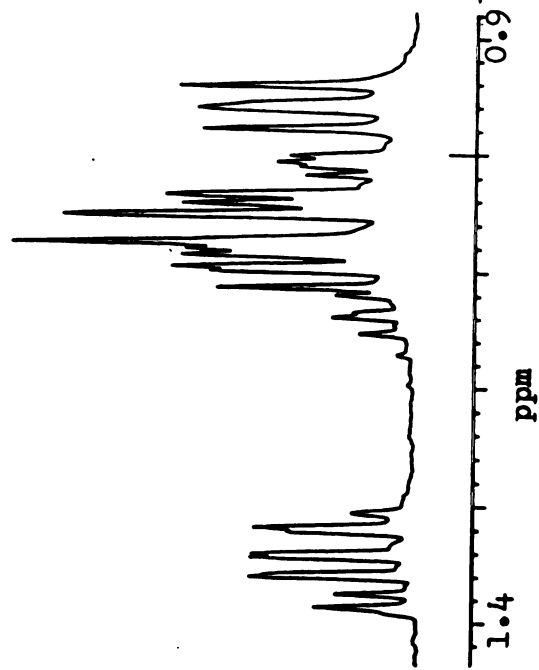


Figure 125. Proton spectrum of the NaSCN·C22l complex in chloroform-d.

Expansion of the ether protons:



Expansion of the amine protons:

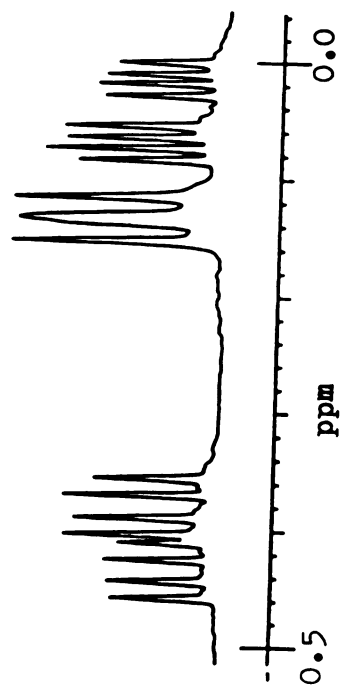


Figure 126. Proton spectrum of the KSCN·C221 complex in chloroform-d.

difference probably reflects the different structures of the two cryptates in solution. The overall high field shift of the ^{13}C resonances in the $\text{Na}^+\cdot\text{C221}$ complex compared to $\text{K}^+\cdot\text{C221}$ has been attributed to an increase of γ -interactions in the $\text{C}-\text{O}(\text{N})-\text{C}-\text{C}$ fragments (141). Likewise the large separation of carbon 4 and 5 resonances for $\text{K}^+\cdot\text{C221}$ (≈ 4.2 ppm) as compared with that for $\text{Na}^+\cdot\text{C221}$ (≈ 0.8 ppm) has been attributed to the absence of γ -interactions in the "crown" N_2O_4 and, therefore, to the opening of that pair upon complexation. But are the structures of the cryptates in solution the same as those in the crystalline state? To find out ≈ 0.5 g samples of the complexes were sent to Nicolet for analysis by solid state NMR. If the splitting patterns of the cryptate in the solid complexes are the same as those observed in solution then the conformations in solution and in the crystalline state are identical. Figure 127 shows the NMR spectra obtained by Nicolet. Obviously, the results are rather inconclusive due to the poor resolution. All that can be concluded is that the conformation of the Na^+ complex is different from that of the K^+ complex.

Close inspection of the proton spectra of the cryptates in chloroform-d suggests that K^+ forms a "crown-like" complex with C221 and not an inclusive complex. The proton spectrum of the $\text{K}^+\cdot\text{cryptate}$ complex (Figure 126) shows two multiplets at 0.96 and 0.14 ppm.

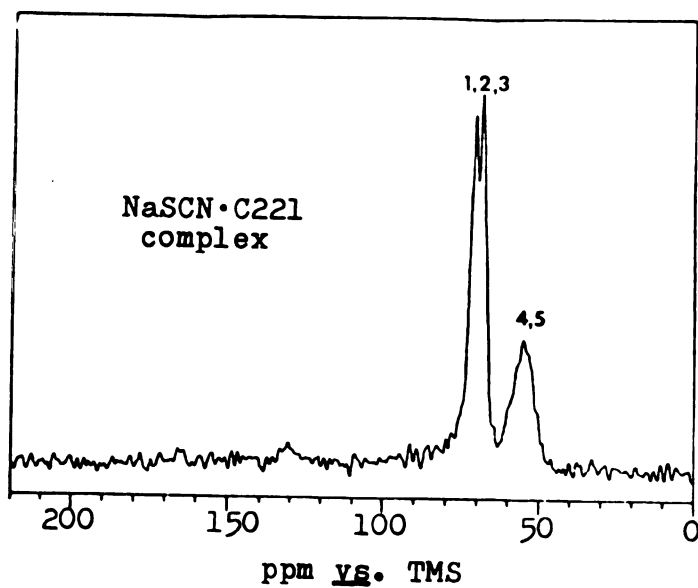
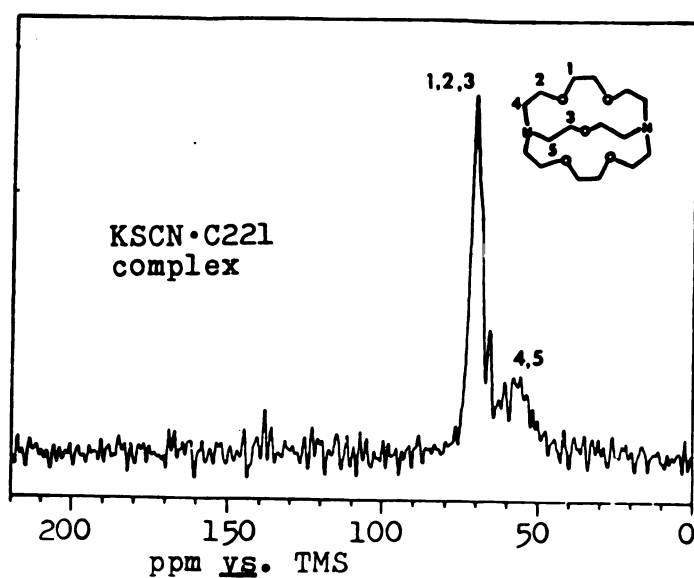


Figure 127 Solid state carbon-13 NMR spectra of the KSCN·C221 and NaSCN·C221 complexes.

These multiplets are similar to those observed for the $\text{N-CH}_2\text{CH}_2\text{-O}$ protons of DA18C6 (discussed in chapter IV). This implies that one face of the cryptand has been forced open and has a DA18C6-like conformation. The absence of these "DA18C6" multiplets in the proton spectrum of the Na^+ cryptate complex (Figure 125) implies that Na^+ forms an inclusive complex with C221.

C. C211 IN DMF AND NM

Schmidt et al. (141) had obtained carbon-13 NMR spectra of C221 in a number of different solvents and at different temperatures. They found that the carbon-13 spectrum of the ligand is strongly influenced by the medium and by temperature. In general the spectra can be separated into two quite distinct classes which were designated by "A" and "B". The "A" spectra, at room temperature or below, are very similar to that of the K^+ C221 complex. In particular there is a very definite separation of the C(4) and C(5) signals which increases as the temperature is lowered. By contrast the "B" spectra resemble that of the Na^+ C221 complex and the C(4) and C(5) signals essentially are superimposed at all accessible temperatures. Schmidt et al. concluded that the "A" spectra were indicative of a specific solvent-ligand interaction where a part of the solvent molecule (e.g., $-\text{OH}$, $-\text{NH}$ or $-\text{CH}_3$) either penetrates into

the cavity of the ligand or hydrogen-bonds with some (or all) hetero-atoms of the latter and forces it into an "open-face" configuration similar to the one observed for the $K^+ \cdot C221$ complex.

It was of interest to see if the carbon-13 spectrum of C211 would also be influenced by the medium. In Schmidt's studies, nitromethane is a class "A" solvent whereas dimethylformamide is a class "B" solvent. Carbon-13 spectra of solutions of C211 in NM and DMF were obtained. The results, shown in Figure 128, indicate that the carbon-13 NMR spectrum of C211 is not strongly influenced by the solvent. Space-filling models (Figure 110 of chapter V) show that C211 is a fairly rigid molecule. Furthermore, unlike C221, the heteroatoms of C211 do not have the proper spatial orientation to overlap with the protons of the methyl group of nitromethane. Therefore, it is not surprising that nitromethane does not interact with C211. The same may not be true of alcohols which have been shown to interact with crown ethers through the hydroxyl group (discussed in chapter V).

Although there is no evidence for specific solvent-ligand interactions, the carbon-13 resonances of C211 in NM and DMF differ somewhat, as shown in Table 39. This implies that the environment of C211 is different in the two solvents; i.e., the solvation shell of the cryptand differs in the two solvents studied.

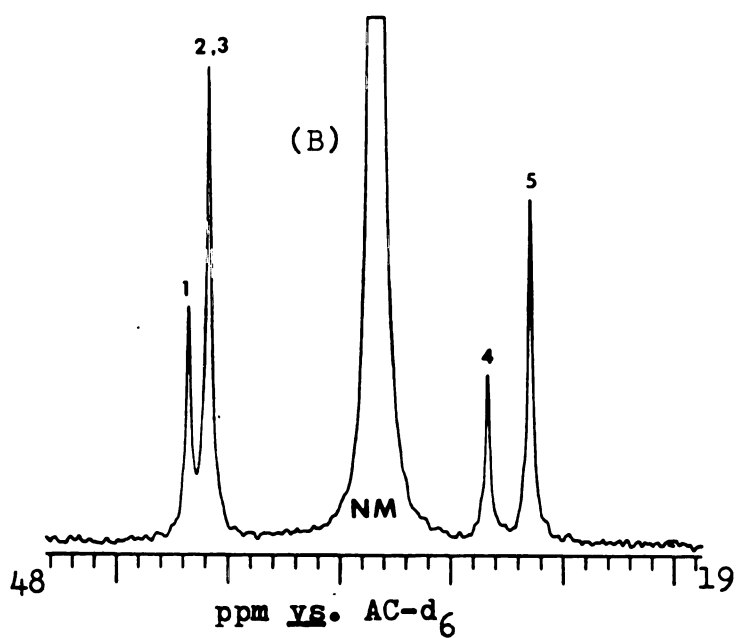
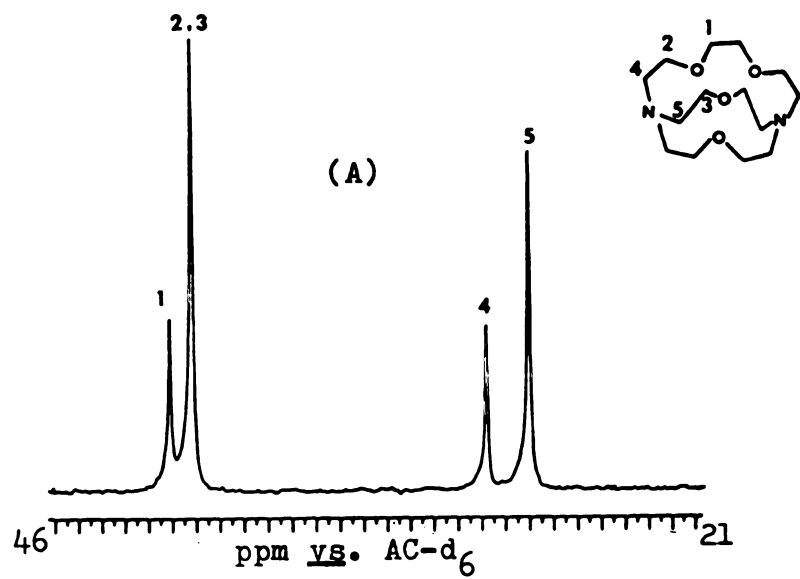
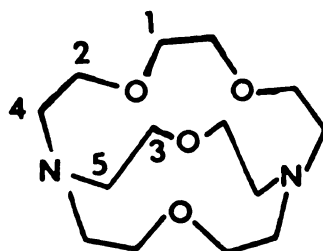


Figure 128. Carbon-13 spectra of C211 in (A) DMF and (B) NM.

Table 39. Carbon-13 Chemical Shift Data for C211 in DMF and NM. ^a

	C211 in DMF	C211 in NM
Concentration of C211	0.3057 M	0.174 M
δ_1	40.62	41.42
δ_2	39.68	40.52
δ_3	39.68	40.52
δ_4	27.28	28.03
δ_5	25.49	26.13

^aChemical shifts are reported relative to acetone- d_6 in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

D. EXCHANGE BETWEEN FREE AND COMPLEXED LIGANDS

Nuclei in different chemical surroundings may have their chemical shift positions averaged by the exchange phenomena. If the exchange is considerably more rapid than the difference between the two chemical shifts (expressed in Hz) then only one sharp resonance signal will appear midway between the two separate chemical shift positions; for a slower exchange, two sharp resonances will be observed at the proper positions, while for intermediate rates either one or two broad resonances occur. The exchange that gives rise to the averaging may be a physical exchange of the nuclei. Such is the case of Li^+ -C211. In NM, DMSO, THF, PC, chloroform, DMF and water, two resonances are observed in the ^7Li NMR spectrum (190). One resonance is due to complexed Li^+ and the other to free Li^+ . Kinetic studies of the complexation of Li^+ and C211 indicate that the rate determining step is decomplexation of the cation (190). Since the rate determining step involves the complexed species, one would expect that the exchange between free and complexed cryptand would also be slow on the NMR time scale. Carbon-13 and proton spectra of solutions of C211 and of LiClO_4 -C211 mixtures at $[\text{LiClO}_4]/[\text{C211}]=0.52$ were obtained in DMF. The results are shown in Figures 129 and 130. As these spectra indicate, exchange is slow at room

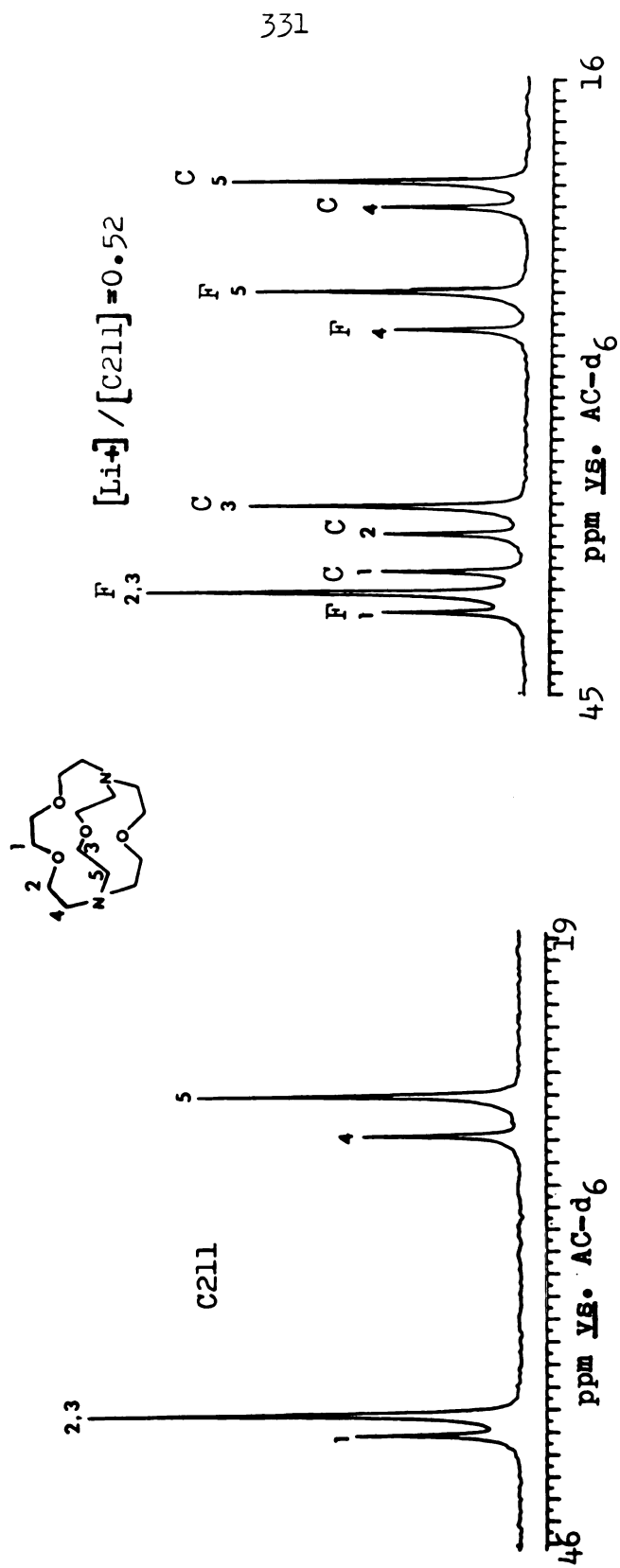


Figure 129. Carbon-13 spectra for solutions of lithium perchlorate and C211 in DMF. The symbols "F" and "C" refer to free and complex, respectively.

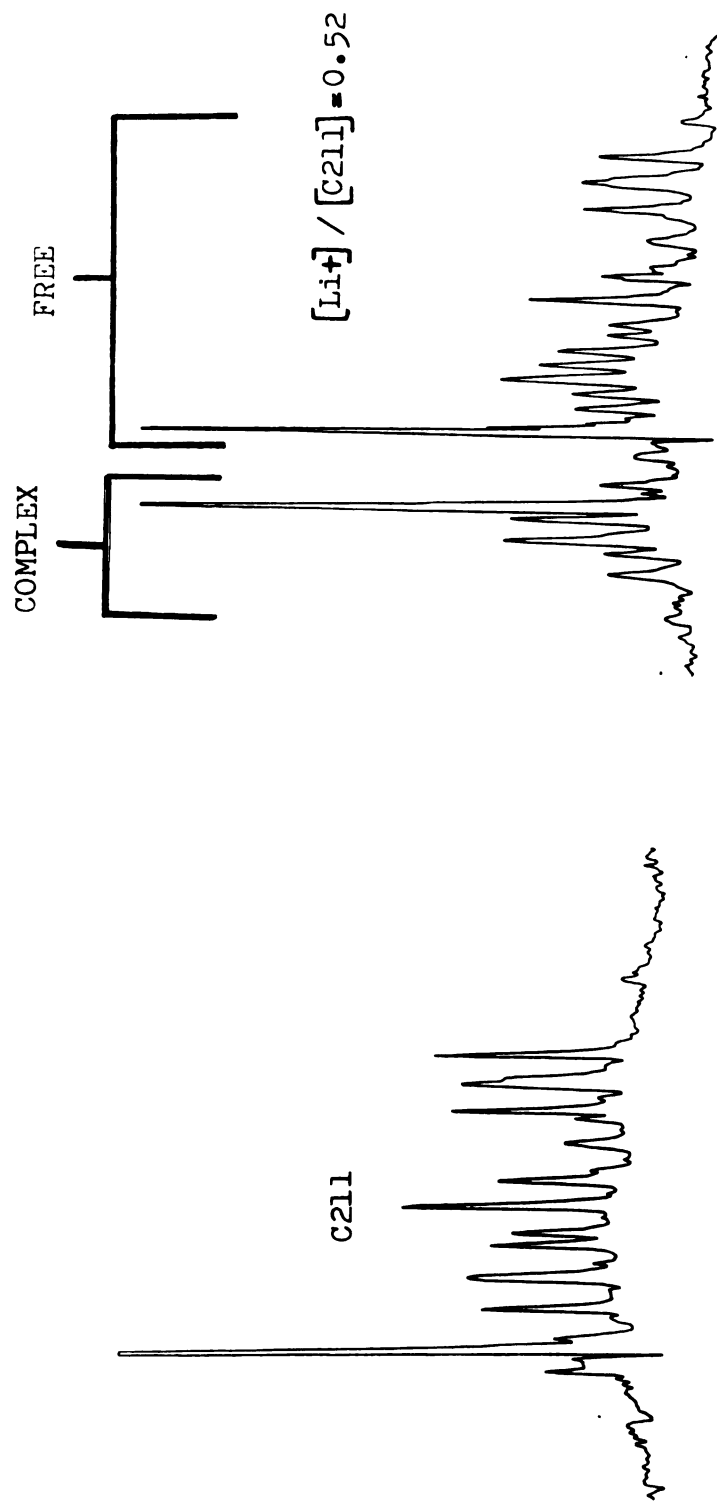
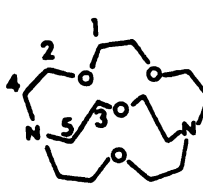


Figure130. Proton spectra of solutions of lithium perchlorate and C211 in DMF.

Table 40. Carbon-13 Chemical Shift^a Data for Solutions of C211 and LiClO₄ in DMF.

	Free C211	Complexed C211
Concentration of C211	0.3057 M	0.4010 M
Concentration of LiClO ₄	0.00	0.2102 M
[Li ⁺]/[C211]	0.00	0.524
 δ_1^F	40.62	40.61
δ_2^F	39.68	39.68
δ_3^F	39.68	39.68
δ_4^F	27.28	27.27
δ_5^F	25.49	25.48
δ_1^C	-----	38.68
δ_2^C	-----	36.91
δ_3^C	-----	35.61
δ_4^C	-----	21.51
δ_5^C	-----	20.32

^aChemical shifts reported relative to acetone-d₆ in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm. Superscripts "F" and "C" refer to free and complex, respectively.

temperature.

The proton spectrum of uncomplexed C211 has a DA18C6-like multiplet, which supports the notion that C211 is a rigid molecule with one "crown-like" face. The proton spectrum of the Li^+ complex is similar to that observed for $\text{Na}^+ \cdot \text{C221}$ suggesting that the lithium cation is encapsulated in the cavity of the cryptand.

