This is to certify that the

thesis entitled

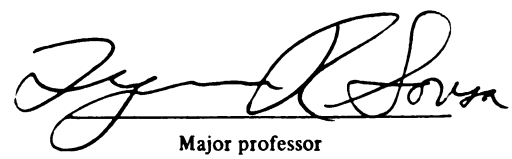
STUDIES OF THE
PROPERTIES, SYNTHESIS, AND STRUCTURE
OF SEVERAL CROWN ETHER MODIFIED CHROMOPHORES

presented by

Houston Slade Brown

has been accepted towards fulfillment
of the requirements for

Ph.D degree in Chemistry



Major professor

Date August 29, 1979

STUDIES OF THE PROPERTIES, SYNTHESIS, AND STRUCTURE OF SEVERAL CROWN ETHER MODIFIED CHROMOPHORES

By

Houston S. Brown

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1979

ABSTRACT

STUDIES OF THE
PROPERTIES, SYNTHESIS, AND STRUCTURE
OF SEVERAL CROWN ETHER MODIFIED CHROMOPHORES

By

Houston S. Brown

Chapter 1 describes the synthesis of a number of new naphthalene crown ethers in moderate yield from the appropriate bis-(halomethyl)naphthalenes and polyethylene glycols. The following crowns were synthesized: 2,3-naphtho-14-crown-4 (15%); 2,3-naphtho-17-crown-5 (19%); 2,3-naphtho-20-crown-6 (36%); 1,8-naphtho-15-crown-4 (20%); 1,8-naphtho-18-crown-5 (7%); 1,8-naphtho-21-crown-6 (38%); 1,2-naphtho-20-crown-6 (4%); 1,5-naphtho-19-crown-5 (11%); 1,5-naphtho-22-crown-6 (14%); 1,4-naphtho-22-crown-6 (9%); and 1,3-naphtho-21-crown-6 (16%). These compounds form a series which is very suitable for the study of naphthalene, as it is perturbed from a specific direction, since the perturber (cation) is situated in the center of the crown ring. The conformational effects of rotation of the ethyleneoxy strand about the naphthalene moiety in the 1,5-naphtho crown have also been investigated. The free energy of rotation for the pentaethyleneoxy strand in 1,5-naphtho-22-crown-6 is 6.2 Kcal, while for the tetraethyleneoxy strand in 1,5-naphtho-19-crown-5, it is greater than 21 Kcal.

Chapter 2 investigates the solid state structure of three crown ethers. They are the potassium thiocyanate complex of 2,3-naphtho-20-crown-6, 1,8-naphtho-21-crown-6, and the potassium thiocyanate complex of 1,8-naphtho-21-crown-6.

Chapter 3 shows the results of preliminary studies on intramolecular energy transfer in two crown ether modified systems using naphthalene and benzophenone as chromophores. The crown ethers do not have a large effect on these systems.

Chapter 4 reveals a new type of crown ether, the ferroceno-crown ether. The crown is capable of "ratcheting" or "squeezing down" on a cation of any size, so long as that cation is smaller than the maximum ring size of the crown.

Chapter 5 describes a computer-fluorescence spectrophotometer interface that has decreased the time required for data-callection and reduction by a factor of 100. The programs described here are listed in Appendix A and Appendix B.

Chapter 6 briefly looks at the synthesis of Farnum et al. of the gypsy moth pheremone, (+)-disparlure. Described here are improvements, additions, and scale-up procedures which have been added to this synthesis.

ACKNOWLEDGMENT

I wish to thank my wife Elene, not only for the friendship, companionship and love that she has shown throughout our college years, but also for the excellent graphics work that she did for this dissertation.

I wish to thank my mother for the loving care with which she raised me, as well as the financial assistance which she and my step father provided. Elene's mother and father are also thanked for their encouragement.

Dr. Lynn Sousa was outstanding as a research director. His many hours of consultation will be forever fondly remembered by me. The old members of the Sousa group were fun to learn chemistry with, as well as being good friends. They were Joe Bucher, Mark Johnson, and Jim Larsen.

Barb Duhl-Emswiler and John Emswiler were also very good friends, who will be always remembered and often missed. Ross and Chrysa Muenchausen, along with Barb, John, and myself, saw many sunrises from the fifth floor while working on the gypsy moth project.

I wish to thank Dr. Eugene Legoff for his friendship and consistently good chemical advice. Dr. Don Farnum (Uncle Don) tremendously helped to organize the way in which I thought about chemistry. Dr. Ring Carde was a pleasure to work with, and a future winner of the Nobel Prize.

I wish to thank Dr. Donald Ward for his help and patience in all the crystal structure determinations. Don is also an extraordinary friend and human being. The use of Dr. Harry Eick's PDP8 for 5 years is

gratefully acknowledged.

Finally, I wish to thank the Michigan State University Department of Chemistry, PRF, AND NSF for financial support.

To Elene, my mother and father, and Mikal and Aron.

Table of Contents

List of Figures

List of Tables

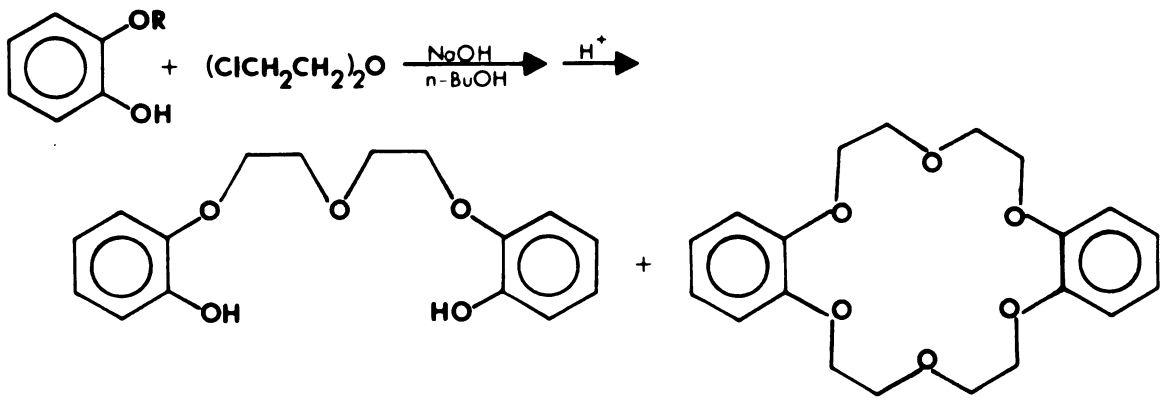
STUDIES OF THE PROPERTIES, SYNTHESIS, AND STRUCTURE OF SEVERAL CROWN ETHER MODIFIED CHROMOPHORES

CHAPTER 1

Synthesis of Crowns Designed to Directionally Orient