It has been previously shown that in THF at room temperature, exchange is slow between free sodium tetraphenylborate and sodium complexed by 18C6. Kinetic studies have shown that decomplexation of the cation is the rate determining step. However, the carbon-13 spectrum of 18C6 in a solution of $[\text{NaBPh}_4]/[\text{18C6}] = 0.735$ in THF shows that the exchange between free and complexed 18C6 is fast. The lifetime of an exchanging system at coalescence, τ , is given by the following expression:

$$\tau = (\pi\sqrt{2} \Delta\nu)^{-1} \quad [18]$$

where $\Delta\nu$ is the separation, in Hz, between free and complexed species. Slow exchange is more likely to occur the further apart the exchanging species are. For C211 in the $\text{Li}^+/\text{C211}/\text{DMF}$ system, $\Delta\nu$ is between 2-5 ppm (or 138-345 Hz). However, $\Delta\nu$ is 0.9 ppm (or 56 Hz) for free and complexed 18C6 in the $18\text{C6}/\text{Na}^+/\text{THF}$ system. These results suggest that the apparent discrepancy of the $18\text{C6}/\text{NaBPh}_4/\text{THF}$ system results because the separation of

Table 41. Carbon-13 Chemical Shift Data^{a,b} for Solutions of 18C6 and NaBPh₄ in THF.

	Free 18C6	Complexed 18C6
Concentration of 18C6	0.1077 M	0.1097 M
Concentration of NaBPh ₄	0.00 M	0.0806 M
[Na ⁺]/[18C6]	0.00	0.735
δ_{18C6}	40.57	39.76
$\delta_{BPh_4}^O$	-----	90.71
$\delta_{BPh_4}^{m,p(?)}$	-----	94.57
$\delta_{BPh_4}^{m,p(?)}$	-----	106.06

^aChemical shifts are reported relative to acetone-d₆ in ppm.
^bUncertainty in the chemical shifts is ± 0.03 ppm.

the resonances of the free and complexed crown is not great enough to result in slow exchange.

CHAPTER VII

SUGGESTIONS FOR
FURTHER STUDIES

There has been a great deal of interest, both past and present, in mixed solvent work. The elucidation of solvent structure is a fundamental problem. It is a problem of interest to theoreticians, biochemists, industrial chemists, etc. Most reactions occur in solution. Therefore, an understanding of reaction rates and mechanisms cannot be complete without a knowledge of solvent structure. The same also applies for solvent-ligand interactions.

Carbon-13 NMR spectroscopy has been shown to be an excellent technique for probing both solvent-solvent interactions and solvent-ligand complexes. The chemical shift range is greater for the carbon-13 nucleus than for proton. Furthermore, carbon-13 spectra are uncomplicated by carbon-carbon coupling as are proton spectra. Consequently, carbon-13 NMR spectroscopy can be used to study many other mixed solvents and crown-solvent complexations besides the ones studied in this investigation.

Proton NMR spectroscopy, however, was useful in studying the conformational changes of substituted crowns. Infrared spectroscopy made it possible to study conformational changes in 18-crown-6 and 15-crown-5. Both techniques can be used to study conformational changes of other ligands.

Further work needs to be done to characterize the

MeOH-CCl₄ and MeOH-C₆H₆ systems. Infrared spectroscopy would probably yield more information about the species occurring in solution. Such a study, however, would require spectral deconvolutions.

APPENDICIES

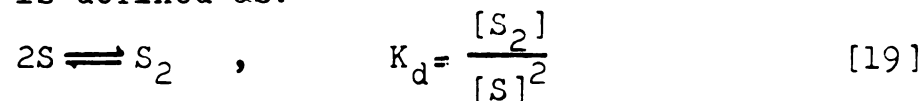
APPENDIX I

SUBROUTINE EQN WHICH INCLUDES SOLVING A GENERALIZED POLYNOMIAL

In order to use the program KINFIT to fit data for systems in which there are multiple equilibria, it is often necessary to solve a high order polynomial (usually either a third or fourth order polynomial). The subroutine which solves such high order polynomials was developed and discussed by R.D. Boss (216). Specific examples of the subroutines used are given. In order for these subroutines to operate properly it is necessary to define the coefficients of the polynomial such that the polynomial is positive when the polynomial is evaluated at zero.

A. MIXED SOLVENT DATA ANALYSIS.

1. Dimerization Model. The dimerization of a solvent, S, is defined as:



The total concentration of S, C_S , is given by:

$$C_S = [S] + 2[S_2] \quad [20]$$

Substituting for $[S_2]$ and rearranging equation [20] yields

$$2K_d[S]^2 + [S] - C_S = 0 \quad [21]$$

Solving the quadratic for $[S]$ gives:

$$[S] = \frac{-1 + \sqrt{1 + 8K_d C_S}}{4K_d} \quad [22]$$

For a system in fast exchange, the observed chemical shift is the weighted average of the chemical shifts of the individual species:

$$\delta_{OBS} = (1/C_S)(\delta_S[S] + 2\delta_{S_2}[S_2]) \quad [23]$$

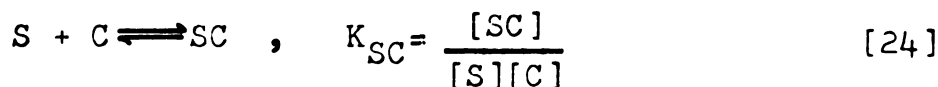
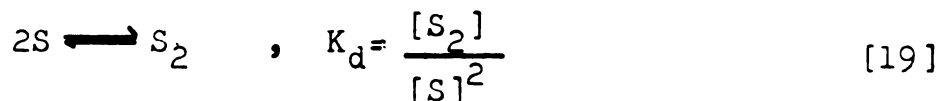
The subroutine used is shown. In the subroutine,

$$XX(1) = C_S \quad \quad \quad XX(2) = \delta_{OBS}$$

$$U(2) = K_d \quad \quad \quad U(1) = \delta_{S_2}$$

$$CONST(1) = \delta_S = \text{chemical shift at infinite dilution}$$

2. Model Which Includes Formation of S_2 and SC. The equilibria occurring in solution are defined as:



The total concentration of S, C_S , is given by:

$$C_S = [S] + [SC] + 2[S_2] \quad [25]$$

$$C_S = [S] + K_{SC}[S][C] + 2K_d[S]^2 \quad [26]$$

The total concentration of the background solvent, C_C , is given by:

$$C_C = [C] + [SC] \quad [27]$$

$$C_C = [C] + K_{SC}[S][C] \quad [28]$$

Solving for $[C]$ yields:

$$[C] = \frac{1}{1 + K_{SC}[S]} \quad [29]$$

Substituting equation [29] into equation [26] and rearranging gives:

$$\begin{aligned} -2K_dK_{SC}[S]^3 - (K_{SC} + 2K_d)[S]^2 - (1 - 2K_{SC}C_S + K_{SC})[S] \\ + C_S = 0 \end{aligned} \quad [30]$$

The observed chemical shift, δ_{OBS} , is given by:

$$\delta_{OBS} = (1/C_S)(\delta_S[S] + \delta_{SC}[SC] + 2\delta_{S_2}[S_2]) \quad [31]$$

The subroutine used is shown. In the subroutine:

$$XX(1) = C_S \quad XX(2) = \delta_{OBS}$$

$$FREEM = [C] \quad FREEL = [S]$$

$$U(1) = K_{SC} \quad U(2) = K_{dS_2}$$

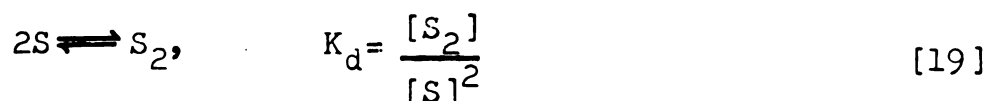
$$U(3) = \delta_{CH_3}^S = \delta_{CH_3}^{S_2} \quad U(4) = \delta_{CN}^{S_2}$$

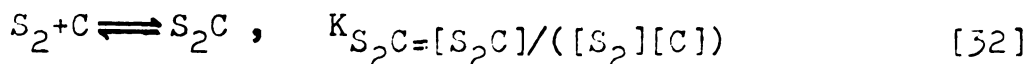
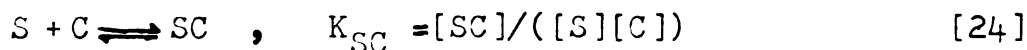
$$CONSTS(1,1) = \delta_{CH_3}^{SC}, \text{ chemical shift at infinite dilution}$$

$$CONSTS(2,1) = \delta_{CN}^S = \delta_{CN}^{S_2}, \text{ the chemical shift at infinite dilution}$$

3. Model Which Includes Formation of S_2 , SC and S_2C .

Equilibria:



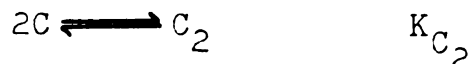
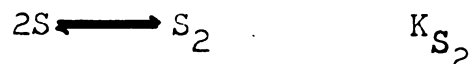


The polynomial has the form:

$$\begin{aligned} & -K_{S_2C}K_d^2[S]^4 - (2K_dK_{SC} + K_dK_{S_2C})[S]^3 + \\ & (3C_SK_dK_{S_2C} - 2K_dK_{S_2C} - K_{SC} - 2K_d)[S]^2 + \\ & (2C_SK_{SC} - K_{SC} - 1)[S] + C_S = 0 \end{aligned} \quad [33]$$

4. Model Which Includes Formation of S_2 , SC , C_2 .

Equilibria:

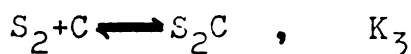
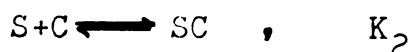


The polynomial has the form:

$$\begin{aligned} & (8K_{S_2}^2K_{C_2}^2 - 2K_{S_2}K_{C_2}K_{SC}^2)[S]^4 + (8K_{C_2}^2K_{S_2} - K_{SC}^2K_{C_2} \\ & - 2K_{S_2}K_{SC}K_{C_2})[S]^3 + (-K_{SC}^2K_{C_2} + 2K_{SC}^2K_{C_2}C_S \\ & - 8C_SK_{S_2}K_{C_2}^2 + 2K_{C_2}^2 - K_{SC}K_{C_2})[S]^2 + \\ & (C_SK_{SC}K_{C_2} - 4C_SK_{C_2}^2)[S] + 2C_S^2K_{C_2}^2 = 0 \end{aligned} \quad [34]$$

5. Model Which Includes Formation of S_2 , C_2 , SC and S_2C .

Equilibria:



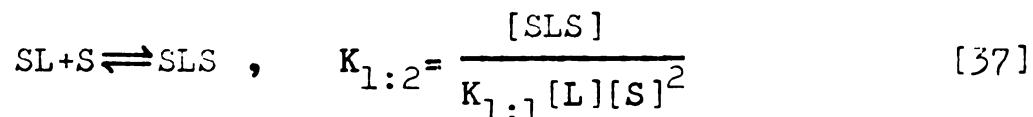
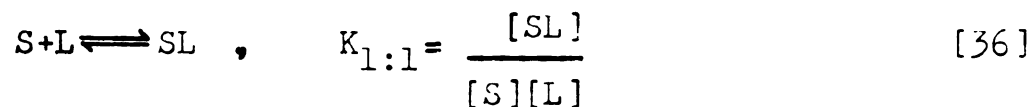
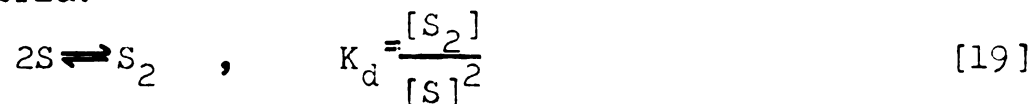


The polynomial has the form:

$$\begin{aligned} & -12K_1^4K_3^4[S]^8 - 20K_1^3K_2K_3^3[S]^7 + (-13K_1^2K_2^2K_3^2 - 8K_1^3K_3^3 \\ & - 32K_1^3K_3^2K_4)[S]^6 + (-2K_1K_2^2K_3 - 8K_1^2K_2K_3^2 - 48K_1^2K_2K_3K_4 \\ & - 16K_1^2K_3^2K_4)[S]^5 + (-2K_1K_2^2K_3 - 32K_1^2K_3^2K_4 + 48C_SK_1^2K_3^2K_4 \\ & + 64K_1^2K_4^2 - 16K_1K_2^2K_4 - 32K_1^2K_3K_4)[S]^4 + (-32K_1K_2K_3K_4 + \\ & 56C_SK_1K_2K_3K_4 + 64K_1K_4^2 - 8K_2^2K_4 - 16K_1K_3K_4 - 16K_1K_2K_4)[S]^3 \\ & + (-8K_2^2K_4 + 16C_SK_2^2K_4 - 64C_SK_1K_4 + 16K_1K_3K_4C_S + 16K_4^2 \\ & - 8K_2K_4)[S]^2 + (8C_SK_2K_4 - 32C_SK_4^2)[S] + 16C_S^2K_4^2 = 0 \end{aligned} \quad [35]$$

B. SOLVENT-LIGAND COMPLEXATION DATA ANALYSIS.

The subroutine shown is for the most complicated model. This model takes into account the following equilibria:



The total concentration of S, C_S , is given by:

$$C_S = [S] + 2[S_2] + [SL] + 2[SLS] \quad [38]$$

$$C_S = [S] + 2K_d[S]^2 + K_{1:1}[S][L] + 2K_{1:1}K_{1:2}[S]^2[L] \quad [39]$$

The total concentration of L, C_L , is given by:

$$C_L = [L] + [SL] + [SLS] \quad [40]$$

$$C_L = [L] + K_{1:1}[S][L] + K_{1:2}K_{1:1}[S]^2[L] \quad [41]$$

Solving for [L] gives:

$$[L] = \frac{1}{1 + K_{1:1}[S] + K_{1:2}K_{1:1}[S]^2} \quad [42]$$

Substituting [42] into [39] and rearranging gives:

$$\begin{aligned} & -2K_dK_{1:1}K_{1:2}[S]^4 - (K_{1:1}K_{1:2} + 2K_{1:1}K_d)[S]^3 + \\ & (K_{1:1}K_{1:2}(C_S - 2C_L) - 2K_d - K_{1:1})[S]^2 + \\ & (K_{1:1}(C_S - C_L) - 1)[S] + C_S = 0 \end{aligned} \quad [43]$$

The observed chemical shift, δ_{OBS} , is given by:

$$\begin{aligned} \delta_{OBS} = (1/C_S)(& \delta_S[S] + 2\delta_{S_2}[S_2] + \delta_{1:1}[SL] + \\ & 2\delta_{1:2}[SLS]) \end{aligned} \quad [44]$$

In the subroutine shown:

FREEL = [S]		FREEM = [L]
XX(1) = C_L	XX(2) = δ_{OBS}	XX(3) = C_S
U(1) = $K_{1:1}$		U(2) = $K_{1:2}$
U(3) = $\delta_{1:1}$		U(4) = $\delta_{1:2}$
CONST(1) = K_d		CONST(2) = δ_S
CONST(3) = δ_{S_2}		

```

SUBROUTINE EQN
COMMON KOUNT,I,TAPE,JTAP,IWT,LAP,XINCR,NOPT,NOVAR,NOUNK,X,U,ITMAX,
1WTX,TEST,I,AV,RESID,IAR,EPS,ITYP,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,E
2IGVAL,XST,T,DT,L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,
3YYY,CONSTS
COMMON/FREDT/IMETH
COMMON/POINT/KOPT,JOPT,XXX
DIMENSION X(4,300),U(20),WTX(4,300),XX(4),FOP(300),FO(300),FU(300)
1,P(20,21),VECT(20,21),ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),
2DY(10),CONST(50,16),NCST(50),ISMN(50),RXTYP(50),DX1I(50),IRX(50)
3,MOPT(50),LOPT(50),YYY(50),CONST(16),XXX(15)
GO TO (2,3,4,5,1,7,8,9,10,11,12),ITYP
1 CONTINUE
ITAPE=60
JTAP=61
RETURN
7 CONTINUE
NOUNK=2
NOVAR=2
RETURN
8 CONTINUE
RETURN
2 CONTINUE
P1=(1.0+(8.0*XX(1)*U(2)))*0.5
P2=4.0*XX(1)*U(2)
CALC=((1.0-P1+P2)/P2)*(U(1)-CONST(1))+CONST(1)
IF(IMETH.NE.-1) GO TO 35
RETURN
35 CONTINUE
RESID=CALC-XX(2)
RETURN
3 CONTINUE
RETURN
4 CONTINUE
RETURN
5 CONTINUE
IF(IMETH.NE.-1) GO TO 20
RETURN
20 CONTINUE

```

EQN4
EQN4
EQN4
EQN4
EQN4
EQN4
EQN4

RETURN
9 CONTINUE
RETURN
10 CONTINUE
RETURN
11 CONTINUE
RETURN
12 CONTINUE
RETURN
END

SUBROUTINE FOR S₂ AND SC:

```

SUBROUTINE CON
COMMON COUNT, ITAPE, JTAPE, INT, LAP, XINCR, NOPT, NOVAR, NOUNK, X, U, ITHAX, EQN4
INTX, TEST, I, V, RESID, IAR, EPS, ITYP, XX, RXTYP, DX11, FOP, FO, FU, P, ZL, TO, EQN4
EIGVAL, XST, I, DT, L, M, JJJ, Y, DY, VEC1, NCST, CONST, NDAT, JDAT, MOPT, LOPT, EQN4
3 YYY, CONSTS
COMMON/FREDT/INETH
COMMON/POINT/KOPT, JOPT, XXX
DIMENSION X(4,300), U(20), VTX(4,300), XX(4), FOP(300), FO(300), FU(300) EQN4
1, P(20,21), VECT(20,21), ZL(300), TO(20), EIGVAL(20), XST(300), Y(10), EQN4
20Y(10), CONSTS(50,16), NCST(50), ISMIN(50), RXTYP(50), DX11(50), IRX(50) EQN4
3, MOPT(50), LOPT(50), YYY(50), CONST(16), XXX(15) EQN4
GO TO (2,3,4,5,1,7,8,9,10,11,12) ITYP EQN4
1 CONTINUE EQN4
ITAPE=60 EQN4
JTAPE=61 EQN4
RETURN EQN4
7 CONTINUE EQN4
NOUNK=4 EQN4
NOVAR=2 EQN4
RETURN EQN4
8 CONTINUE EQN4
RETURN EQN4
2 CONTINUE EQN4
U(1)=ABS(U(1))
U(2)=ABS(U(2))
U(3)=ABS(U(3))
U(4)=ABS(U(4))
A=2.0*U(1)*U(2)
A1=-A
B=-(2.0*U(2)+U(1))
C=2.0*U(1)*XX(1)-1.0*U(1)
IF(XX(1).EQ.0.0) GOTO 2008
FREEL1=0.00
VALUE1=XX(1)
FREEL2=XX(1)/2.0
2005 CONTINUE
VALUE2=((A1+FREEL2*B)+FREEL2*C)+FREEL2*XX(1)
IF(VALUE2.GT.0.0) GOTO 2000
IF(VALUE2.EQ.0.0) GOTO 2001
2004 CONTINUE
FREEL3=(FREEL2-FREEL1)/(VALUE1-VALUE2)+VALUE1+FREEL1
VALUE3=((A1+FREEL3*B)+FREEL3*C)+FREEL3*XX(1)
IF(VALUE3.EQ.0.0) GOTO 2002
IF(VALUE3.GT.0.0) GOTO 2003
IF(ABS(VALUE3).LT.0.000001) GOTO 2002
VALUE2=VALUE3
FREEL2=FREEL3
GOTO 2004
2003 CONTINUE
IF(FREEL1.NE.0.0) GOTO 2010
FREEL1=1.0E-10
2010 CONTINUE
IF(ABS(VALUE3).LT.0.000001) GOTO 2002
VALUE1=VALUE3
FREEL1=FREEL3
GOTO 2004
2000 CONTINUE
IF(FREEL1.EQ.FREEL2) GOTO 2006
VALUE1=VALUE2
FREEL1=FREEL2
FREEL2=XX(1)
GOTO 2004
2001 CONTINUE
FREEL=FREEL2
GOTO 2007
2002 CONTINUE
FREEL=FREEL3
GOTO 2007
2006 CONTINUE
WRITE(JTAPE,996)
996 FORMAT(5X,50H..... WARNING ...../,
15X,5X,50H..... NO NEGATIVE "VALUE" FOUND .....))
2008 CONTINUE
FREEL=C
2007 CONTINUE
VALUE=((A1+FREEL*B)+FREEL*C)+FREEL*XX(1)
FREEL=((1.0-XX(1))/(1.0*U(1)+FREEL)

```

CONFIDENTIAL

[illegible]

4444
2222
0000
3333

```

2004 CONTINUE
FREEEL3=(FREEEL2-FREEEL1)/(VALUE1-VALUE2)*VALUE1+FREEEL1
VALUE3=((A1*FREEEL3+B)*FREEEL3+C)*FREEEL3+D)*FREEEL3+XX(3)
IF(VALUE3.EQ.0.0)GOTO2002
IF(VALUE3.GT.0.0) GOTO 2003
IF(ABS(VALUE3).LT.0.000001) GOTO 2002
VALUE2=VALUE3
FREEEL2=FREEEL3
GOTO 2004

2003 CONTINUE
IF(FREEEL1.NE.0.0) GOTO 2010
FREEEL1=1.0E-10

2010 CONTINUE
IF(ABS(VALUE3).LT.0.000001) GOTO 2002
VALUE1=VALUE3
FREEEL1=FREEEL3
GOTO 2004

2000 CONTINUE
IF(FREEEL1.EQ.FREEEL2) GOTO 2006
VALUE1=VALUE2
FREEEL1=FREEEL2
FREEEL2=XX(3)
GOTO 2005

2001 CONTINUE
FREEEL=FREEEL2
GOTO 2007

2002 CONTINUE
FREEEL=FREEEL3
GOTO 2007

2006 CONTINUE
FREEEL=XX(3)
GOTO 2007

2008 CONTINUE

```

```

FREEEL=0.0
CONTINUE
VALUE=(( (A1*FREEEL+B)*FREEEL+C)*FREEEL+D)*FREEEL+XX(3)
FREEEM=XX(1)/(1.0+U(1)*FREEEL+U(1)*U(2)*(FREEEL**2.0))
P1=CONST(2)*FREEEL
P2=2.0*CONST(3)*CONST(1)*(FREEEL**2.0)
P3=U(3)*U(1)*FREEEL*FREEEM
P4=2.0*U(4)*U(1)*U(2)*FREEEM*(FREEEL**2.0)
CALC=(P1+P2+P3+P4)/XX(3)
CONTINUE
IF(IMETH.NE.-1) GO TO 35
RETURN
35 CONTINUE
RESID=CALC-XX(2)
RETURN
3 CONTINUE
4 CONTINUE
5 CONTINUE
IF(IMETH.NE.-1) GO TO 20
RETURN
20 CONTINUE
9 CONTINUE
10 CONTINUE
11 CONTINUE
12 CONTINUE
END

```

APPENDIX II

DESCRIPTION OF COMPUTER PROGRAM KINFIT
AND SUBROUTINE EQN FOR THE RESOLUTION
OF OVERLAPPING INFRARED BANDS

The lineshape of an infrared band can be described as a Lorentzian-Gaussian product:

$$I = I_0 \{ \exp[-(\nu - \nu_0)^2 / 2\sigma^2] \} \{ 1 + (\nu - \nu_0)^2 / \sigma^2 \}^{-1} \quad [5]$$

where I is the arbitrary intensity at frequency ν ; ν_0 is the position of the line center with maximum intensity, I_0 ; and σ is the variance ($\sigma = 1.46 \Delta\nu_{\frac{1}{2}}$ where $\Delta\nu_{\frac{1}{2}}$ is the halfwidth). Equation [5] describes one peak. To resolve two or more overlapping peaks, a linear sum of two or more equations similar to [5] is required. It was found that in instances where there are three or more overlapping bands, the unknowns were too highly correlated to properly converge. To avoid this problem, the peak positions were fixed for a particular run. The peak positions were then changed and the data was refit until further variation of the positions (within a $\pm 0.01 \text{ cm}^{-1}$) did not improve the fit. In these deconvolutions, the baseline was corrected for.

The subroutine is shown. The comment statements are

self-explanatory. In the subroutine, PGAUS# and PLORN# refer to the gaussian and lorentzian portions of peak#. Absorbance and percent transmittance are referred to as A and TR. The expression for the calculated intensity, CALC, is given as:

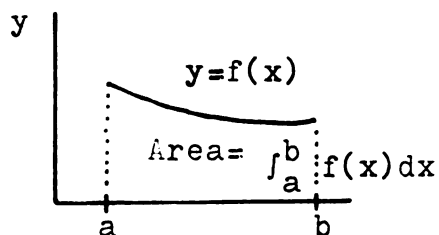
$$\text{CALC} = ((100.0 - \text{TR}) / 0.25) + ((\text{CONSTS}(1,1) * \text{XX}(1) + \text{CONSTS}(1,2)) \quad [45]$$

In the expression for CALC, 0.25 is a scaling factor which converts the intensity from percent transmittance to millimeters.

After final convergence, the areas under the vibrational bands were integrated using Simpson's rule. In the method known as Simpson's rule, a second-degree polynomial or parabolic segment is constructed through each set of three evenly spaced points. It can be shown by calculus that the area under a given parabolic segment, P_k , is given by:

$$P_k = \frac{\Delta x}{3} [f(x_{k-1}) + 4f(x_k) + f(x_{k+1})] \quad [46]$$

where x is the interval between $x=a$ and $x=b$ to be integrated as shown:



The k^{th} subinterval is denoted by x_k . Using the above expression, the formula for the Simpson's rule approximation of the area can be deduced by considering that the total area is the summation of all of the areas under the series of parabolic segments. The formula is then:

$$P = \left(\frac{2}{3}\right) \Delta x \left[\frac{f(a)}{2} + 2f(x_1) + f(x_2) + 2f(x_3) + \dots \right. \\ \left. + 2f(x_{n-1}) + \frac{f(b)}{2} \right] \quad [47]$$

or

$$P = \left(\frac{2}{3}\right) \Delta x \left\{ \frac{f(a)}{2} + \frac{f(b)}{2} + 2[f(x_1) + f(x_3) + \dots \right. \\ \left. + f(x_{n-1})] + [f(x_2) + f(x_4) + \dots + f(x_{n-2})] \right\} \quad [48]$$


```

SUBROUTINE EQN
COMMON KOUNT,ITAPE,JTAPE,IVT,LAP,XINCR,NOPT,NOVAR,NOUNK,X,U,ITMAX,
1VTX,TEST,1,AV,RESID,IAR,EPS,ITYP,XX,XYTYP,DX11,FOP,F0,FU,FU,ZL,TO,E
2IGVAL,XST,T,DT,L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,
3YYY,CONSTS
COMMON/PJOINT/KDPT,JOPT,XXX
DIMENSION X(4,300),U(20),VTX(4,300),XX(4),FOP(300),F0(300),FU(300)
1,P(20,21),VECT(20,21),ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),
2DY(10),CONSTS(50,16),NCST(50),ISMIN(50),XYTYP(50),DX11(50),IRX(50)
3,MOPT(50),LOPT(50),YYY(50),CONST(16),XXX(15)
GO TO (2,3,4,5,1,7,8,9,10,11,12) ITPY
1 CONTINUE
ITAPE=60
JTAPE=51
NOUNK=6
NOVAR=2
RETURN
7 CONTINUE
RETURN
8 CONTINUE
RETURN
2 CONTINUE
=====
C
C      THIS SET OF EQUATIONS WILL FIT THREE LORENTZ-GAUSSIAN PRODUCT
C      FUNCTIONS TO THE DATA PROVIDED
C
C=====
C=====
C
C      THE VARIABLES
C
C      XX(1)=THE FREQUENCY (THE UNITS ARE OF THE USERS CHOICE)
C      XX(2)=THE INTENSITY (THE UNITS ARE OF THE USERS CHOICE)
C
C      THE UNKNOWNS
C
C      U(1)=THE LINEWIDTH OF THE FIRST PEAK DIVIDED BY 1.46
C           (THE UNITS ARE THE SAME AS FOR XX(1) )
C      U(2)=THE INTENSITY OF THE FIRST PEAK
C           (THE UNITS ARE THE SAME AS FOR XX(2) )
C      U(3)=THE LINEWIDTH OF THE SECOND PEAK DIVIDED BY 1.46
C           (THE UNITS ARE THE SAME AS FOR XX(1) )
C      U(4)=THE INTENSITY OF THE SECOND PEAK
C           (THE UNITS ARE THE SAME AS FOR XX(2) )
C      U(5)=THE LINEWIDTH OF THE THIRD PEAK DIVIDED BY 1.46
C           (THE UNITS ARE THE SAME AS FOR XX(1) )
C      U(6)=THE INTENSITY OF THE THIRD PEAK
C           (THE UNITS ARE THE SAME AS FOR XX(2) )
C
C      THE CONSTANTS
C
C      CONSTS(1,1)=THE SLOPE OF THE BASELINE INTENSITY
C      CONSTS(1,2)=THE INTERCEPT OF THE BASELINE INTENSITY
C      CONSTS(1,3)=THE POSITION OF THE FIRST PEAK
C           (THE UNITS ARE THE SAME AS FOR XX(1) )
C      CONSTS(1,4)=THE POSITION OF THE SECOND PEAK
C           (THE UNITS ARE THE SAME AS FOR XX(1) )
C      CONSTS(1,5)=THE POSITION OF THE THIRD PEAK
C           (THE UNITS ARE THE SAME AS FOR XX(1) )
C      CONSTS(1,6)=A "COUNTER"
C=====

```

```

      PGAUS1=EXP(-((ABS(XX(1)-CONSTS(1,3))*2.0)/(2.0*(U(1)+2.0)))
      PLORN1=(1.0/(1.0+(ABS((XX(1)-CONSTS(1,3))/(U(1)))+2.0)))
      PEAK1=U(2)*PGAUS1*PLORN1
      PGAUS2=EXP(-((ABS(XX(1)-CONSTS(1,4))*2.0)/(2.0*(U(3)+2.0)))
      PLORN2=(1.0/(1.0+(ABS((XX(1)-CONSTS(1,4))/(U(3)))+2.0)))
      PEAK2=U(4)*PGAUS2*PLORN2
      PGAUS3=EXP(-((ABS(XX(1)-CONSTS(1,5))*2.0)/(2.0*(U(5)+2.0)))
      PLORN3=(1.0/(1.0+(ABS((XX(1)-CONSTS(1,5))/(U(5)))+2.0)))
      PEAK3=U(6)*PGAUS3*PLORN3
      A=PEAK1+PEAK2+PEAK3
      TR=100.0*(10.0+(-A))
      CALC=((100.0-TR)/0.25)+((CONSTS(1,1)*XX(1))+CONSTS(1,2))
      IF(IMETH.NE.-1) GO TO 35
      RETURN
35 CONTINUE
      RESID=CALC-XX(2)
      IF(LAP.NE.3)GOTO1000
C=====
C      THIS PORTION OF THE SUBROUTINE USES SIMPSON'S RULE TO
C      INTEGRATE THE AREAS UNDER THE VIBRATIONAL BANDS.
C=====
C      IF(CONSTS(1,6).NE.0)GOTO1001
C=====
C      FREQMN=THE MINIMUM FREQUENCY (THE LOWER LIMIT OF INTEGRATION)
C      FREQMX=THE MAXIMUM FREQUENCY (THE UPPER LIMIT OF INTEGRATION)
C      *NOPANS*MUST BE AN EVEN NUMBER
C=====
C      NOPANS=200.0
C      FREQMN=2220.0
C      FREQMX=2314.0
C      DELTAV=(FREQMX-FREQMN)/NOPANS
C      M1=NOPANS-1.0
C      M2=NOPANS-2.0
C=====
C      DOES THE INTEGRATION UNDER THE FIRST PEAK
C=====
301 CONTINUE
      S1=0.0
      D050011=1,M1,2
      V=FREQMN+I1*(DELTAV)
      PGAUS1=EXP(-((ABS(V-CONSTS(1,3))*2.0)/(2.0*(U(1)+2.0)))
      PLORN1=(1.0/(1.0+(ABS((V-CONSTS(1,3))/(U(1)))+2.0)))
      PEAK1=U(2)*PGAUS1*PLORN1
      S1=S1+2.0*(PEAK1)
300 CONTINUE
      S2=0.0
      D050511=2,M2,2
      V=FREQMN+I1*(DELTAV)
      PGAUS1=EXP(-((ABS(V-CONSTS(1,3))*2.0)/(2.0*(U(1)+2.0)))
      PLORN1=(1.0/(1.0+(ABS((V-CONSTS(1,3))/(U(1)))+2.0)))
      PEAK1=U(2)*PGAUS1*PLORN1
      S2=S2+PEAK1
305 CONTINUE
      SUM1=0.0
      V=FREQMN
      PGAUS1=EXP(-((ABS(V-CONSTS(1,3))*2.0)/(2.0*(U(1)+2.0)))
      PLORN1=(1.0/(1.0+(ABS((V-CONSTS(1,3))/(U(1)))+2.0)))
      PEAK1=U(2)*PGAUS1*PLORN1
      SUM1=SUM1+(PEAK1/2.0)
      V=FREQMX
      PGAUS1=EXP(-((ABS(V-CONSTS(1,3))*2.0)/(2.0*(U(1)+2.0)))
      PLORN1=(1.0/(1.0+(ABS((V-CONSTS(1,3))/(U(1)))+2.0)))
      PEAK1=U(2)*PGAUS1*PLORN1
      SUM1=SUM1+(PEAK1/2.0)
      AREA1=(2.0/3.0)*(DELTAV)*(SUM1)
      WRITE(JTAPE,510)AREA1
310 FORMAT(/,5X,30THE AREA UNDER THE FIRST PEAK=,E10.4)

```

[illegible]

EQN4
EQN4
EQN4
EQN4
EQN4
EQN4
EQN4
EQN4
EQN4
EQN4
EQN4
EQN4
E2N4
EQN4
EQN4
EQN4
EQN4
EQN4

APPENDIX III

CHEMICAL SHIFT AND VISCOSITY
DATA FOR THE SYSTEMS STUDIED

Table 1. Carbon-13 Chemical Shift Data for Solutions of Acetonitrile in Carbon Tetrachloride.

X_{MeCN}	$\text{MeCN}^{\text{a, b}}$ δ_{CN}	MeCN δ_{CH_3}	CCl_4 δ
0.0326	115.52	2.60	97.11
0.0331	115.38	2.57	97.11
0.0332	115.44	2.56	97.14
0.0426	115.62	2.57	97.12
0.0483	115.64	2.57	97.14
0.0511	115.75	2.60	97.14
0.0517	115.69	2.57	97.12
0.0545	115.75	2.56	97.13
0.0551	115.75	2.59	97.11
0.0555	115.75	2.56	97.10
0.0587	115.72	2.55	97.11
0.0619	115.79	2.55	97.12
0.0666	115.86	2.56	97.10
0.0749	115.95	2.57	97.11
0.0875	115.98	2.54	97.13
0.0892	116.02	2.54	97.12
0.1031	116.11	2.53	97.13
0.1067	116.17	2.54	97.11
0.1151	116.17	2.51	97.14
0.1302	116.28	2.51	97.11
0.1352	116.36	2.54	97.10
0.1363	116.36	2.54	97.10

Table 1. Continued.

x_{MeCN}	$\delta_{\text{CN}}^{\text{MeCN}^{\text{a,b}}}$	$\delta_{\text{CH}_3}^{\text{MeCN}}$	δ^{CCl_4}
0.1571	116.44	2.50	97.09
0.1864	116.55	2.49	97.08
0.1890	116.57	2.47	97.07
0.2121	116.65	2.44	97.07
0.2414	116.70	2.43	97.06
0.2557	116.81	2.42	97.08
0.2587	116.78	2.41	97.08
0.2986	116.94	2.41	97.06
0.3339	116.95	2.34	97.07
0.3376	117.03	2.39	97.04
0.3652	117.02	2.31	97.04
0.3724	117.11	2.37	97.02
0.4362	-----	2.30	96.99
0.4409	117.20	2.27	97.03
0.4767	117.30	2.25	96.99
0.5550	117.45	2.20	96.95
0.5759	117.47	2.16	96.94
0.5922	117.49	2.15	96.95
0.59673	117.53	2.18	96.92
0.63313	-----	2.09	96.97
0.65373	117.63	2.11	96.90
0.65403	117.60	2.08	96.91

Table 1. Continued.

X_{MeCN}	$\delta_{\text{CN}}^{\text{MeCN}^{\text{a}, \text{b}}}$	$\delta_{\text{CH}_3}^{\text{MeCN}}$	δ_{CCl_4}
0.65426	117.64	2.11	96.88
0.68714	-----	2.08	-----
0.73275	117.77	2.03	96.83
0.76872	117.84	2.02	96.82
0.78385	117.87	1.99	96.80
0.81783	117.92	1.94	96.75
0.82335	117.94	1.97	96.77
0.83823	117.97	1.94	96.75
0.85889	118.00	1.91	-----
0.89594	118.05	1.85	96.71
0.94214	118.15	1.79	96.65
0.95137	118.15	1.77	96.64
0.99048	118.24	1.73	-----
1.00000	118.24	1.69	-----

^aChemical shifts are reported in ppm relative to TMS in acetone- d_6 .

^bUncertainty in the chemical shifts is ± 0.06 ppm.

Table 2. Carbon-13 Chemical Shift Data for Solutions of Acetonitrile in Benzene.

X_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}^{a,b}}$	$\delta_{\text{CN}}^{\text{MeCN}}$	$\delta_{\text{C}_6\text{H}_6}$
0.00	-----	-----	98.91
0.0257	-29.45	86.35	98.97
0.0351	-29.47	86.34	98.34
0.0406	-29.44	86.42	98.95
0.0568	-29.40	86.45	98.96
0.0665	-29.37	86.54	98.98
0.0728	-29.31	86.54	99.00
0.0729	-29.33	86.55	98.99
0.0970	-29.30	86.62	98.98
0.0987	-29.26	86.65	99.01
0.0996	-29.26	86.65	99.01
0.1073	-29.23	86.68	99.03
0.1186	-29.22	86.72	99.02
0.1278	-29.22	86.75	99.01
0.1495	-29.15	86.78	99.05
0.1692	-29.10	86.87	99.07
0.1820	-29.09	86.88	99.05
0.1941	-29.08	86.91	99.05
0.2091	-29.06	86.95	99.05
0.2235	-29.02	87.00	99.07
0.2277	-29.02	87.00	99.06
0.2323	-28.98	87.06	99.10

Table 2 . Continued.

x_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}^{\text{a}, \text{b}}}$	$\delta_{\text{CN}}^{\text{MeCN}}$	$\delta_{\text{C}_6\text{H}_6}^{\text{C}_6\text{H}_6}$
0.2363	-29.00	87.04	99.07
0.2524	-28.94	87.10	99.11
0.2573	-28.94	87.10	99.11
0.2690	-28.95	87.11	99.09
0.2934	-28.88	87.18	99.12
0.3063	-28.88	87.19	99.11
0.3194	-28.86	87.22	99.11
0.3307	-28.81	87.27	99.14
0.3504	-28.79	87.31	99.15
0.3785	-28.75	87.35	99.15
0.3910	-28.76	87.34	99.15
0.4030	-28.73	87.36	99.16
0.4303	-28.68	87.45	99.18
0.4440	-28.67	87.46	99.19
0.44939	-28.66	87.47	99.21
0.45346	-28.66	87.49	99.18
0.47471	-28.62	87.53	99.23
0.47814	-28.62	87.54	99.20
0.52459	-28.56	87.61	99.24
0.54888	-28.52	87.67	99.26
0.57578	-28.50	87.70	99.24
0.58443	-28.49	87.71	99.27
0.61203	-28.43	87.81	99.30

Table 2. Continued.

x_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}^{a,b}}$	$\delta_{\text{CN}}^{\text{MeCN}}$	$\delta_{\text{C}_6\text{H}_6}^{\text{C}_6\text{H}_6}$
0.63316	-28.40	87.84	99.30
0.64445	-28.41	87.86	99.31
0.66474	-28.40	87.88	99.30
0.67032	-28.39	87.87	99.30
0.68345	-28.36	87.90	99.32
0.68729	-28.35	87.93	99.34
0.68974	-28.37	87.93	99.32
0.69369	-28.35	87.91	99.33
0.72437	-28.32	87.99	99.35
0.73099	-28.31	88.01	99.36
0.74832	-28.29	88.04	99.37
0.75945	-28.28	88.05	99.38
0.76959	-28.28	88.06	99.36
0.80154	-28.26	88.19	99.36
0.83200	-28.20	88.19	99.42
0.87622	-28.15	88.27	99.45
0.90978	-28.12	88.33	99.48
0.93474	-28.09	88.38	99.49
0.94024	-28.08	88.41	99.49
0.96644	-28.06	88.44	99.51
0.97552	-28.05	88.46	99.50

Table 2 . Continued.

x_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}^{a,b}}$	$\delta_{\text{CN}}^{\text{MeCN}}$	$\delta_{\text{C}_6\text{H}_6}^{\text{C}_6\text{H}_6}$
0.99002	-28.03	88.50	99.52
1.00000	-28.04	88.49	-----

^aChemical shifts are reported relative to the methyl carbon of acetone- d_6 in ppm.

^bUncertainty in the chemical shifts is ± 0.03 ppm.

Table 3 . Proton Chemical Shift Data for Solutions of Acetonitrile in Benzene.

X_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}^{a,b}}$	$\delta_{\text{C}_6\text{H}_6}^{\text{C}_6\text{H}_6}$
0.00	-----	6.736
0.2900	0.923	6.931
0.5439	1.365	7.094
0.8188	1.786	7.297
1.0000	2.066	-----

^aChemical shifts reported in ppm relative to TMS in acetone- d_6 .

^bUncertainty in chemical shifts is ± 0.01 ppm.

Table 4. Carbon-13 Chemical Shift Data for Solutions of Acetonitrile in Chloroform.

X_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}^{\text{a}, \text{b}}}$	$\delta_{\text{CN}}^{\text{MeCN}}$	δ_{CHCl_3}
0.00	----	-----	78.16
0.0172	2.80	117.27	78.19
0.0356	2.81	117.36	78.24
0.0714	2.81	117.45	78.32
0.1090	2.77	117.50	78.39
0.1448	2.75	117.56	78.45
0.1604	2.74	117.58	78.47
0.1673	2.72	117.56	78.48
0.2106	2.68	117.61	78.54
0.2744	2.65	117.70	78.65
0.3311	2.58	117.73	78.73
0.3936	2.51	117.79	78.80
0.4488	2.45	117.84	78.86
0.50630	2.39	117.86	78.91
0.50774	2.34	117.86	78.92
0.52631	2.39	117.86	78.93
0.55327	2.33	117.90	78.95
0.57984	2.29	117.92	78.97
0.59808	2.26	117.93	78.98
0.63020	2.23	117.95	79.00
0.74533	2.06	118.04	79.05
0.75002	2.06	118.02	79.04

Table 4 . Continue.

X_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}^{a,b}}$	$\delta_{\text{CN}}^{\text{MeCN}}$	δ_{CHCl_3}
0.79633	2.00	118.07	79.07
0.82867	1.93	118.08	79.06
0.85938	1.90	118.11	79.09
0.89892	1.83	118.13	79.08
0.93196	1.80	118.17	79.09
0.96594	1.74	118.18	79.09
1.00000	1.68	118.23	-----

^aChemical shifts are reported relative to TMS in acetone- d_6 in ppm.

^bUncertainty in the chemical shifts is ± 0.03 ppm.

Table 5. Proton Chemical Shift Data for Solutions of Acetonitrile in Chloroform.

X_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}^{a,b}}$	δ_{CHCl_3}	X_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}}$	δ_{CHCl_3}
0.00	-----	7.378	0.50854	2.089	7.562
0.0176	2.124	7.385	0.55959	2.086	7.578
0.0355	2.123	7.392	0.60451	2.084	7.592
0.0548	2.121	7.398	0.65326	2.078	7.603
0.0729	2.120	7.406	0.70167	2.078	7.618
0.1091	2.116	7.419	0.74756	2.073	7.628
0.1465	2.112	7.431	0.78803	2.071	7.637
0.1801	2.112	7.447	0.82688	2.070	7.646
0.2133	2.106	7.484	0.85825	2.067	7.653
0.2776	2.106	7.484	0.89618	2.067	7.661
0.3362	2.100	7.504	0.93237	2.064	7.669
0.3941	2.097	7.526	0.97172	2.062	7.676
0.4526	2.091	7.544	1.00000	2.062	-----

^aChemical shifts reported relative to TMS in acetone- d_6 in ppm.

^bUncertainty in chemical shifts is ± 0.01 ppm.

Table 6. Carbon-13 Chemical Shift Data for Solutions of Acetonitrile in Acetone.

X_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}^{a,b}}$	$\delta_{\text{CN}}^{\text{MeCN}}$	$\delta_{\text{CH}_3}^{\text{AC}}$	$\delta_{\text{CO}}^{\text{AC}}$
0.00	-----	-----	-47.47	127.66
0.0161	-76.94	39.42	-47.47	-----
0.0242	-76.93	39.50	-47.46	127.71
0.0343	-76.92	39.51	-47.45	-----
0.0473	-76.91	39.50	-47.44	-----
0.0674	-----	39.57	-----	-----
0.0811	-76.91	39.51	-47.45	127.76
0.0996	-----	39.59	-----	-----
0.1101	-76.88	39.56	-47.43	127.86
0.1302	-----	39.61	-47.47	-----
0.1382	-76.87	39.55	-47.44	127.88
0.1630	-76.92	39.63	-47.45	-----
0.1965	-76.83	39.63	-47.41	-----
0.1973	-76.83	39.64	-47.41	128.03
0.2272	-76.82	39.63	-47.40	-----
0.2573	-76.80	39.66	-47.39	-----
0.2683	-76.78	39.67	-47.39	-----
0.2771	-76.76	39.71	-47.36	-----
0.3029	-76.78	39.68	-47.40	128.17
0.3449	-76.74	39.71	-47.37	128.24
0.3688	-76.72	39.73	-47.35	-----
0.4054	-76.70	39.75	-47.35	128.35

Table 6 • Continued.

X_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}^{\text{a}, \text{b}}}$	$\delta_{\text{CN}}^{\text{MeCN}}$	$\delta_{\text{CH}_3}^{\text{AC}}$	$\delta_{\text{CO}}^{\text{AC}}$
0.4319	-76.77	39.81	-47.40	-----
0.4596	-76.68	39.80	-47.34	-----
0.4836	-76.73	39.87	-47.37	-----
0.50976	-76.62	39.86	-47.31	128.55
0.53189	-76.62	39.84	-47.30	-----
0.55860	-76.61	39.87	-47.29	-----
0.58387	-76.58	39.88	-47.30	128.64
0.58750	-76.58	39.90	-47.30	-----
0.63409	-76.55	39.91	-47.28	-----
0.65373	-76.53	39.95	-47.26	128.78
0.67830	-76.52	39.97	-47.27	-----
0.72345	-76.49	40.02	-47.25	-----
0.73865	-76.47	40.02	-47.23	128.91
0.76584	-76.46	40.05	-47.24	-----
0.81088	-76.42	40.09	-47.21	-----
0.82793	-76.41	40.08	-47.20	129.06
0.84500	-76.41	40.11	-47.21	-----
0.88314	-76.35	40.16	-47.16	-----
0.92291	-76.34	40.18	-47.18	-----

Table 6 . Continued.

x_{MeCN}	$\delta_{\text{CH}_3}^{\text{MeCN}^{\text{a}, \text{b}}}$	$\delta_{\text{CN}}^{\text{MeCN}}$	$\delta_{\text{CH}_3}^{\text{AC}}$	$\delta_{\text{CO}}^{\text{AC}}$
0.92549	-76.34	40.18	-47.19	129.22
0.96714	-76.30	40.21	-47.14	-----
0.98699	-76.30	40.21	-47.16	129.32
1.00000	-76.28	40.24	-----	-----

^aChemical shifts reported relative to chloroform-d in ppm.

^bUncertainty in the chemical shifts is ± 0.03 ppm.

Table 7. Carbon-13 Chemical Shift Data for Solutions of Nitromethane in Benzene.

x_{MeNO_2}	$\delta_{\text{CH}_3}^{\text{NM}^{\text{a}, \text{b}}}$	$\delta_{\text{C}_6\text{H}_6}$	x_{MeNO_2}	$\delta_{\text{CH}_3}^{\text{NM}}$	$\delta_{\text{C}_6\text{H}_6}$
0.0082	31.52	98.99	0.53631	32.56	-----
0.0201	31.53	98.97	0.55812	32.60	-----
0.0403	31.62	98.95	0.61392	32.67	99.22
0.0771	31.68	98.98	0.64924	32.71	99.23
0.1181	31.81	98.98	0.66266	32.71	99.21
0.1528	31.84	99.04	0.67323	32.73	99.23
0.1752	31.90	98.99	0.72405	32.80	99.23
0.2235	32.00	99.03	0.78811	32.87	99.27
0.2543	32.09	99.05	0.80354	32.90	99.28
0.2891	32.16	99.09	0.84191	32.92	99.26
0.3231	32.21	99.09	0.85785	32.93	99.27
0.3539	32.28	99.11	0.90255	32.98	99.28
0.4199	32.37	99.12	0.93650	33.00	99.29
0.4718	32.46	99.14	0.97539	33.05	99.30
0.51489	32.53	99.16	1.00000	33.07	-----
0.52327	32.54	99.17			

^aChemical shifts are reported relative to acetone- d_6 in ppm.

^bUncertainty in the chemical shifts is ± 0.03 ppm.

Table 8. Carbon-13 Chemical Shift Data for Solutions of Chloroform in Benzene.

X_{CHCl_3}	$\delta_{\text{CHCl}_3}^{a,b}$	$\delta_{\text{C}_6\text{H}_6}$	X_{CHCl_3}	δ_{CHCl_3}	$\delta_{\text{C}_6\text{H}_6}$
0.00	-----	98.91	0.49114	48.23	99.28
0.0516	48.03	98.97	0.53111	48.24	99.29
0.0811	48.03	98.99	0.53886	48.24	99.29
0.1076	48.06	99.01	0.62377	48.27	99.33
0.1252	48.07	99.02	0.67420	48.30	99.38
0.1326	48.05	99.03	0.71697	48.33	99.40
0.2331	48.11	99.09	0.75850	48.35	99.44
0.2604	48.12	99.11	0.81402	48.36	99.47
0.2658	48.12	99.11	0.86102	48.39	99.50
0.2951	48.14	99.12	0.90727	48.40	99.52
0.3743	48.17	99.19	0.94734	48.42	99.56
0.3935	48.17	99.19	1.00000	48.44	-----
0.4401	48.21	99.24			

^aChemical shifts are reported relative to the methyl carbon of acetone- d_6 in ppm.

^bUncertainty in chemical shifts is ± 0.03 ppm.

Table 9 . Carbon-13 Chemical Shift Data for Solutions of N,N-Dimethylformamide in Benzene.

X_{DMF}	$\delta_{\alpha\text{CH}_3}^{\text{DMF}^{\text{a}, \text{b}}}$	$\delta_{\beta\text{CH}_3}^{\text{DMF}}$	$\delta_{\text{CO}}^{\text{DMF}}$	$\delta_{\text{C}_6\text{H}_6}^{\text{C}}$
0.00	----	----	-----	98.94
0.0230	1.03	5.45	132.02	98.96
0.0231	1.04	5.47	132.08	98.97
0.0576	1.05	5.55	132.13	98.98
0.0837	1.08	5.62	132.20	99.01
0.1127	1.10	5.70	132.27	99.03
0.1414	1.11	5.76	132.33	99.04
0.1691	1.14	5.80	132.37	99.05
0.2250	1.16	5.89	132.46	99.09
0.2777	1.20	5.97	132.54	99.12
0.3335	1.22	6.05	132.62	99.16
0.3858	1.25	6.12	132.70	99.20
0.4319	1.26	6.16	132.74	99.20
0.45655	1.26	6.18	132.76	99.22
0.48060	1.30	6.22	132.81	99.24
0.52754	1.30	6.26	132.86	99.26
0.54711	1.32	6.27	132.88	99.27
0.58277	1.32	6.31	132.92	99.30
0.62438	1.33	6.33	132.96	99.32
0.69215	1.34	6.36	133.02	99.32
0.72584	1.35	6.40	133.07	99.36
0.77279	1.37	6.42	133.11	99.37

Table 9. Continued.

X_{DMF}	$\delta_{\alpha\text{CH}_3}^{\text{DMF}^{a,b}}$	$\delta_{\beta\text{CH}_3}^{\text{DMF}}$	$\delta_{\text{CO}}^{\text{DMF}}$	$\delta_{\text{C}_6\text{H}_6}^{\text{C}}$
0.82142	1.39	6.44	132.16	99.40
0.86566	1.39	6.47	132.20	99.41
0.91691	1.40	6.49	133.25	99.43
0.96249	1.41	6.51	133.28	99.45
1.00000	1.40	6.52	133.29	-----

^aChemical shifts are reported in ppm relative to the methyl carbon of acetone- d_6 .

^bUncertainty in the chemical shifts is ± 0.03 ppm.

Table 10. Carbon-13 Chemical Shift Data for Solutions of Acetone in Benzene.

x_{AC}	$\delta_{CH_3}^{AC^{a,b}}$	δ_{CO}^{AC}	$\delta_{C_6H_6}^C$
0.00	-----	-----	50.71
0.0109	-47.77	125.81	50.70
0.0230	-47.79	125.81	50.71
0.0216	-47.79	125.79	50.70
0.0417	-47.75	125.95	50.72
0.0565	-47.73	125.98	50.71
0.0866	-47.73	126.14	50.74
0.0964	-47.71	126.15	50.75
0.1137	-47.71	126.24	50.75
0.1404	-47.68	126.30	50.77
0.1819	-47.65	126.40	50.79
0.2430	-47.63	126.56	50.80
0.2998	-47.60	126.67	50.82
0.3471	-47.57	126.79	50.85
0.4101	-47.57	126.90	50.86
0.4592	-47.55	126.97	50.90
0.51876	-47.55	127.07	50.90
0.58080	-47.53	127.17	50.93
0.59281	-47.52	127.18	50.94
0.61352	-47.49	127.23	50.95
0.64406	-47.51	127.25	50.95
0.65582	-47.50	127.29	50.97

Table 10. Continue.

X_{AC}	$\delta_{CH_3}^{AC^{a,b}}$	δ_{CO}^{AC}	$\delta_{C_6H_6}$
0.69009	-47.50	127.32	50.98
0.73859	-47.48	127.39	50.99
0.78060	-47.47	127.45	51.00
0.82804	-47.47	127.51	51.01
0.87355	-47.46	127.58	51.04
0.91831	-47.47	127.62	51.05
0.96274	-47.45	127.67	51.08
1.00000	-47.47	127.70	-----
1.00000	-47.45	127.70	-----

^aChemical shifts are reported relative to chloroform-d in ppm.

^bUncertainty in the chemical shifts is ± 0.03 ppm.

Table 11.. Carbon-13 Chemical Shift Data for Solutions
of Methanol in Carbon Tetrachloride.

x_{MeOH}	$\delta_{\text{CH}_3}^{\text{MeOH}}$	δ^{CCl_4}	x_{MeOH}	$\delta_{\text{CH}_3}^{\text{MeOH}}$	δ^{CCl_4}
0.00	-----	97.15	0.58302	50.05	96.99
0.0215	50.98	97.13	0.66988	49.96	96.96
0.0453	50.74	97.14	0.71187	49.92	96.94
0.0549	50.66	97.12	0.74091	49.88	96.92
0.1065	50.53	97.11	0.77688	49.85	96.92
0.1520	50.44	97.11	0.80938	49.81	96.90
0.2003	50.38	97.10	0.85274	49.72	96.84
0.2552	50.33	97.10	0.87465	49.69	96.83
0.2911	50.30	97.10	0.90463	49.64	96.81
0.3823	50.22	97.06	0.93147	49.58	96.77
0.4543	50.17	97.07	0.95793	49.52	96.75
0.4709	50.16	97.06	0.98203	49.46	96.71
0.51504	50.12	97.03	1.00000	49.42	-----
0.56569	50.07	97.00			

^aChemical shifts reported in ppm relative to TMS in acetone-d₆.

^bUncertainty in the chemical shifts is ± 0.03 ppm.

Table 12. Proton Chemical Shift Data for Solutions of Methanol in Carbon Tetrachloride.

X_{MeOH}	$\delta_{\text{CH}_3}^{\text{MeOH}^{\text{a}, \text{b}}}$	$\delta_{\text{OH}}^{\text{MeOH}}$	X_{MeOH}	$\delta_{\text{CH}_3}^{\text{MeOH}}$	$\delta_{\text{OH}}^{\text{MeOH}}$
0.0215	3.487 ^c	1.996 ^c	0.66988	3.404	4.824
0.0549	3.467	3.410	0.71187	3.395	4.836
0.1065	3.452	3.965	0.74091	3.392	4.852
0.1520	3.449	4.226	0.77688	3.386	4.862
0.2003	3.442	4.381	0.80938	3.383	4.873
0.2552	-----	4.501	0.85274	3.376	4.884
0.2911	3.438	4.552	0.87465	3.372	4.886
0.3823	3.430	4.653	0.90463	3.366	4.894
0.4543	3.423	4.711	0.93147	3.363	4.898
0.4709	3.421	4.720	0.95793	3.356	4.907
0.51504	3.420	4.749	0.98203	3.350	4.909
0.56569	3.413	4.775	1.00000	3.343	4.900
0.58302	3.407	4.788			

^aChemical shifts are reported relative to TMS in acetone- d_6 in ppm.

^bUncertainty in the chemical shifts is ± 0.01 ppm.

^cMethyl group appears as a doublet and the hydroxyl group as a quartet.

Table 13. Carbon-13 Chemical Shift Data for Solutions of Methanol in Benzene.

a, b					
X_{MeOH}	δ_{MeOH}	$\delta_{\text{C}_6\text{H}_6}$	X_{MeOH}	δ_{MeOH}	$\delta_{\text{C}_6\text{H}_6}$
0.00	-----	128.65	0.54064	49.71	128.68
0.0214	50.31	128.66	0.59135	49.68	128.68
0.0454	50.20	128.66	0.64571	49.66	128.69
0.0500	50.20	128.66	0.68265	49.65	128.69
0.0751	50.13	128.67	0.72000	49.60	128.69
0.0927	50.09	128.68	0.75941	49.58	128.69
0.1184	50.04	128.67	0.79711	49.57	128.70
0.1441	50.00	128.67	0.83822	49.53	128.71
0.1902	49.94	128.68	0.86812	49.52	128.70
0.2362	49.89	128.68	0.89798	49.50	128.72
0.2422	49.90	128.68	0.92884	49.48	128.71
0.2980	49.86	128.68	0.95906	49.44	128.72
0.3513	49.82	128.69	0.97870	49.43	128.72
0.4252	49.77	128.68	1.00000	49.42	-----
0.48631	49.74	128.69			

^aChemical shifts reported relative to TMS in acetone- d_6 in ppm.

^bUncertainty in chemical shifts is ± 0.03 ppm.

Table 14. Proton Chemical Shift Data for Solutions of Methanol in Benzene.

X_{MeOH}	MeOH a, b δ_{CH_3}	MeOH δ_{OH}	$\delta_{\text{C}_6\text{H}_6}$
0.00	-----	-----	6.736
0.0233	2.646 ^c	0.294 ^c	6.745
0.0454	2.708	1.247	6.752
0.0500	2.714	1.367	6.752
0.0751	2.760	2.024	6.758
0.0927	2.788	2.376	6.766
0.1184	2.815	2.750	6.770
0.1855	2.866	3.366	6.785
0.2284	2.894	3.612	6.800
0.2422	2.902	3.683	6.803
0.2980	2.927	3.899	6.818
0.3821	2.962	4.134	6.846
0.4863	3.003	4.350	6.885
0.59135	3.041	4.504	6.929
0.68265	3.082	4.618	6.981
0.75941	3.121	4.693	7.033
0.83822	3.175	4.765	7.102
0.89798	3.222	4.811	7.164
0.95906	3.286	4.856	7.242

Table 14 . Continued.

X_{MeOH}	$\delta_{\text{CH}_3}^{\text{MeOH}^{a,b}}$	$\delta_{\text{OH}}^{\text{MeOH}}$	$\delta_{\text{C}_6\text{H}_6}^{\text{C}_6\text{H}_6}$
0.97870	3.312	4.883	7.274
1.00000	3.343	4.900	-----

^aChemical shifts are reported in ppm relative to TMS in acetone- d_6 .

^bUncertainty in the chemical shifts is ± 0.01 ppm.

^cMethyl group appears as a doublet and the hydroxyl group as a quartet.

Table 15. Carbon-13 and Proton Chemical Shift Data for
Solutions of 18-Crown-6 in Carbon Tetrachloride.

X_{18C6}	$^1H_{\delta_{18C6}}$ a, b	$^{13}C_{\delta_{18C6}}$ a, c	$^{13}C_{\delta_{CCl_4}}$ a, c
1.8×10^{-3}	3.67	71.66	97.12
1.9×10^{-3}	3.68	71.69	97.12
2.1×10^{-3}	3.68	71.67	97.12
2.2×10^{-3}	3.67	71.69	97.12
3.0×10^{-3}	3.68	71.67	97.12
4.7×10^{-3}	3.68	71.67	97.12
5.6×10^{-3}	3.68	71.69	97.12
9.1×10^{-3}	3.68	71.69	97.12
1.35×10^{-2}	3.68	71.67	97.12
1.78×10^{-2}	3.68	71.67	97.12
2.85×10^{-2}	3.68	71.69	97.14
2.92×10^{-2}	3.68	71.67	97.14
3.01×10^{-2}	3.68	71.67	97.12

^aProton and carbon-13 chemical shifts are reported
relative to TMS in acetone- d_6 in ppm.

^bUncertainty in the proton chemical shifts is ± 0.01 ppm.

^cUncertainty in the carbon-13 chemical shifts is ± 0.03 ppm.

Table 16. Proton Chemical Shift Data for Solutions of 18-Crown-6 in Acetonitrile.

X_{18C6}	$\delta_{CH_3}^{MeCN^{a,b}}$	δ^{18C6}	X_{18C6}	$\delta_{CH_3}^{MeCN}$	δ^{18C6}
0.5×10^{-3}	2.06	3.60	4.0×10^{-3}	2.05	3.59
0.7×10^{-3}	2.06	3.60	4.4×10^{-3}	2.05	3.59
1.3×10^{-3}	2.06	3.60	4.8×10^{-3}	2.05	3.59
1.5×10^{-3}	2.06	3.60	5.1×10^{-3}	2.05	3.59
1.8×10^{-3}	2.06	3.60	5.2×10^{-3}	2.05	3.59
1.9×10^{-3}	2.06	3.60	5.2×10^{-3}	2.05	3.59
2.5×10^{-3}	2.06	3.60	5.6×10^{-3}	2.05	3.59
2.5×10^{-3}	2.06	3.60	6.3×10^{-3}	2.04	3.58
2.8×10^{-3}	2.06	3.60	6.5×10^{-3}	2.04	3.58
3.3×10^{-3}	2.05	3.59	7.0×10^{-3}	2.04	3.58
3.7×10^{-3}	2.05	3.59	7.2×10^{-3}	2.04	3.58
4.0×10^{-3}	2.05	3.59			

^aChemical shifts are reported relative to TMS in acetone- d_6 in ppm.

^bUncertainty in the chemical shifts is ± 0.01 ppm.

Table 17. Carbon-13 Chemical Shifts of Solutions of 18-Crown-6 in Acetonitrile.

X_{18C6}	$\delta_{CH_3}^{MeCN}$	δ_{CN}^{MeCN}	δ_{18C6}
0.00	1.70	118.25	-----
0.2×10^{-3}	1.69	118.26	71.13
0.5×10^{-3}	1.69	118.26	71.15
0.6×10^{-3}	1.69	118.25	71.15
0.7×10^{-3}	1.69	118.26	71.15
0.9×10^{-3}	1.69	118.26	71.15
1.5×10^{-3}	1.69	118.26	71.15
1.6×10^{-3}	1.69	118.26	71.15
1.9×10^{-3}	1.69	118.26	71.15
2.1×10^{-3}	1.71	118.26	71.16
2.3×10^{-3}	1.69	118.24	71.15
2.8×10^{-3}	1.71	118.27	71.15
3.6×10^{-3}	1.69	118.26	71.14
3.7×10^{-3}	1.71	118.27	71.15
3.8×10^{-3}	1.69	118.09	71.15
4.3×10^{-3}	1.69	118.26	71.13
5.1×10^{-3}	1.69	118.27	71.15
5.2×10^{-3}	1.69	118.26	71.15
5.6×10^{-3}	1.69	118.27	71.13
6.3×10^{-3}	1.69	118.26	71.13
6.5×10^{-3}	1.69	118.27	71.13

^aChemical shifts reported relative to TMS in acetone- d_6 in ppm.

^bUncertainty in the δ is ± 0.03 ppm.

Table 18. Carbon-13 Chemical Shift Data for Solutions of 18-Crown-6 in Benzene.

x_{18C6}	$\delta^{18C6^{a,b}}$	$\delta^{C_6H_6}$	x_{18C6}	δ^{18C6}	$\delta^{C_6H_6}$
0.00	-----	99.02	2.61×10^{-2}	41.56	98.98
1.2×10^{-3}	41.56	98.95	3.35×10^{-2}	41.56	99.00
3.0×10^{-3}	41.55	99.02	3.92×10^{-2}	41.56	99.05
4.0×10^{-3}	41.61	99.09	4.64×10^{-2}	41.56	98.99
4.7×10^{-3}	41.56	99.02	5.36×10^{-2}	41.56	99.01
5.8×10^{-3}	41.56	98.96	8.03×10^{-2}	41.56	99.02
8.3×10^{-3}	41.56	98.96	9.74×10^{-2}	41.55	99.06
1.03×10^{-2}	41.56	98.99	1.160×10^{-1}	41.56	99.02
1.18×10^{-2}	41.56	99.04	1.434×10^{-1}	41.55	99.10
2.46×10^{-2}	41.56	99.05	1.811×10^{-1}	41.56	99.17

^aChemical shifts reported relative to the methyl carbon of acetone- d_6 in ppm.

^bUncertainty in the chemical shifts is ± 0.03 ppm.

Table 19. Carbon-13 Chemical Shift Data for Solutions of 18-Crown-6 in Chloroform.

X_{18C6}	$\delta_{18C6}^{a,b}$	δ_{CHCl_3}
9.43×10^{-3}	41.99	48.50
4.14×10^{-2}	41.99	48.71
7.30×10^{-2}	41.97	48.88
1.028×10^{-1}	41.99	49.07
1.753×10^{-1}	42.00	49.48

^aChemical shifts are reported relative to acetone- d_6 in ppm.

^bUncertainty in the chemical shifts is ± 0.03 ppm.

Table 20. Carbon-13 Chemical Shift Data for Solutions of 18-Crown-6 in Acetone.

X_{18C6}	δ_{18C6}^a	δ_{CH_3}	δ_{CO}
3.46×10^{-3}	-6.74	-47.45	-----
5.98×10^{-3}	-6.79	-47.44	127.79
1.19×10^{-2}	-6.80	-47.42	127.79
2.03×10^{-2}	-----	-47.45	-----
2.57×10^{-2}	-6.83	-47.44	127.76
4.06×10^{-2}	-6.83	-47.45	127.70
4.15×10^{-2}	-6.85	-47.45	127.69
6.25×10^{-2}	-6.85	-47.44	127.63
6.99×10^{-2}	-6.89	-47.46	127.66
9.44×10^{-2}	-6.92	-47.47	127.64
1.229×10^{-1}	-6.94	-47.47	-----
1.669×10^{-1}	-6.98	-47.46	-----

^bChemical shifts are reported relative to $CDCl_3$ in ppm.
 Uncertainty in the chemical shifts is ± 0.03 ppm.

Table 21. Carbon-13 and Proton Chemical Shift Data for Solutions of 18-Crown-6 in Methanol.

X_{18C6}	1H_6CH_3 a	1H_6OH	$^1H_6^{18C6}$	$^{13}C_6^{18C6}$ b	$^{13}C_6CH_3$
0.00	3.34	4.91	----	----	49.40
6.4×10^{-4}	3.34	4.89	3.62	----	----
1.93×10^{-3}	3.33	4.88	3.62	70.98	49.43
2.19×10^{-3}	3.33	4.89	3.61	71.01	49.43
3.4×10^{-3}	3.33	4.87	3.61	71.00	49.42
3.87×10^{-3}	3.33	4.87	3.61	71.01	49.43
4.8×10^{-3}	3.33	4.87	3.61	71.01	49.43
9.97×10^{-3}	3.30	4.83	3.58	71.04	49.46
1.25×10^{-2}	3.29	4.80	3.58	70.95	49.37
1.65×10^{-2}	3.28	4.78	3.56	70.98	49.43
2.34×10^{-2}	3.26	4.73	3.54	70.95	49.40
3.69×10^{-2}	3.22	4.63	3.50	70.95	49.43
3.86×10^{-2}	3.21	4.62	3.50	70.95	49.43
6.01×10^{-2}	3.16	4.49	3.44	70.92	49.43
7.07×10^{-2}	3.14	4.42	3.42	70.92	49.46

- ^aProton chemical shifts are reported relative to TMS in acetone-d₆ in ppm.
Uncertainty in the proton chemical shifts is ± 0.01 ppm.
- ^bCarbon-13 chemical shifts are reported relative to TMS in acetone-d₆ in ppm.
Uncertainty in the carbon-13 chemical shifts is ± 0.06 ppm.

Table 22. Viscosity Data for Solutions of 18-Crown-6 in Water at 26°C.

[18C6] (M)	c _{18C6} (g/100ml)	VISCOMETER NUMBER	AVERAGE TIME (sec.)	η (cp)	η_{sp}	η_{sp}/c	$\frac{1}{c}(\ln \frac{\eta}{\eta_0})$
0.00	0.00	^a #25	470.38	0.8705	-----	-----	-----
0.00	0.00	^b #75	117.65	0.8705	-----	-----	-----
0.1012	2.6743	#25	509.7	0.9433	0.0836	3.13×10^{-2}	3.00×10^{-2}
0.3011	7.9569	#75	151.45	1.1206	0.2873	3.61×10^{-2}	3.17×10^{-2}
0.5015	13.2526	#75	180.92	1.3386	0.5377	4.06×10^{-2}	3.25×10^{-2}
0.6016	15.8979	#75	198.30	1.4672	0.6855	4.31×10^{-2}	3.28×10^{-2}
0.7519	19.8697	#75	230.56	1.7059	0.9597	4.83×10^{-2}	3.39×10^{-2}
0.8908	23.5403	#75	264.26	1.9553	1.2461	5.29×10^{-2}	3.44×10^{-2}

At 26°C, $\rho_{H_2O} = 0.99681$ g/ml and $\eta_{H_2O} = 0.8705$ cp.

^a $B_{\#25} = 1.8566 \times 10^{-3}$ ml·cp·g⁻¹·sec⁻¹ and ^b $B_{\#75} = 7.4227 \times 10^{-3}$ ml·cp·g⁻¹·sec⁻¹.

Table 23. Viscosity Data for Solutions of 18-Crown-6 in Acetonitrile at 26°C.

[18C6] (M)	c _{18C6} (g/100ml)	VISCOMETER NUMBER	AVERAGE TIME (sec.)	η (cp)	η_{sp}	η_{sp}/c	$(\frac{1}{c})(\ln \frac{\eta}{\eta_0})$
0.00	0.00	#25 ^a	231.98	0.3404	-----	-----	-----
0.00	0.00	#75 ^b	61.23	0.3404	-----	-----	-----
0.0526	1.3900	#25	237.43	0.3484	0.02349	1.69×10^{-2}	1.67×10^{-2}
0.0764	2.0189	#25	240.25	0.3525	0.03565	1.77×10^{-2}	1.73×10^{-2}
0.1177	3.1103	#25	246.28	0.3614	0.06164	1.98×10^{-2}	1.92×10^{-2}

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At 26°C, $\rho_{AN} = 0.77559$ g/ml. Therefore,

$$^a B_{\#25} = 1.8919 \times 10^{-3} \text{ ml cp g}^{-1} \text{ sec}^{-1} \text{ and } ^b B_{\#75} = 7.1679 \times 10^{-3} \text{ ml cp g}^{-1} \text{ sec}^{-1}.$$

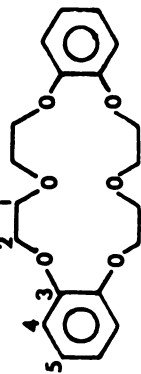
Table 24 Viscosity Data for Solutions of 18-Crown-6 in Carbon Tetrachloride at 26°C.

[18C6] (M)	c _{18C6} (g/100ml)	VISCOMETER NUMBER	AVERAGE TIME (sec.)	η (cp)	η_{sp}	η_{sp}/c	$(\frac{1}{c})(\ln \frac{\eta}{\eta_0})$
0.00	0.00	#25	298.42	0.8934	-----	-----	-----
0.00	0.00	#75	77.4	0.8934	-----	-----	-----
0.0501	1.324	#25	308.90	0.9247	0.0351	2.65×10^{-2}	2.60×10^{-2}
0.0937	2.476	#25	318.30	0.9529	0.0666	2.69×10^{-2}	2.60×10^{-2}
0.1508	3.985	#25	330.57	0.9896	0.1077	2.70×10^{-2}	2.57×10^{-2}
0.2009	5.308	#25	342.00	1.0238	0.1460	2.75×10^{-2}	2.57×10^{-2}
0.2250	5.945	#25	347.68	1.0408	0.1650	2.78×10^{-2}	2.57×10^{-2}
0.2805	7.412	#75	93.48	1.0789	0.2077	2.80×10^{-2}	2.55×10^{-2}
0.3070	8.112	#25	366.70	1.0978	0.2287	2.82×10^{-2}	2.54×10^{-2}
0.4079	10.780	#75	101.43	1.1708	0.3105	2.88×10^{-2}	2.51×10^{-2}
0.5003	13.221	#75	108.38	1.2510	0.4003	3.03×10^{-2}	2.55×10^{-2}
0.7098	18.756	#75	126.35	1.4584	0.6324	3.37×10^{-2}	2.61×10^{-2}

At 26°C, $\rho_{CCl_4} = 1.5825$. Therefore, ^a $B_{\#25} = 1.8917 \times 10^{-3}$ ml cp g⁻¹ sec⁻¹ and

^b $B_{\#75} = 7.2939 \times 10^{-3}$ ml cp g⁻¹ sec⁻¹.

Table 25. Carbon-13 Chemical Shift Data of 0.0118 M Dibenzo-18-Crown-6 in Acetonitrile as a function of Temperature.



TEMP. (°C)	δ_5^c	δ_4	δ_3	δ_2	δ_1	$\delta_5-\delta_4$	$\delta_2-\delta_1$	$\delta_3-\delta_5$
^a 62	60.05	52.20	87.69	8.51	7.26	7.85	1.25	27.64
52	59.85	51.70	87.44	8.33	6.94	8.14	1.40	27.59
42	59.70	51.27	87.22	8.20	6.67	8.42	1.53	27.52
33	59.58	50.92	87.03	8.10	6.45	8.66	1.65	27.45
25	59.48	50.64	86.85	7.98	6.27	8.84	1.71	27.37
13 ^b	91.77	82.76	119.07	40.24	38.51	9.01	1.73	27.30
9	91.71	82.66	118.97	40.17	38.43	9.06	1.73	27.26
5	91.71	82.60	118.94	40.14	38.39	9.12	1.74	27.23
3	91.70	82.55	118.91	40.12	38.39	9.14	1.73	27.21
-6	91.64	82.42	118.79	40.02	38.31	9.22	1.71	27.15
-16	91.61	82.33	118.69	39.95	38.26	9.28	1.69	27.02
-26	91.56	82.26	118.59	39.86	38.21	9.31	1.65	27.02

Table 25. Continue.

- ^aFor temperatures greater than 20°C, nitromethane-d₃ was used as the external lock and reference. Chemical shifts are reported relative to NM-d₃ in ppm.
- ^bFor temperatures less than 20°C, acetone-d₆ was used as the external lock and reference. Chemical shifts are reported relative to acetone-d₆ in ppm.
- ^cUncertainty in the chemical shifts is ±0.03 ppm.

Table 26. ^{13}C Chemical Shift Data for DB18C6 in NM-d_3 as a Function of Temperature.^a

TEMP. (°C)	δ_4	δ_5	δ_3	δ_2	δ_1	$\delta_4 - \delta_5$	$\delta_2 - \delta_1$	$\delta_3 - \delta_5$
72	-41.12	-49.01	-13.33	-92.60	-93.98	7.89	1.38	27.78
62	-41.15	-49.29	-13.42	-92.60	-94.11	8.14	1.51	27.72
52	-41.26	-49.23	-13.60	-92.70	-94.35	8.42	1.65	27.67
42	-41.37	-50.02	-13.76	-92.79	-94.55	8.66	1.76	27.61
32	-41.48	-50.36	-13.97	-92.92	-94.77	8.88	1.85	27.52
21	-41.57	-50.61	-14.11	-93.01	-94.91	9.04	1.90	27.46
12	-41.59	-50.75	-14.19	-93.05	-94.96	9.16	1.91	27.40
2	-41.60	-50.83	-14.26	-93.10	-94.99	9.23	1.90	27.34
-7	-41.62	-50.91	-14.35	-93.15	-95.02	9.29	1.87	27.27
-17	-41.62	-50.97	-14.41	-93.20	-95.02	9.35	1.82	27.21

^aChemical shifts are reported relative to the amide carbon of DMF in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm. Chemical shift assignment is:



Table 27. Proton and Carbon-13 Chemical Shift Data for Solutions of Acetonitrile and 18-Crown-6 in Carbon Tetrachloride.

a	b, c		b, d			
	$^1\text{H}_{\text{MeCN}}$ CH_3	$^1\text{H}_{\text{C}_6}$	$^{13}\text{C}_{\text{MeCN}}$ CH_3	$^{13}\text{C}_{\text{MeCN}}$ CN	$^{13}\text{C}_{\text{C}_6}$	$^{13}\text{C}_{\text{CCl}_4}$
$\frac{[\text{18C6}]}{[\text{MeCN}]}$						
0.00	-----	-----	2.60	115.59	-----	97.11
0.0248	-----	-----	2.59	115.65	71.51	97.11
0.0323	-----	-----	2.58	115.65	71.51	97.12
0.0407	-----	-----	2.57	115.75	71.51	97.12
0.0640	2.08	3.67	-----	115.77	71.53	97.12
0.0751	2.08	3.66	2.56	115.81	71.53	97.12
0.0876	2.08	3.66	2.55	115.82	71.53	97.12
0.1013	-----	-----	2.56	115.88	71.53	97.12
0.1275	2.09	3.66	2.51	116.12	71.54	97.12
0.3089	2.09	3.66	2.50	116.25	71.54	97.12

^aSolutions were prepared by adding 50 μl of MeCN to a known amount of 18C6 and diluting to 2ml with carbon tetrachloride.

^bChemical shifts are reported relative to TMS in acetone- d_6 in ppm.

^cUncertainty in the ^1H chemical shifts is ± 0.01 ppm; in the ^{13}C is ± 0.03 ppm.

Table 28. Carbon-13 Chemical Shift Data for Solutions of 18-Crown-6 and Acetonitrile in Chloroform.

$\frac{[18C6]^a}{[MeCN]}$	$\delta_{CH_3}^{MeCN^{b,c}}$	δ_{CN}^{MeCN}	δ^{18C6}	δ^{CHCl_3}
0.00	-26.90	87.63	-----	48.51
0.1797	-26.88	87.65	41.94	48.54
0.4994	-26.90	87.76	41.94	48.63
0.5570	-26.91	87.73	41.95	48.63
0.9160	-26.92	87.90	41.94	48.73
1.6586	-26.96	88.06	41.95	48.89
2.2581	-27.01	88.26	41.95	49.05
2.2696	-27.01	88.30	41.94	49.09
2.6104	-27.04	88.36	41.95	49.14
3.5522	-27.13	88.64	41.94	49.37

^aSolutions were prepared by adding 50 μ l of MeCN to a known amount of 18C6 and diluting to 2 ml with benzene.

^bChemical shifts are reported relative to the methyl carbon of acetone- d_6 in ppm.

^cUncertainty in the chemical shifts is ± 0.03 ppm.

Table 29. Carbon-13 Chemical Shift Data for Solutions of Acetonitrile and 18-Crown-6 in Benzene.

Solutions were prepared by adding 25 μ l of AN to a known amount of 18C6 and diluting to 2ml with benzene:

[18C6] [AN]	$\delta_{\text{CH}_3}^{\text{AN}^a}$	$\delta_{\text{CN}}^{\text{AN}}$	$\delta_{18\text{C}6}$	$\delta_{\text{C}_6\text{H}_6}$
0.00	-29.49	86.28	-----	-----
0.2268	-29.40	-----	41.59	99.02
0.5143	-29.35	-----	41.57	99.00
0.6406	-29.32	-----	41.59	99.04
0.7864	-29.28	-----	41.59	99.04
0.8386	-29.35	86.59	41.53	98.97
0.8729	-29.28	-----	41.56	99.00
0.9498	-29.25	86.80	41.53	99.00
0.9993	-29.26	-----	41.60	99.03
1.0545	-29.26	-----	41.59	99.04
1.0995	-29.26	-----	41.59	99.04
1.1436	-29.20	86.84	41.55	99.02
1.3679	-29.19	-----	41.59	99.04
1.6000	-29.16	-----	41.57	99.03
1.8313	-29.16	-----	41.53	99.00
1.9871	-29.09	-----	41.59	99.05
2.0177	-29.07	-----	41.59	99.05
2.0911	-29.09	-----	41.59	99.05
2.1907	-29.08	87.17	41.52	99.00
2.3622	-29.11	-----	41.58	99.03
2.8808	-28.97	-----	41.61	99.08

Table 29. Continue.

Solutions were prepared by adding 50 μ l AN to a known amount of 18C6 and diluting to 2ml with benzene:

[18C6] [AN]	^a		δ_{18C6}	$\delta_{C_6H_6}$
	$\delta_{CH_3}^{AN}$	δ_{CN}^{AN}		
0.00	-29.43	86.36	-----	-----
0.0266	-29.40	86.43	41.47	98.98
0.1092	-29.35	86.52	41.48	98.98
0.1806	-29.35	86.53	41.51	99.00
0.2105	-29.34	86.62	41.48	98.98
0.2983	-29.28	86.71	41.48	99.00
0.3644	-29.25	86.81	41.47	99.00

^aChemical shifts are reported relative to acetone- d_6 in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

Table 30. Carbon-13 Chemical Shift Data for Solutions of 18-Crown-6 and Acetonitrile in Acetone.

Solutions were prepared by adding 100 μ l AN to a known amount of 18C6 and diluting to 2ml with AC:

$\frac{[18C6]}{[AN]}$	AN a $\delta_{CH_3}^{AN}$	AN δ_{CN}^{AN}	$\delta_{CH_3}^{AC}$	δ_{CO}^{AC}	δ_{18C6}
0.00	-76.90	39.53	-47.44	-----	-----
0.1439	-76.89	39.66	-47.44	127.81	-6.80
1.0821	-76.83	40.10	-47.41	127.72	-6.92

Solutions were prepared by adding 50 μ l of AN and diluting to 2ml with AC:

$\frac{[18C6]}{[AN]}$	$\delta_{CH_3}^{AN}$	δ_{CN}^{AN}	$\delta_{CH_3}^{AC}$	δ_{CO}^{AC}	δ_{18C6}
0.00	-76.92	39.50	-47.45	-----	-----
0.0969	-76.99	39.59	-47.50	-----	-6.73
0.3027	-77.01	39.59	-47.51	-----	-6.74
0.6741	-76.98	39.71	-47.51	-----	-6.79
0.7685	-76.94	39.75	-47.46	127.74	-6.81
0.8003	-76.89	39.72	-47.45	-----	-6.80
0.9210	-76.96	39.85	-47.51	127.86	-6.82
1.0952	-76.86	39.85	-47.43	-----	-6.83
1.1561	-76.86	39.84	-47.43	127.74	-6.84
1.2466	-76.96	39.91	-47.51	127.84	-6.85
1.4985	-76.85	39.97	-47.43	-----	-6.85
1.5719	-76.78	39.97	-47.45	127.71	-6.87
1.6567	-76.95	40.02	-47.51	127.81	-6.88
1.7191	-76.85	40.02	-47.44	-----	-6.88
1.8544	-76.95	40.05	-47.53	127.80	-6.89
1.9191	-76.88	40.04	-47.44	127.70	-6.90
2.3058	-76.95	40.14	-47.51	127.78	-6.89
3.5834	-76.92	40.39	-47.52	127.71	-7.02

^aChemical shifts are reported relative to chloroform-d
in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

Table 31. Carbon-13 Chemical Shift Data for Solutions of Nitromethane and 18-Crown-6 in Benzene.

Solutions prepared by adding 25 μ l of NM to a known amount of 18C6 and diluting to 2 ml.:

$\frac{[18C6]}{[MeNO_2]}$	$\delta^{NM}_{CH_3}$ ^{a, b}	δ^{18C6}	$\delta^{C_6H_6}$
0.0	31.53	-----	98.97
0.0329	31.53	41.30	98.94
0.0778	31.69	41.38	98.96
0.1125	31.67	41.36	98.95
0.2200	31.82	41.38	98.97
0.3959	32.08	41.39	98.95
0.4144	32.04	41.39	98.95
0.5050	32.11	41.41	98.98
0.6113	32.17	41.44	98.97
0.6721	32.14	41.43	98.96
0.7206	32.28	41.42	98.97
0.7326	32.23	41.45	98.97
0.9660	32.45	41.44	98.98
0.9689	32.37	41.45	98.97
0.9919	32.41	41.47	98.97
1.0355	32.47	41.44	98.98
1.1549	32.54	41.46	98.97
1.3418	32.60	41.47	98.98
1.6304	32.69	41.48	98.98
1.7609	32.76	41.48	98.98
1.9319	32.79	41.48	98.98

Table 32. Continue.

25 μ l NM diluted to 2 ml with benzene:

$\frac{[^{18}\text{C6}]}{[\text{MeNO}_2]}$	$\delta_{\text{CH}_3}^{\text{NM}^{\text{a,b}}}$	$\delta^{18}\text{C6}$	$\delta^{\text{C}_6\text{H}_6}$
1.9397	32.86	41.48	98.98
2.0098	32.91	41.46	98.98
2.3527	33.11	41.48	99.00

25 μ l NM diluted to 5 ml with benzene:

$\frac{[^{18}\text{C6}]}{[\text{MeNO}_2]}$	$\delta_{\text{CH}_3}^{\text{NM}^{\text{a,b}}}$	$\delta^{18}\text{C6}$	$\delta^{\text{C}_6\text{H}_6}$
0.00	31.52	-----	98.99
0.8810	31.94	41.47	98.96
1.3098	32.05	41.52	98.97
1.5747	32.12	41.52	98.97
1.7895	32.21	41.53	98.97
1.9444	32.22	41.52	98.97
2.2445	32.21	41.56	99.00
2.8448	32.47	41.52	98.97

^aChemical shifts are reported relative to the methyl carbon of acetone- d_6 in ppm.

^bUncertainty in the chemical shifts is ± 0.03 ppm.

Table 33. Carbon-13 Chemical Shift Data for Solutions of 18-Crown-6 and Chloroform in Benzene.

$[^{18}\text{C}6]^a$ $[\text{CHCl}_3]$	$\delta^b_{\text{CHCl}_3}$	$\delta_{\text{C}_6\text{H}_6}$	$\delta_{^{18}\text{C}6}$
0.00	48.00	98.96	-----
0.4205	48.16	98.96	41.55
0.7246	48.31	98.98	41.55
1.1329	48.46	98.99	41.55
1.2103	48.49	98.99	41.55
1.4892	48.59	98.99	41.55
1.6147	48.62	99.00	41.55
1.6675	48.62	98.99	41.55
1.8634	48.69	99.01	41.55
2.0148	48.72	99.00	41.55
2.1259	48.74	99.00	41.55
2.2702	48.78	99.02	41.55
2.4519	48.86	99.02	41.55
2.6446	48.90	99.02	41.55
2.6731	48.91	99.02	41.55
3.6538	49.18	99.05	41.53

^aSolutions were prepared by adding 50 μl of CHCl_3 to a known amount of $^{18}\text{C}6$ and diluting to 2ml with benzene.

^bChemical shifts are reported relative to acetone- d_6 in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

Table 34. Carbon-13 Chemical Shift Data for Solutions of 18-Crown-6 and N,N-Dimethylformamide in Benzene.

$\frac{[18C6]^a}{[DMF]}$	$\delta_{\alpha CH_3}^{DMF^b}$	$\delta_{\beta CH_3}^{DMF}$	δ_{CO}^{DMF}	δ_{18C6}	$\delta_{C_6H_6}$
0.00	1.04	5.47	132.08	-----	98.97
0.2751	1.06	5.48	132.05	41.54	98.97
1.0039	1.08	5.54	132.11	41.54	98.98
1.2917	1.08	5.57	132.12	41.54	99.00
1.9418	1.11	5.63	132.15	41.54	99.01
2.4942	1.14	5.69	132.18	41.54	99.03
2.9017	1.16	5.72	132.21	41.54	99.04
3.1578	1.16	5.73	132.23	41.54	99.04
3.7483	1.17	5.77	132.25	41.53	99.04
4.4099	1.25	5.83	132.30	41.53	99.07
4.6595	1.23	5.86	132.28	41.53	99.07
5.5535	1.29	5.94	132.33	41.53	99.09
6.1476	1.30	5.97	132.36	41.53	99.10
6.3703	1.32	5.99	132.37	41.53	99.12

^aSolutions were prepared by adding 40 μ l of DMF to a known amount of 18C6 and diluting to 2ml with benzene.

^bChemical shifts are reported relative to acetone- d_6 in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

Table 35. Carbon-13 Chemical Shift Data for Solutions of 18-Crown-6 and Acetone in Benzene.

$\frac{[18C6]^a}{[AC]}$	$\delta_{CH_3}^{ACb}$	δ_{CO}^{AC}	δ_{18C6}	$\delta_{C_6H_6}$
0.00	-47.79	125.82	-----	50.70
0.9699	-47.68	125.91	-6.64	50.77
2.4947	-47.66	126.05	-6.70	50.75
3.0983	-47.61	126.14	-6.70	50.77
3.9634	-47.54	126.26	-6.68	50.81
4.5318	-47.54	126.29	-6.70	50.81
4.5782	-47.54	126.34	-6.73	50.80
5.1423	-47.51	126.41	-6.71	50.81
5.2338	-47.50	126.42	-6.70	50.83
5.6964	-47.44	126.52	-6.70	50.85
6.0410	-47.47	126.54	-6.73	50.84
6.6566	-47.42	126.61	-6.70	50.87

^aSolutions were prepared by adding 40 μ l AC to a known amount of 18C6 and diluting to 2 ml with benzene.

^bChemical shifts are reported relative to chloroform-d in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

Table 36. Carbon-13 Chemical Shift Data for Solutions of 18-Crown-6 and Methanol in Benzene.

$\frac{[18C6]}{[MeOH]}$	^a	MeOH δ_{CH_3}	^{b, c}	18C6 δ	C_6H_6 δ
0.00		50.20		-----	128.66
0.1840		50.19		71.12	128.67
0.2740		50.22		71.15	128.69
0.3604		50.22		71.15	128.69
0.9070		50.19		71.18	128.71
0.9979		50.20		71.18	128.72
1.0476		50.22		71.20	128.72
1.8761		50.19		71.21	128.76
2.0634		50.17		71.20	128.77
2.4440		50.17		71.20	128.79
3.2167		50.19		71.24	128.80
4.3015		50.17		71.23	128.82

^aSolutions were prepared by adding 40 μ l of methanol to a known amount of 18-crown-6 and diluting to 2 ml with benzene.

^bChemical shifts are reported relative to TMS in acetone- d_6 in ppm.

^cUncertainty in the chemical shifts is ± 0.03 ppm.

Table 37. Proton Chemical Shift Data for Solutions of 18-Crown-6 and Methanol in Benzene.

$\frac{[18C6]^a}{[MeOH]}$	$\delta_{OH}^{MeOH^{b,c}}$	$\delta_{CH_3}^{MeOH}$	δ_{18C6}	$\delta_{C_6H_6}$
0.00	1.25 ^d	2.71 ^d	----	6.75
0.1472	1.26	2.75	3.09	6.75
0.2912	1.32	2.78	3.09	6.76
0.6634	1.58 ^d	2.85 ^d	3.11	6.77
0.7304	1.84	2.88	3.11	6.77
1.0293	1.95 ^d	2.91 ^d	3.12	6.78
1.3556	2.13 ^d	2.93 ^d	3.12	6.79
1.4611	2.22 ^d	2.96 ^d	3.13	6.80
1.9091	2.35 ^d	2.99 ^d	3.14	6.82
1.9098	2.37 ^d	2.99 ^d	3.14	6.82
2.0041	2.38 ^d	2.99 ^d	3.15	6.82
2.1800	2.45 ^d	3.01 ^d	3.15	6.83
2.3330	2.29 ^d	2.99 ^d	3.15	6.82
2.4029	2.46 ^d	3.01 ^d	3.16	6.84
3.2167	2.56 ^d	3.04 ^d	3.18	6.87
4.3015	2.58 ^d	3.04 ^d	3.20	6.89

^aSolutions were prepared by adding 40 μ l MeOH to a known amount of 18C6 and diluting to 2 ml with benzene.

^bChemical shifts are reported relative to TMS in AC-d₆ in ppm.

^cUncertainty in the chemical shifts is ± 0.01 ppm.

^dResonances of the hydroxyl and methyl groups appear as a quartet and doublet, respectively.

Table 38. Carbon-13 Chemical Shift Data for Solutions of 15-Crown-5 and Acetonitrile in Benzene.

$\frac{[15C5]^a}{[AN]}$	$\delta_{CH_3}^{AN^{b,c}}$	δ_{CN}^{AN}	δ_{15C5}	$\delta_{C_6H_6}$
0.00	-29.43	86.42	-----	98.97
0.2702	-29.37	86.50	41.60	98.98
0.6611	-29.29	86.62	41.58	98.99
0.8919	-29.26	86.69	41.58	98.99
1.5780	-29.15	86.88	41.58	99.02
1.8232	-29.12	86.94	41.55	99.02
2.0589	-29.07	87.00	41.57	99.04
2.1565	-29.07	87.01	41.55	99.02
2.2798	-29.03	87.06	41.57	99.05
2.4986	-29.00	87.13	41.55	99.05
2.6764	-28.97	87.19	41.55	99.07
3.1637	-28.91	87.26	41.58	99.08
3.5201	-28.85	87.36	41.58	99.10
4.1019	-28.80	87.47	41.57	99.10
4.5417	-28.72	87.57	41.57	99.12
6.4496	-28.61	87.80	41.57	99.17

^aSolutions were prepared by adding 50 μ l AN to a known amount of 15C5 and diluting to 2 ml with benzene.

^bChemical shifts are reported relative to acetone-d₆ in ppm.

^cUncertainty in the chemical shifts is ± 0.03 ppm.

Table 39. Carbon-13 Chemical Shift Data for Solutions of 15-Crown-5 and Nitromethane in Benzene.

Solutions prepared by adding 30 μ l of NM to a known amount of 15C5 and diluting to 2 ml with benzene:

$\frac{[15C5]}{[NM]}$	$\delta_{NM}^{a,b}$	δ_{15C5}	$\delta_{C_6H_6}$
0.00	31.54	-----	98.96
0.2822	31.64	41.61	98.97
0.6012	31.68	41.59	98.97
0.9454	31.79	41.58	98.97
1.1151	31.85	41.59	98.99
1.3135	31.92	41.59	98.99
1.6040	32.01	41.61	99.00
1.9011	32.09	41.59	99.00
2.1375	32.11	41.56	98.99
2.2570	32.14	41.59	99.00
2.4966	32.21	41.56	98.99
2.5174	32.24	41.59	99.00
2.8528	32.27	41.56	98.99
2.9676	32.26	41.56	98.99
3.1997	32.33	41.56	99.00
3.9146	32.48	41.59	99.03
4.5603	32.59	41.56	99.03

Table 39. Continue.

20 μ l of NM diluted to 2 ml with benzene:

$\frac{[^{15}\text{C}5]}{[\text{NM}]}$	$\overset{\text{a,b}}{\delta}_{\text{NM}}$	$\delta_{^{15}\text{C}5}$	$\delta_{\text{C}_6\text{H}_6}$
0.00	31.51	-----	98.95
0.2355	31.56	41.60	98.95
0.9163	31.63	41.61	98.97
2.1094	31.91	41.60	98.98
6.0446	32.36	41.60	99.02

^aChemical shifts are reported relative to acetone- d_6 in ppm.

^bUncertainty in the chemical shifts is ± 0.03 ppm.

Table 40. Carbon-13 Chemical Shift Data for Solutions of Chloroform and 15C5 in Benzene.

$\frac{[15C5]^a}{[CHCl_3]}$	$\delta_{CHCl_3}^{b,c}$	δ_{15C5}	$\delta_{C_6H_6}$
0.00	48.00	-----	98.96
0.3281	48.12	41.63	98.96
0.3375	48.13	41.63	98.96
0.6604	48.22	41.63	98.96
0.9199	48.29	41.62	98.97
1.0717	48.35	41.62	98.97
1.5134	48.47	41.62	98.99
1.8222	48.54	41.62	98.99
1.8957	48.56	41.62	98.99
2.1323	48.65	41.61	99.00
2.2367	48.65	41.62	99.00
2.6841	48.75	41.62	99.02
2.9988	48.82	41.61	99.02
3.2662	48.91	41.62	99.03
3.7847	49.00	41.61	99.03
4.4459	49.10	41.61	99.06
5.1651	49.16	41.61	99.05
6.5336	49.26	41.60	99.07

^aSolutions were prepared by adding 50 μ l of $CHCl_3$ to a known amount of 15C5 and diluting to 2 ml with benzene.

^bChemical shifts are reported relative to acetone- d_6 in ppm.

^cUncertainty in the chemical shifts is ± 0.03 ppm.

Table 41. Carbon-13 Chemical Shift Data for Solutions of 15-Crown-5 and Acetone in Benzene.

$[15C5]^a$ [AC]	^b δ_{AC}^{CO}	$\delta_{AC}^{CH_3}$	δ_{15C5}	$\delta_{C_6H_6}$
0.00	125.76	-47.77	-----	50.73
0.9418	125.89	-47.74	-6.59	50.73
1.6225	126.00	-47.70	-6.59	50.74
2.2756	126.08	-47.66	-6.60	50.75
2.8258	126.15	-47.64	-6.60	50.78
3.7548	126.25	-47.61	-6.61	50.78
4.0833	126.29	-47.58	-6.60	50.81
4.6945	126.33	-47.55	-6.60	50.81
5.8037	126.45	-47.51	-6.61	50.83
6.4484	126.47	-47.46	-6.61	50.84
7.3277	126.52	-47.50	-6.61	50.86
10.1073	126.72	-47.36	-6.63	50.90

^aSolutions were prepared by adding 40 μ l of AC to a known amount of 15C5 and diluting to 2ml with benzene.

^bChemical shifts are reported relative to $CDCl_3$ in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

Table 42. Carbon-13 Chemical Shift Data for Solutions of 15-Crown-5 and N,N-Dimethylformamide in Benzene.

$\frac{[15C5]^a}{[DMF]}$	$\delta_{\alpha CH_3}^{DMF}$	$\delta_{\beta CH_3}^{DMF}$	δ_{CO}^{DMF}	δ_{15C5}	$\delta_{C_6H_6}$
0.00	1.03	5.45	132.02	-----	98.96
0.8702	1.06	5.54	132.17	41.60	98.97
1.6620	1.11	5.61	132.24	41.59	98.98
2.6110	1.16	5.69	132.33	41.59	99.01
3.1171	1.17	5.75	132.39	41.57	99.03
3.6863	1.17	5.77	132.42	41.57	99.03
4.4857	1.25	5.86	132.49	41.56	99.06
4.9304	1.25	5.89	132.52	41.56	99.06
5.1028	1.25	5.91	132.53	41.56	99.07
5.6293	1.25	5.92	132.55	41.54	99.06
5.9632	1.30	5.98	132.59	41.56	99.09
6.1872	1.30	5.99	132.62	41.56	99.09
6.9399	1.32	6.04	132.65	41.54	99.10
8.0768	1.35	6.13	132.72	41.54	99.13

^aSolutions were prepared by adding 40 μ l of DMF to a known amount of 15C5 and diluting to 2ml with benzene.

^bChemical shifts are reported relative to acetone- d_6 in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

Table 43. Carbon-13 Chemical Shift Data for Solutions of Methanol and 15-Crown-5 in Benzene.

^a <u>[15C5]</u> [MeOH]	^b δ_{MeOH}	$\delta_{15\text{C}5}$	$\delta_{\text{C}_6\text{H}_6}$
0.00	50.26	-----	128.67
0.4300	50.19	71.20	128.68
1.3264	50.17	71.23	128.71
2.2519	50.14	71.23	128.74
2.5287	50.10	71.21	128.74
3.5825	50.10	71.23	128.79
3.7629	50.07	71.22	128.81

^aSolutions were prepared by adding 40 μl of MeOH to a known amount of 15C5 and diluting to 2ml with benzene.

^bChemical shifts are reported relative to TMS in acetone- d_6 in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

Table 44. Proton Chemical Shift Data for Solutions of Methanol and 15-Crown-5 in Benzene.

$\frac{[15C5]}{[MeOH]}$ ^e	$\delta_{CH_3}^{MeOH}$ ^{a, b}	δ_{OH}^{MeOH}	δ^{15C5}	$\delta^{C_6H_6}$
0.00	2.69 ^c	0.97 ^c	----	6.75
0.2129	2.76	1.37	3.08	6.76
0.4973	2.82	1.67	3.09	6.76
0.7302	2.86	1.87	3.07	6.77
0.8427	2.87	1.95	3.10	6.77
0.9796	2.89	2.08	3.11	6.80
1.0446	2.90	2.11	3.09	6.78
1.3467	2.93	2.25	3.11	6.79
1.6050	2.95	2.45	3.12	6.80
1.9013	2.96	2.52	3.12	6.80
2.2089	3.00	d	3.12	6.81
2.5299	2.99	d	3.14	6.82
2.7003	3.02	d	3.13	6.82
2.9883	3.02	d	3.13	6.83
3.0305	3.03	d	3.14	6.84
3.2812	3.04	d	3.15	6.84
3.6966	3.05	d	3.16	6.86
3.7589	3.05	d	3.16	6.86
3.8951	3.05	d	3.17	6.87

Table 44. Continue.

$\frac{[15C5]}{[MeOH]}^e$	$\delta_{CH_3}^{MeOH^{a,b}}$	δ_{OH}^{MeOH}	δ^{15C5}	$\delta^{C_6H_6}$
3.7629	3.04	d	3.18	6.89

^aChemical shifts are reported relative to TMS in acetone- d_6 in ppm.

^bUncertainty in the chemical shifts is ± 0.01 ppm.

^cThe resonance of the methyl group appears as a doublet and the hydroxyl group as a quartet.

^dThe resonance was too broad to measure.

^eSolutions were prepared by adding 40 μ l of methanol to a known amount of 15C5 and diluting to 2 ml with benzene.

Table 45. Carbon-13 Chemical Shift Data for Solutions of Acetonitrile and Tetraglyme in Benzene.

$\frac{[\text{TG}]^a}{[\text{MeCN}]}$	$\delta_{\text{CH}_3}^{\text{MeCN}^b, c}$	$\delta_{\text{CN}}^{\text{MeCN}}$	$\delta_{\text{C}_6\text{H}_6}^d$	$\delta_{\text{A}}^{\text{TG}^d}$	$\delta_{\text{B}}^{\text{TG}}$	$\delta_{\text{C}}^{\text{TG}}$	$\delta_{\text{D}}^{\text{TG}}$
0.00	-29.44	86.35	98.98	-----	-----	-----	-----
0.2806	-29.40	86.44	98.98	42.76	41.45	41.28	29.06
0.7586	-29.32	86.57	99.00	42.78	41.45	41.29	29.07
1.6037	-29.23	86.76	99.03	42.79	41.47	41.31	29.09
2.6460	-29.12	87.00	99.07	42.81	41.47	41.31	29.10
3.4559	-29.01	87.16	99.10	42.82	41.48	41.32	29.13
3.8344	-28.99	87.25	99.12	42.83	41.50	41.33	29.13
3.9648	-28.97	87.28	99.13	42.83	41.50	41.33	29.15
4.9442	-28.88	87.47	99.17	42.86	41.51	41.35	29.16
5.4923	-28.87	87.54	99.17	42.85	41.50	41.33	29.16
6.1749	-28.81	87.63	99.19	42.88	41.49	41.35	29.17
6.3853	-28.81	87.67	99.20	42.88	41.51	41.35	29.17
7.0976	-28.78	87.78	99.21	42.88	41.52	41.35	29.17

Table 46. Carbon-13 Chemical Shift Data for Tetraglyme and Chloroform in Benzene.

$\frac{[\text{TG}]^a}{[\text{CHCl}_3]}$	$\delta_{\text{CHCl}_3}^b$	$\delta_{\text{C}_6\text{H}_6}^c$	$\delta_{\text{A}}^{\text{TG}}$	$\delta_{\text{B}}^{\text{TG}}$	$\delta_{\text{C}}^{\text{TG}}$	$\delta_{\text{D}}^{\text{TG}}$
0.00	48.03	98.95	-----	-----	-----	-----
0.2235	48.07	98.96	42.75	41.44	41.44	29.08
1.0591	48.31	98.97	42.77	41.46	41.30	29.09
1.6255	48.44	99.00	42.79	41.47	41.32	29.11
1.7074	48.45	98.99	42.78	41.46	41.31	29.09
2.0954	48.53	98.99	42.78	41.46	41.29	29.09
3.3220	48.84	99.04	42.82	41.50	41.35	29.14
3.3556	48.84	99.03	42.80	41.47	41.33	29.12
3.5326	48.87	99.05	42.80	41.47	41.33	29.12
3.8550	48.93	99.05	42.81	41.47	41.33	29.12
4.0646	48.96	99.06	42.81	41.49	41.33	29.12
4.7251	49.06	99.08	42.81	41.49	41.33	29.14
4.8724	49.07	99.09	42.84	41.52	41.37	29.17
5.2024	49.15	99.09	42.83	41.49	41.34	29.15
5.6373	49.21	99.09	42.83	41.49	41.34	29.15
5.9680	49.24	99.09	42.83	41.49	41.34	29.15
6.5920	49.34	99.12	42.84	41.50	41.34	29.15
7.9517	49.50	99.15	42.86	41.52	41.36	29.17

Table 47. Carbon-13 Chemical Shift Data for Nitromethane and Tetraglyme in Benzene.

$\frac{[\text{TG}]^a}{[\text{NM}]}$	δ_{NM}^b	$\delta_{\text{C}_6\text{H}_6}^{\text{C}}$	$\delta_{\text{A}}^{\text{TG}}$	$\delta_{\text{B}}^{\text{TG}}$	$\delta_{\text{C}}^{\text{TG}}$	$\delta_{\text{D}}^{\text{TG}}$
0.00	31.52	98.97	-----	-----	-----	-----
0.5247	31.77	98.97	42.75	41.43	41.30	29.03
1.1158	31.94	99.00	42.76	41.42	41.28	29.04
1.9402	32.22	99.03	42.78	41.44	41.29	29.06
2.4904	32.41	99.06	42.79	41.45	41.29	29.07
2.8490	32.44	99.07	42.80	41.47	41.32	29.10
3.1465	32.53	99.07	42.81	41.47	41.31	29.09
3.3595	32.59	99.08	42.80	41.47	41.32	29.09
3.7100	32.66	99.10	42.83	41.48	41.32	29.12
4.0094	32.72	99.10	42.82	41.47	41.32	29.10
4.2539	32.75	99.11	42.83	41.48	41.33	29.12
4.6659	32.86	99.14	42.85	41.49	41.35	29.13
5.5003	33.00	99.17	42.86	41.51	41.36	29.14
6.1307	33.13	99.20	42.87	41.51	41.34	29.16

^aSolutions were prepared by adding 40 μl of NM to a known amount of TG and diluting to 2ml with benzene.

^bChemical shifts are reported relative to AC-d₆ in ppm. Uncertainty is ± 0.03 ppm.

cChemical shift assignment for TG is:

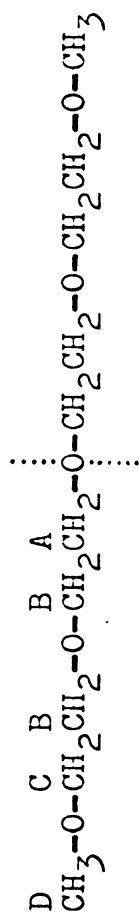


Table 48. Proton Chemical Shift Data for Methanol and Tetraglyme in Benzene.

$\frac{[\text{TG}]^e}{[\text{MeOH}]}$	$\delta_{\text{OH}}^{\text{MeOH}}$	$\delta_{\text{CH}_3}^{\text{MeOH}^c}$	$\delta_{\text{C}_6\text{H}_6}$	$\delta_{\text{A}}^{\text{TG}^d}$	$\delta_{\text{B}}^{\text{TG}}$	$\delta_{\text{C}}^{\text{TG}}$	$\delta_{\text{D}}^{\text{TG}}$
0.00	0.89	2.69	6.75	-----	-----	-----	-----
0.1964	1.21	2.75	6.76	3.04	3.06	2.92	2.71
0.5786	1.59	2.85	6.78	3.06	3.08	2.94	2.73
0.9792	1.72	2.89	6.79	3.08	3.09	2.95	2.75
1.2262	1.98	2.94	6.82	3.10	3.11	2.97	2.77
1.8538	2.22	-----	6.85	3.13	3.14	3.01	2.80
2.0027	2.29	-----	6.85	3.12	3.13	3.00	2.79
2.1471	2.26	-----	6.87	3.14	3.15	3.02	2.82
2.5086	2.42	-----	6.88	3.14	3.16	3.03	2.82
3.0458	2.53	-----	6.92	3.18	3.19	3.06	2.86
3.4268	2.58	3.12	6.94	3.20	3.21	3.08	2.88
3.5625	2.61	3.13	6.95	3.21	3.22	3.09	2.89
4.1816	2.67	-----	7.00	3.25	3.25	3.13	2.94

Table 49. Carbon-13 Chemical Shifts of Acetonitrile and Benzene for Solutions of Bl5C5 and AN in Benzene.

$\frac{[\text{Bl5C5}]^a}{[\text{AN}]}$	$\delta_{\text{CH}_3}^{\text{AN}^b}$	$\delta_{\text{CN}}^{\text{AN}}$	$\delta_{\text{C}_6\text{H}_6}$
0.00	-29.51	86.27	98.94
0.4213	-29.47	86.36	98.94
0.9464	-29.45	86.43	98.96
1.3203	-29.45	86.46	98.94
2.0887	-29.39	86.55	98.94
2.7940	-29.41	86.59	98.94
3.0549	-----	86.65	98.96
3.0884	-29.38	86.64	98.94
3.8975	-29.36	86.69	98.94
4.0646	-29.38	86.73	98.94
4.0665	-29.32	86.74	98.94
4.1771	-----	86.77	98.94
4.3801	-29.30	86.81	98.94
5.4088	-----	86.89	98.96
6.3958	-29.25	86.98	98.96

^aSolutions were prepared by adding 20 μl of AN to a known amount of Bl5C5 and diluting to 2ml with benzene.

^bChemical shifts are reported relative to acetone- d_6 in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

^cChemical shifts of Bl5C5 varied:

$\delta_1 = 39.74\text{--}39.69$ ppm

$\delta_2 = 40.40\text{--}40.30$ ppm

Table 49. Continue.

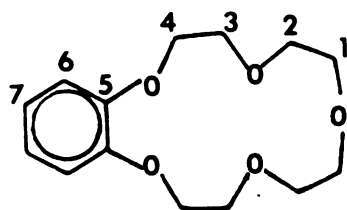
 $\delta_3 = 41.74-41.59$ ppm $\delta_4 = 42.21-42.09$ ppm $\delta_5 = 120.45-120.35$ ppm $\delta_6 = 84.95-84.92$ ppm $\delta_7 = 91.92-91.89$ ppm

Table 5Q. Carbon-13 Chemical Shift Data for Solutions of B15C5 and Nitromethane in Benzene.^b

Solutions were prepared by adding 30 μ l of NM to a known amount of B15C5 and diluting to 2ml with benzene:

$\frac{[\text{B15C5}]}{[\text{NM}]}$	$\delta_{\text{NM}}^{\text{a}}$	$\delta_{\text{C}_6\text{H}_6}$	$\frac{[\text{B15C5}]}{[\text{NM}]}$	δ_{NM}	$\delta_{\text{C}_6\text{H}_6}$
0.00	31.51	98.95	2.8045	32.08	98.95
0.3351	31.61	98.95	3.3675	32.17	98.95
0.7907	31.68	98.95	3.8550	32.26	98.95
1.6287	31.82	98.95	4.5014	32.33	98.95
2.2687	31.99	98.95			

Solutions were prepared by adding 20 μ l of NM to a known amount of B15C5 and diluting to 2ml with benzene:

$\frac{[\text{B15C5}]}{[\text{NM}]}$	$\delta_{\text{NM}}^{\text{a}}$	$\delta_{\text{C}_6\text{H}_6}$	$\frac{[\text{B15C5}]}{[\text{NM}]}$	δ_{NM}	$\delta_{\text{C}_6\text{H}_6}$
0.00	31.53	98.95	3.6824	32.00	98.95
0.5886	31.60	98.95	4.5792	32.10	98.95
1.8566	31.79	98.95	5.2104	32.19	98.97
2.5132	31.84	98.95	6.5035	32.32	98.97

^aChemical shifts are reported relative to acetone- d_6 in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

^bChemical shifts of B15C5 varied:

$\delta_1 = 39.70\text{--}39.65$ ppm

$\delta_2 = 40.38\text{--}40.27$ ppm

$\delta_3 = 41.72\text{--}41.52$ ppm

$\delta_4 = 42.19\text{--}42.14$ ppm

$\delta_5 = 120.43\text{--}120.29$ ppm

$\delta_6 = 91.90\text{--}91.89$ ppm

$\delta_7 = 84.91\text{--}84.88$ ppm

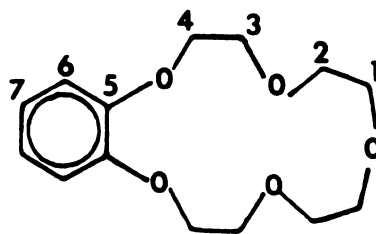


Table 51. Carbon-13 Chemical Shift Data for^c Solutions of B15C5 and Chloroform in Benzene.

$\frac{[\text{B15C5}]^a}{[\text{CHCl}_3]}$	^b δ_{CHCl_3}	$\delta_{\text{C}_6\text{H}_6}$	$\frac{[\text{B15C5}]}{[\text{CHCl}_3]}$	δ_{CHCl_3}	$\delta_{\text{C}_6\text{H}_6}$
0.00	48.01	98.94	4.7708	48.47	98.95
0.3603	48.05	98.94	5.1443	48.54	98.94
1.0590	48.13	98.95	5.1551	48.51	98.94
1.6115	48.17	98.94	6.0408	48.58	98.95
2.6642	48.31	98.94	6.3012	48.61	98.94
3.4201	48.35	98.94	6.5315	48.61	98.94
4.1017	48.42	98.94	7.3214	48.66	98.94

^aSolutions were prepared by adding 40 μl of CHCl_3 to a known amount of B15C5 and diluting to 2ml with^bbenzene.

^bChemical shifts are reported relative to acetone- d_6 in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

^cChemical shifts of B15C5 varied:

$\delta_1 = 39.73\text{--}39.68$ ppm

$\delta_2 = 40.41\text{--}40.31$ ppm

$\delta_3 = 41.76\text{--}41.59$ ppm

$\delta_4 = 42.23\text{--}42.10$ ppm

$\delta_5 = 120.46\text{--}120.32$ ppm

$\delta_6 = 84.94\text{--}84.88$ ppm

$\delta_7 = 91.90\text{--}91.88$ ppm

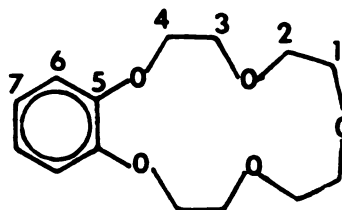


Table 52. Carbon-13 Chemical Shift Data for Solutions of Methanol and B15C5 in Benzene.^c

$\frac{[\text{B15C5}]^a}{[\text{MeOH}]}$	^b δ_{MeOH}	$\delta_{\text{C}_6\text{H}_6}$	$\frac{[\text{B15C5}]}{[\text{MeOH}]}$	δ_{MeOH}	$\delta_{\text{C}_6\text{H}_6}$
0.00	50.23	128.66	1.5566	50.16	128.66
0.1894	50.22	128.66	1.7289	50.16	128.66
0.3644	50.22	128.66	1.7554	50.17	128.65
0.3843	50.22	128.66	1.8555	50.14	128.66
0.8188	50.17	128.64	2.0380	50.14	128.66
1.0184	50.19	128.66	2.0539	50.14	128.66
1.1593	50.17	128.66	2.3211	50.14	128.66
1.2699	50.16	128.64	2.6342	50.11	128.66
1.4660	50.16	128.66			

^aSolutions were prepared by adding 40 μl of MeOH to a known amount of B15C5 and diluting to 2ml with benzene.

^bChemical shifts are reported relative to TMS in AC-d_6 in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

^cChemical shifts of B15C5 varied:

$\delta_1 = 69.36\text{--}69.39$ ppm

$\delta_2 = 69.99\text{--}70.07$ ppm

$\delta_3 = 71.24\text{--}71.32$ ppm

$\delta_4 = 71.74\text{--}71.80$ ppm

$\delta_5 = 150.01\text{--}150.09$ ppm

$\delta_6 = 114.60\text{--}114.65$ ppm

$\delta_7 = 121.61\text{--}121.64$ ppm

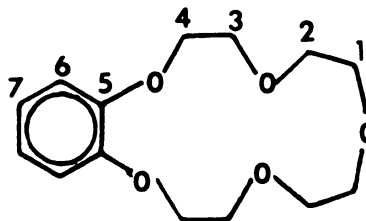


Table 53. Proton Chemical Shift Data for Solutions of B15C5 and Methanol in Benzene.^c

[B15C5] ^a [MeOH]	$\delta_{\text{MeOH}}^{\text{b,d}}$ δ_{OH}	δ_{MeOH} δ_{CH_3}	$\delta_{\text{C}_6\text{H}_6}$
0.00	1.08	2.69	6.75
0.1894	1.25	2.72	6.74
0.3418	1.28	2.74	6.74
0.3644	1.30	2.73	6.74
0.3843	1.34	2.74	6.74
0.6601	1.48	2.76	6.74
0.8188	1.60	2.77	6.73
1.0184	1.68	2.79	6.73
1.1593	1.78	2.79	6.72
1.2699	1.83	2.79	6.72
1.4660	1.86	2.80	6.72
1.7289	1.92	2.80	6.72
1.8555	1.97	2.80	6.72
2.0539	2.00	2.80	6.71
2.3211	2.04	2.80	6.71
2.6342	2.09	2.80	6.71

^aSolutions were prepared by adding 40 μl of MeOH to a known amount of B15C5 and diluting to 2ml with benzene.

^bUncertainty in the chemical shifts is ± 0.01 ppm. The chemical shifts are reported relative to TMS in acetone- d_6 in ppm.

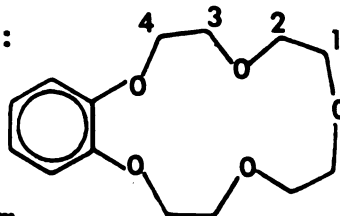
^cChemical shifts of B15C5 varied:

$\delta_{1,2} = 3.19\text{--}3.15$ ppm.

$\delta_3 = 3.15\text{--}3.14$ ppm.

$\delta_4 = 3.35\text{--}3.36$ ppm.

$\delta_{\text{aromatic}} = 6.31\text{--}6.29$ ppm.



^dResonances of the methyl and hydroxyl groups of methanol appeared as a doublet and quartet, respectively.

Table 54. Carbon-13 Chemical Shift Data for Solutions of Pentaglyme and NM in Benzene.

$\frac{[\text{PG}]}{[\text{NM}]}$ ^a	^{b, c} δ_{NM}	$\delta_{\text{C}_6\text{H}_6}$	δ_1^{PG} ^d	$\delta_2^{\text{PG}}, \delta_3$	δ_4^{PG}
0.00	31.59	98.97	-----	-----	-----
0.2344	31.69	98.99	29.05	41.43	42.75
0.5862	31.81	98.99	29.05	41.41	42.77
0.8162	31.90	99.00	29.06	41.43	42.77
1.1361	32.06	99.02	29.06	41.43	42.76
1.2244	32.11	99.03	29.08	41.44	42.78
1.4972	32.21	99.03	29.08	41.44	42.78
1.8952	32.33	99.06	29.09	41.44	42.79
2.2098	32.43	99.04	29.08	41.44	42.78
2.3447	32.52	99.06	29.09	41.44	42.79
2.5453	32.49	99.06	29.08	41.43	42.78
2.7094	32.60	99.07	29.09	41.44	42.79
3.1656	32.75	99.12	29.12	41.47	42.82
3.5072	32.81	99.11	29.12	41.45	42.80
3.9384	32.91	99.14	29.15	41.48	42.85
4.2282	32.98	99.14	29.13	41.47	42.83
4.7727	33.08	99.16	29.14	41.46	42.83
5.5682	33.23	99.20	29.17	41.49	42.86
6.7455	33.42	99.25	29.20	41.50	42.89

Table 54. Continue.

^aSolutions were prepared by adding 40 μ l of NM to a known amount of PG and diluting to 2 ml with benzene.

^bChemical shifts are reported relative to acetone-d₆ in ppm.

^cUncertainty in the chemical shifts is ± 0.03 ppm.

^dChemical shift assignment for pentaglyme is:

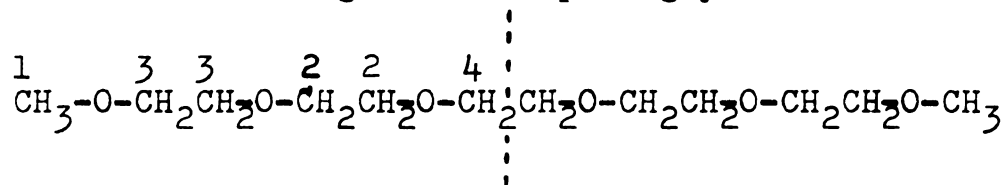


Table 55. Carbon-13 Chemical Shift Data for Solutions of 21C7 and NM in Benzene.

$\frac{[21C7]^a}{[NM]}$	$\delta_{NM}^{a,b}$	δ_{21C7}	$\delta_{C_6H_6}$
0.00	31.55	-----	98.99
0.5243	31.83	41.61	98.96
1.0021	32.13	41.63	98.98
1.3545	32.29	41.63	98.98
1.5759	32.41	41.61	98.99
1.8766	32.52	41.54	98.99
2.2796	32.71	41.60	98.99
2.5482	32.79	41.54	99.01
3.1231	33.01	41.61	99.02
5.1702	33.49	41.53	99.08

^aSolutions were prepared by adding 25 μ l of NM to a known amount of 21C7 and diluting to 2 ml with benzene.

^bChemical shifts are reported relative to acetone- d_6 in ppm.

^cUncertainty in the chemical shifts is ± 0.03 ppm.

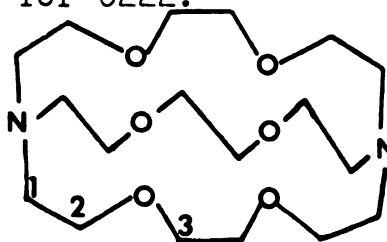
Table 56. Carbon-13 Chemical Shift Data for Solutions of C222 and NM in Benzene.

$\frac{[\text{C222}]^a}{[\text{NM}]}$	δ_{NM}^b	$\delta_{\text{C}_6\text{H}_6}^b$	δ_{C222}^c	δ_{C222}^c	δ_{C222}^c
			δ_1	δ_2	δ_3
0.00	31.55	98.95	-----	-----	-----
0.2794	31.57	98.95	27.41	40.82	41.76
1.0310	31.70	98.95	27.38	40.79	41.74
1.1883	31.74	-----	-----	-----	-----
2.1302	31.88	98.98	27.39	40.77	41.73
4.2939	32.30	-----	-----	-----	-----
6.2327	32.46	-----	-----	-----	-----

^aSolutions were prepared by adding 25 μl of NM to a known amount of C222 and diluting to 2 ml with benzene.

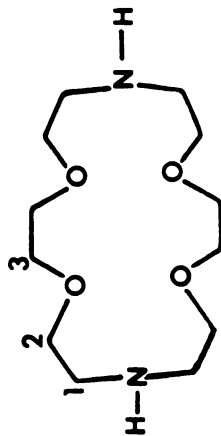
^bChemical shifts are reported relative to acetone- d_6 in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

^cChemical shift assignment for C222:



* In benzene, $\delta_1 = 27.42$ ppm
 $\delta_2 = 40.81$ ppm
 $\delta_3 = 41.78$ ppm

Table 57. Carbon-13 Chemical Shift Data for Solutions of DA18C6 and Acetonitrile in Benzene.



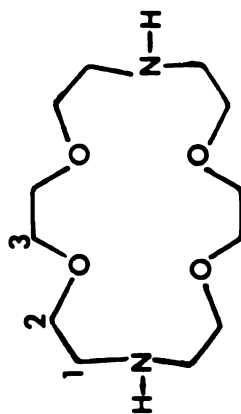
$\frac{[\text{DA18C6}]^a}{[\text{MeCN}]}$	$\delta_{\text{CH}_3}^{\text{MeCN}^b, c}$	$\delta_{\text{CN}}^{\text{MeCN}}$	δ_1^{DA18C6}	δ_2^{DA18C6}	δ_3^{DA18C6}	$\delta_{\text{C}_6\text{H}_6}$
0.00	-29.52	86.23	-----	-----	-----	98.98
0.6650	-29.45	86.29	20.58	41.19	41.49	98.98
0.7159	-29.45	86.29	20.58	41.20	41.49	98.97
0.9967	-29.42	-----	20.60	41.24	41.54	99.00

^aSolutions were prepared by adding 25 μl of acetonitrile to a known amount of DA18C6 and diluting to 5 ml with benzene.

^bChemical shifts are reported relative to acetone- d_6 in ppm.

^cUncertainty in the chemical shifts is ± 0.03 ppm.

Table 58. Carbon-13 Chemical Shift Data for DAL8C6 and Acetonitrile in Chloroform.



$\frac{[\text{DAL8C6}]}{[\text{MeCN}]}$ ^a	$\delta_{\text{MeCN}}^{\text{b,c}}$ δ_{CH_3}	$\delta_{\text{MeCN}}^{\text{b,c}}$ δ_{CN}	$\delta_{\text{DAL8C6}}^{\text{b,c}}$ δ_1	$\delta_{\text{DAL8C6}}^{\text{b,c}}$ δ_2	$\delta_{\text{DAL8C6}}^{\text{b,c}}$ δ_3	δ_{CHCl_3}
0.00	-26.93	87.56	-----	-----	-----	48.55
0.5700	-26.93	87.66	20.73	41.66	41.82	48.70
0.7659	-26.96	87.64	20.73	41.66	41.82	48.76
1.5379	-26.99	87.76	20.76	41.65	41.81	49.02
0.3939	-26.90	87.66	20.72	41.63	41.81	48.64

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^aSolutions were prepared by adding 50 μl of MeCN to a known amount of DAL8C6 and diluting to 2 ml with chloroform.

^bChemical shifts are reported relative to acetone- d_6 in ppm.

^cUncertainty in the chemical shifts is ± 0.03 ppm.

Table 59. Carbon-13 Chemical Shift Data for Solutions of Silver Nitrate in Acetonitrile.

X_{AgNO_3}	$\delta_{\text{CH}_3}^a$	δ_{CN}
0.00	1.71	118.24
8.83×10^{-3}	1.69	118.34
1.19×10^{-2}	1.69	118.37
2.18×10^{-2}	1.72	118.49
3.62×10^{-2}	1.69	118.59
3.73×10^{-2}	1.69	118.61
4.86×10^{-2}	1.72	118.73
6.02×10^{-2}	1.68	118.80
6.43×10^{-2}	1.65	118.83
8.14×10^{-2}	1.63	118.96
8.90×10^{-2}	1.62	119.03
1.039×10^{-1}	1.60	119.18
1.097×10^{-1}	1.60	119.23
1.209×10^{-1}	1.57	119.33
1.415×10^{-1}	1.55	119.46
1.682×10^{-1}	1.53	119.67
1.886×10^{-1}	1.52	119.87
1.905×10^{-1}	1.52	119.89

^aChemical shifts are reported relative to TMS in AC-d₆ in ppm. Uncertainty in the chemical shifts is ± 0.03 ppm.

Table 60. Proton Chemical Shift Data for Solutions of Silver Nitrate in Acetonitrile.

X_{AgNO_3}	$\delta_{\text{CH}_3}^a$
0.00	2.06
2.18×10^{-2}	2.03
3.73×10^{-2}	2.00
4.86×10^{-2}	1.98

^aChemical shifts are reported relative to TMS in AC-d₆ in ppm. Uncertainty in the chemical shifts is ± 0.01 ppm.

REFERENCES

REFERENCES

1. J.D. Lamb, R.M. Izatt and J.J. Christensen in "Progress in Macrocyclic Chemistry, Vol. II", R.M. Izatt and J.J. Christensen, eds., John Wiley and Sons (1981).
2. S. Khazaeli, Ph.D. Thesis, Michigan State University, East Lansing, MI (1982).
3. P. Szczygiel, M.S. Thesis, Michigan State University, East Lansing, MI (1984).
4. B. Strasser, Ph.D. Thesis, Michigan State University, East Lansing, MI (1984).
5. G.W. Gokel, D.J. Cram, C.L. Liotta, H.P. Harris and F.L. Cook, J. Org. Chem., 39, 2445 (1974).
6. S.N. Ghosh, R. Trambarulo and W. Gordy, J. Chem. Phys., 21, 308 (1953).
7. J.D. Lambert, G.A.H. Roberts, J.S. Rowlinson and V.J. Wilkinson, Proc. Roy. Soc. (London), A196, 113 (1949).
8. J.M. Prausnitz and W.B. Carter, A.I.Ch.E.J., 6, 611 (1960).
9. A.M. Saum, J. Polymer Sci., 42, 66,57 (1960).
10. A.D. Buckingham and R.E. Raab, J. Chem. Soc., 5511 (1961).
11. W. Dannhauser and A.F. Flueckinger, J. Phys. Chem., 68, 1814 (1964).
12. T.B. Freedman and E.R. Nixon, Spectrochim. Acta, 28A, 1375 (1972).
13. F.E. Murray and W.G. Schneider, Can. J. Chem., 33, 797 (1955).

14. R.W. Taft, E. Price, I.R. Fox, I.C. Lewis, K.K. Andersen and G.T. Davis, J. Am. Chem. Soc., 85, 709 (1963).
15. B.H. Thomas and W.J. Orville-Thomas, J. Mol. Struct., 3, 191 (1969).
16. K.F. Purcell and R.S. Drago, J. Am. Chem. Soc., 88, 919 (1966).
17. E.L. Zhukova, Opt. i. Spektroskopiya, 5, 270 (1958).
18. K.F. Purcell, J. Am. Chem. Soc., 89, 247 (1967).
19. R.K. Thomas, Proc. Roy. Soc. (London), A325, 133 (1971).
20. R.K. Thomas and H.W. Thompson, Proc. Roy. Soc. (London), A316, 303 (1970).
21. J.P. Roche and P. van Huong, J. Chim. Phys., 67, 211 (1970).
22. C.C. Mohr, W.D. Wilk and G.M. Barrow, J. Am. Chem. Soc., 87, 3048 (1965).
23. C.D. Ritchie and A.L. Pratt, J. Am. Chem. Soc., 86, 1571 (1964).
24. J.V. Hatton and W.G. Schneider, Can. J. Chem., 40, 1285 (1962).
25. R.J. Abraham, J. Chem. Phys., 34, 1062 (1961).
26. A.D. Buckingham, T. Schaefer and W.G. Schneider, J. Chem. Phys., 34, 1064 (1961).
27. I. Brown and W. Fock, Aust. J. Chem., 8, 361 (1955); 9, 180 (1956); 10, 417 (1957).
28. K. Amaya, Bull. Chem. Soc. Jpn., 34, 1271, 1278, 1349 (1961).
29. R.V. Arye and J.M. Prausnitz, Trans. Faraday Soc., 61, 1338 (1965).
30. J.R. Goates, J.B. Ott and A.H. Budge, J. Phys. Chem., 65, 2162 (1961).
31. J. Yarwood, R. Arndt and G. Doge, Chem. Phys., 25, 387 (1977).

32. J. Timmermans, "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions, Vol. I", Interscience Publishers (1959), p. 766.
33. P.J. Berkeley and M.W. Hanna, J. Phys. Chem., 67, 846 (1963).
34. W. Lin and S. Tsay, J. Phys. Chem., 74, 1037 (1970).
35. Y.P. Handa and D.E. Jones, Can. J. Chem., 55, 2977 (1977).
36. A. Kreglewski, Bull. Acad. Polon. Sci. Ser. Sci. Chim., 13, 723 (1965).
37. F. Mato and M. Sanchez, An. Real. Soc. Espan. Fis. Quin. Ser. B, 63, 1 (1967).
38. Y.P. Handa, J. Chem. Thermodyn., 9, 117 (1977).
39. I. Brown and F. Smith, Aust. J. Chem., 7, 269 (1954).
40. M.L. McGlashan, J.E. Prue, and I.E.J. Sainsbury, Trans. Faraday Soc., 50, 1284 (1954).
41. J.W. Lorimer and D.E. Jones, Can. J. Chem., 55, 2977 (1977).
42. G.W. Williams, J. Am. Chem. Soc., 47, 2644 (1925).
43. R.O. Herzog, Z. Physik. Chem., A147, 118 (1930).
44. H. Pestimer and O. Fruhwirth, Monatsh. Chem., 70, 146 (1937).
45. G.C. Danielson and K. Lark-Horowitz, Phys. Rev., 59, 110 (1941).
46. B. Jacobson, Acta Chem. Scand., 6, 1485 (1952).
47. P.A.D. de Maine, M.M. de Maine and A.G. Goble, Trans. Faraday Soc., 53, 427 (1957).
48. E. Tannenbaum, R.J. Myers and W.D. Gwinn, J. Chem. Phys., 25, 42 (1956).
49. P.A.D. de Maine, M.M. de Maine, A.A. Briggs and G.E. McAlonie, J. Mol. Spectrosc., 4, 398 (1960).
50. P.A.D. de Maine, L.H. Daly and M.M. de Maine, Can. J. Chem., 38, 1921 (1960).

51. P.A.D. de Maine, J. Mol. Spectrosc., 4, 407 (1960).
52. H.H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", John Wiley and Sons (1962).
53. S. Nagakura, Mol. Phys., 3, 152 (1960).
54. A. Balasubramanian and C.N.R. Rao, Spectrochim. Acta, 18, 1337 (1962).
55. W.F. Baitinger, P.v.R. Schleyer, T.S.S.R. Murty and L. Robinson, Tetrahedron, 20, 1635 (1964).
56. H.E. Ungnade and L.W. Kissinger, Tetrahedron, Suppl. 1, 19, 121 (1963).
57. H.E. Ungnade, E.D. Loughrom and L.W. Kissinger, J. Phys. Chem., 66, 2643 (1962).
58. O.A. Reutov and I.P. Beletskaya, "CH-Acids", Pergamon Press (1978), pp. 34-65.
59. C.F. Jumper, M.T. Emerson and B.B. Howard, J. Chem. Phys., 35, 1911 (1961).
60. B.B. Howard, C.F. Jumper and M.T. Emerson, J. Mol. Spectrosc., 10, 117 (1963).
61. A.L. McClellan, S.W. Nicksic and J.C. Guffy, J. Mol. Spectrosc., 11, 340 (1963).
62. S.N. Vinogradov and R.H. Linnell, "Hydrogen Bonding", Van Nostrand Reinhold (1971).
63. L. Pauling, "The Nature of the Chemical Bond", Cornell University Press (1948).
64. R.M. Meighan and R.H. Cole, J. Phys. Chem., 68, 503 (1964).
65. R.J. Kurland and E.B. Wilson, Jr., J. Chem. Phys., 27, 585 (1957).
66. J. Zabicky, "The Chemistry of Amides", John Wiley and Sons (1970).
67. R.D. McLachlan and R.A. Nyquest, Spectrochim. Acta, 20, 1397 (1964).

68. I.M. Klotz and J.J. Franzen, J. Am. Chem. Soc., 84, 3461 (1962).
69. L.A. LaPlanche and M.T. Rogers, J. Am. Chem. Soc., 86, 337 (1964).
70. R.C. Neuman, Jr., W. Snider and V. Jonas, J. Phys. Chem., 72, 2469 (1968).
71. J.C. Woodbrey and M.T. Rogers, J. Am. Chem. Soc., 84, 13 (1962).
72. A.G. Whittaker and S. Siegel, J. Chem. Phys., 42, 3320 (1965).
73. R.C. Neuman, Jr. and L.B. Young, J. Phys. Chem., 69, 2570 (1965).
74. R.L. Adelman, J. Org. Chem., 29, 1837 (1964).
75. J.V. Hattin and R.E. Richards, Mol. Phys., 5, 139 (1962).
76. C.D. Gutsche, "The Chemistry of Carbonyl Compounds", Prentice-Hall (1967), pp.15-19.
77. E.D. Becker, Spectrochim. Acta, 17, 436 (1961).
78. H. Saito, Y. Tanaka, S. Nagata and K. Nukada, Can. J. Chem., 51, 2118 (1973).
79. W. Weltner and K.S. Pitzer, J. Am. Chem. Soc., 73, 2606 (1951).
80. N.S. Berman, A.I.Ch.E.J., 14, 497 (1968).
81. S.C. Stanford and W. Gordy, J. Am. Chem. Soc., 62, 1247 (1940).
82. R. Mecke, Discussions Faraday Soc., 9, 161 (1950).
83. N.D. Goggeshall and E.L. Saier, J. Am. Chem. Soc., 73, 5414 (1951).
84. A. Ens and F.E. Murray, Can. J. Chem., 35, 170 (1957).
85. U. Liddel and E.D. Becker, Spectrochim. Acta, 10, 70 (1957).
86. L.J. Bellamy and R.J. Pace, Spectrochim. Acta, 22, 525 (1966).

87. L.J. Bellamy, K.J. Morgan and R.J. Pace, Spectrochim. Acta, 22, 535 (1966).
88. A.N. Fletcher and C.A. Heller, J. Phys. Chem., 71, 3742 (1967).
89. L.K. Patterson and R.M. Hammaker, Spectrochim. Acta, 23A, 2333 (1967).
90. M. van Thiel, E.D. Becker and G.C. Pimentel, J. Chem. Phys., 27, 95, 486 (1957).
91. A. Hall and J.L. Wood, Spectrochim. Acta, 23A, 2657 (1967).
92. H.C. van Ness, J. van Winkle, H.H. Richtol and H.B. Hollinger, J. Phys. Chem., 71, 1483 (1967).
93. H. Ratajczak and W.J. Orville-Thomas, J. Mol. Struct., 1, 449 (1968).
94. P. Sohar and G. Varsanji, Spectrochim. Acta, 23A, 1947 (1967).
95. A.D. Cohen and C. Reid, J. Chem. Phys., 25, 790 (1956).
96. M. Saunders and J.B. Hyne, J. Chem. Phys., 29, 1319 (1958).
97. J.C. Davis, K.S. Pitzer and C.N.R. Rao, J. Phys. Chem., 64, 1744 (1960).
98. H. Elmgren, J. Chem. Soc., 65, 206 (1968).
99. L.H. Thomas and R. Meatyard, J. Chem. Soc., 1986 (1963).
100. L.H. Thomas, J. Chem. Soc., 1995 (1963).
101. R.H. Stokes, Aust. J. Chem., 21, 1343 (1968).
102. W. Gordy and S.C. Stanford, J. Chem. Phys., 9, 204 (1941).
103. R.G. Inskeep, F.E. Dickson and J.M. Kelliker, J. Mol. Spectrosc., 4, 477 (1960).
104. J.E. Gordon, J. Org. Chem., 26, 738 (1961).
105. N.S. Bayliss and N.W. Cant, Spectrochim. Acta, 18, 1287 (1962).

106. M.L. McGlashan, D. Stubley and H. Watts, J. Chem. Soc. A, 1969, 673.
107. R.P. Rastogi and R.K. Nigam, Trans. Faraday Soc., 55, 2005 (1959).
108. B.J. Ott, J.R. Goates and A.H. Budge, J. Phys. Chem., 66, 1387 (1962).
109. J.R. Goates, R.J. Sullivan and J.B. Ott, J. Phys. Chem., 63, 589 (1959).
110. R. Anderson and J.M. Prausnitz, J. Chem. Phys., 39, 1225 (1963).
111. R. Anderson and J.M. Prausnitz, J. Chem. Phys., 40, 3443 (1964).
112. F.P. Hinz and D.W. Margerum, J. Am. Chem. Soc., 96, 4993 (1974).
113. F.P. Hinz and D.W. Margerum, Inorg. Chem., 13, 2941 (1974).
114. D.K. Cabbiness and D.W. Margerum, J. Am. Chem. Soc., 91, 6540 (1969).
115. G.F. Smith and D.W. Margerum, J. Chem. Soc., Chem. Comm., 1975, 807.
116. A. Dei and R. Gori, Inorg. Chim. Acta, 14, 157 (1975).
117. B.L. Haymore, J.D. Lamb, R.M. Izatt and J.J. Christensen, Inorg. Chem., 21, 1598 (1982).
118. P. Paoletti, L. Fabbrizzi and R. Barbucci, Inorg. Chem., 12, 1961 (1973).
119. P. Paoletti, L. Fabbrizzi, and A.B.P. Lever, Inorg. Chem., 15, 1502 (1976).
120. P. Paoletti, L. Fabbrizzi, A. Anichini and R. Clay, Inorg. Chim. Acta, 22, L25 (1977).
121. M. Kodama and E. Kimura, J. Chem. Soc., Chem. Comm., 1975, 326.
122. M. Kodama and E. Kimura, J. Chem. Soc., Dalton Trans., 1976, 116.

123. M. Kodama and E. Kimura, J. Chem. Soc., Dalton Trans., 1977, 2269.
124. A. Anichini, L. Fabbrizzi, P. Paoletti, and R.M. Clay, J. Chem. Soc., Dalton Trans., 1978, 577.
125. F. Arnaud-Neu, M.J. Schwing-Weill, J. Juillard, R. Louis and R. Weiss, Inorg. Nucl. Chem. Lett., 14, 367 (1978).
126. G.W. Liesegang, M.M. Farrow, F.A. Vazquez, N. Purdie and E.M. Eyring, J. Am. Chem. Soc., 99, 3240 (1977).
127. G.W. Liesegang, M.M. Farrow, N. Purdie and E.M. Eyring, J. Am. Chem. Soc., 98, 6905 (1976).
128. L.J. Rodriguez, G.W. Liesegang, R.D. White, M.M. Farrow, N. Purdie and E.M. Eyring, J. Phys. Chem., 81, 2118 (1977).
129. D. Live and S.I. Chan, J. Am. Chem. Soc., 98, 3769 (1976).
130. G.W. Liesegang, M.M. Farrow, L.J. Rodriguez, R.K. Burnham, N. Purdie and E.M. Eyring, Int. J. Chem. Kin., X, 471 (1978).
131. C.C. Chen and S. Petrucci, J. Phys. Chem., 86, 2601 (1982)
132. V. Kryukov, V.K. Pogorelyi, and Y.A. Tarasenko, Teoreticheskaya i. Eksperimental'maya Khim., 17, 553 (1981).
133. Ting-Po I and E. Grunwald, J. Am. Chem. Soc., 96, 2879 (1974).
134. M.H. Abraham, A.F. Danil DeNamor and W.H. Lee, J. Chem. Soc., Chem. Comm., 1977, 892.
135. M.H. Abraham and H.C. Ling, Tetrahedron Lett., 23, 469 (1982).
136. J. Dale and P.O. Kristiansen, Acta Chem. Scand., 26, 1471 (1972).
137. J. Dale, Isr. J. Chem., 20, 3 (1980).
138. J. Dale, Tetrahedron, 30, 1683 (1974).
139. J.D. Dunitz, M. Dobler, P. Seiler and R.P. Phizackerley, Acta Crystallogr., B30, 2733 (1974).

140. C.J. Pedersen, J. Am. Chem. Soc., 89, 7017 (1967).
141. E. Schmidt, J.-M. Tremillon, J.-P. Kintzinger and A.I. Popov, J. Am. Chem. Soc., 105, 7563 (1983).
142. F. Vogtle and W.M. Muller, Naturwissenschaften, 67, 255 (1980).
143. F. Vogtle, W.M. Muller and E. Weber, Chem. Ber., 113, 1130 (1980).
144. A. Elbasyouny, H.J. Brugge, K. von Deuten, M. Dickel, A. Knochel, K.U. Koch, J. Kopf, D. Melzer and G. Rudolph, J. Am. Chem. Soc., 105, 6568 (1983).
145. Shell Internationals Research Maatschappij, Brit. Appl. 77/26,333,23 June 1977; 7pp.
146. Charles L. Liotta (duPont de Nemours, E.I. and Co.), Appl. 511,000,01 Oct. 1974; 4pp.
147. J.A.A. de Boer, D.N. Reinhoudt, S. Harkema, G.J. van Hummel and F. de Jong, J. Am. Chem. Soc., 104, 4073 (1982).
148. R. Kaufmann, A. Knochel, J. Kopf, J. Oehler and G. Rudolph, Chem. Ber., 110, 2249 (1977).
149. I. Goldberg, Acta Crystallogr., B31, 754 (1975).
150. R.D. McLachlan, Spectrochim. Acta, 30A, 2153 (1974).
151. H.S. Gold and M.R. Rice, Talanta, 29, 637 (1982).
152. A. Elbasyony, J. Klimes, A. Knochel, J. Oehler and G. Rudolph, Z. Naturforsch., 31B, 1192 (1976).
153. F. de Jong, D.N. Reinhoudt and C.J. Smit, Tetrahedron Lett., 1976, 1371.
154. A. van Zon, Y. Onwezen and H.P.M. Tomassen, Recl. Trav. Chim. Pays-Bas, 102, 290 (1983).
155. J.A. Bandy, M.R. Truter and F. Vogtle, Acta Crystallogr., B37, 1568 (1981).
156. W.H. Watson, J. Galloy and D.A. Grossie, J. Org. Chem., 49, 347 (1984).
157. I. Goldberg, Acta Crystallogr., B34, 3387 (1978).

158. G.R. Newkome, F.R. Fronczek, H.C.R. Taylor, T.J. Delord and D.K. Kohli, J. Am. Chem. Soc., 103, 7376 (1981).
159. F. Vogtle, H. Puff, E. Friedrichs and W.M. Muller, J. Chem. Soc., Chem. Comm., 1982, 1398.
160. D.J. Cram, K.D. Stewart, I. Goldberg and K.N. Trueblood, J. Am. Chem. Soc., 107, 2574 (1985).
161. K. von Deuten, A. Knochel, J. Kopf, J. Oehler and G. Rudolph, J. Chem. Res. (S), 1979, 358.
162. D. Leutloff and E. Knozinger, Spectrosc. Lett., 12, 815 (1979).
163. D.R. Petzold and R. Radeaglia, Z. Phys. Chem. (Leipzig), 249, 253 (1972).
164. R. Anderson, R. Cambio and J.M. Prausnitz, A.I.Ch.E.J., 8, 66 (1962).
165. J. Homer and A.R. Dudley, J. Chem. Soc., Faraday Trans. I, 69, 1995 (1973).
166. J. Feeney and P.J.S. Pauwells, J. Chem. Soc. B, 1971, 515.
167. H.-J. Bittrich and E. Kietz, Z. Phys. Chem. (Leipzig), 261, 17 (1980).
168. H. Farber and S. Petrucci, J. Phys. Chem., 85, 1396 (1981).
169. K.J. Maynard, D.E. Irish, E.M. Eyring and S. Petrucci, J. Phys. Chem., 88, 729 (1984).
170. C.C. Chen, W. Wallace, E.M. Eyring and S. Petrucci, J. Phys. Chem., 88, 2541 (1984).
171. A.D.H. Claque, G. Govil and H.J. Bernstein, Can. J. Chem., 47, 625 (1969).
172. C.B. Kretschmer and R. Wieke, J. Amer. Chem. Soc., 76, 2579 (1954).
173. R.G. Inskeep, J.M. Kelliher, P.E. McMahon and B.G. Somers, J. Chem. Phys., 28, 1033 (1958).
174. R.G. Inskeep, F.E. Dickson and H.M. Olsen, J. Mol. Spectrosc., 5, 284 (1960).

175. E. Shchori and J. Jagur-Grodzinski, Isr. J. Chem., 10, 935 (1972).
176. R.N. Greene, Tetrahedron Lett., 1793 (1972).
177. J.A. Riddick and W.B. Bunger, "Techniques of Chemistry-Volume II: Organic Solvents", 3rd. Edition, A. Weissberger ed., Wiley-Interscience (1970).
178. H.M. McNair and E.J. Bonelli, "Basic Gas Chromatography", Varian (1968), pp. 59-64.
179. M.L. Martin, J.J. Delpuech and G.J. Martin, "Practical NMR Spectroscopy", Heyden and Sons Ltd. (1980).
180. M.S. Greenberg and A.I. Popov, Spectrochim. Acta, 31A, 697 (1975).
181. C. Brevard and P. Granger, "Handbook of High Resolution Multinuclear NMR", John Wiley and Sons (1981).
182. J.B. Lambert, H.F. Shurvell, L. Verbit, R.G. Cooks and G.H. Stout, "Organic Structural Analysis", Macmillan Publishing Co., Inc. (1976).
183. J.L. Dye and V.A. Nicely, J. Chem. Ed., 48, 443 (1971).
184. A.R. Davis, D.E. Irish, R.B. Roden and A.J. Weerheim, Appl. Spectrosc., 26, 384 (1972).
185. J.D. Ingle, Jr. and S.R. Crouch, "CEM 835: Analytical Optical Spectroscopy Notes", Michigan State University, East Lansing, MI (1982).
186. D.P. Shoemaker, C.W. Garland and J.I. Steinfeld. "Experiments in Physical Chemistry", 3rd Edition, McGraw-Hill, Inc. (1974).
187. A.J. Gordon and R.A. Ford, "The Chemist's Companion: A Handbook of Practical Data, Techniques, and References", John Wiley and Sons (1972).
188. M.S. Greenberg, Ph.D. Thesis, Michigan State University, East Lansing, MI (1974).
189. V. Gutmann and E. Wyckera, Inorg. Nucl. Chem. Lett., 2, 257 (1965).

190. Y.M. Cahen, Ph.D. Thesis, Michigan State University, East Lansing (1975).
191. W.J. Moore, "Physical Chemistry" 4th Edition, Prentice-Hall, Inc. (1972).
192. S.L. Whittenberg and C.H. Wang, J. Chem. Phys., 66, 4255 (1977).
193. "Handbook of Chemistry and Physics", 57th Edition, R.C. Weast Ed., Chemical Rubber Co. (1976).
194. J. Gmehling, U. Onken and W. Arlt, "Vapor-Liquid Equilibrium Data Collection: Aldehydes and Ketones, Ethers", Deckema (1979).
195. B. Swanson, D.F. Shriver and J.A. Ibers, Inorg. Chem., 10, 2182 (1969).
196. J. Gmehling, U. Onken and W. Arlt, "Vapor-Liquid Equilibrium Data Collection: Aromatic Compounds", Deckema (1979).
197. A. Engdahl and B. Nelander, J. Phys. Chem., 89, 2860 (1985).
198. I.N. Levine, "Physical Chemistry", 2nd Edition, McGraw-Hill Book Co. (1983).
199. J.R. van Wazer, J.W. Lyons, K.Y. Kim and R.E. Colwell, "Viscosity and Flow Measurement: A Laboratory Handbook of Rheology", John Wiley and Sons (1963).
200. A.J. Smetana, Ph.D. Thesis, Michigan State University, East Lansing, MI (1979).
201. K.F. Purcell and J.C. Kotz, "Inorganic Chemistry", W.B. Saunders Co. (1977).
202. Y. Jayathirtha and V. Krishnan, Proc. Indian Acad. Sci., 86, 465 (1977).
203. Y.C. Lee, Ph.D. Thesis, Michigan State University, East Lansing, MI (1983).
204. D.L. Ward, personal communication.
205. J.W. Rovang, personal communication.

206. Y.C. Lee, A.I. Popov and J.Allison, Inter. J. of Mass Spect. and Ion Physics, 51, 267 (1983).
207. J.L. Duncan, D.C. McKean, F. Tullini, G.D. Nivellini and J.P. Pena, J. Mol. Spectrosc., 69, 123 (1978).
208. J. Rebek, Jr., Acc. Chem. Res., 17, 258 (1984).
209. M. Shamsipur, G. Rounaghi, and A.I. Popov, J. Soln. Chem., 9, 701 (1980).
210. B.G. Cox, J. Garcia-Rosas and H. Schneider, J. Am. Chem. Soc., 103, 1384 (1981).
211. B.G. Cox, H. Schneider and J. Stroka, J. Am. Chem. Soc., 100, 4746 (1978).
212. J.E. Huheey, "Inorganic Chemistry", 2nd Edition, Harper and Row (1978).
213. J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structures", McGraw-Hill Inc. (1977).
214. S. Patai, "The Chemistry of Amidines and Imidates", John Wiley and Sons, Ltd. (1975).
215. J.C. Grivas and A. Taurins, Can. J. Chem., 39, 761 (1961). N. Naulet, M.L. Filleux, G.J. Martin and J. Pornet, Org. Magnetic Res., 7, 326 (1975).
216. R.D. Boss, Ph.D. Thesis, Michigan State University, East Lansing, MI (1985).
217. G.J. Janz and K. Balasubrahmanyam, J. Am. Chem. Soc., 92, 4189 (1970).
218. F.A. Cotton and G. Wilkenson, "Basic Inorganic Chemistry", John Wiley and Sons (1976).
219. E. Breitmaier and W. Voelter, "Carbon-13 NMR Spectroscopy", Verlag Chemie, (1974).
220. F. Mathieu, B. Metz, D. Moras and R. Weiss, J. Am. Chem. Soc., 100, 4412 (1978).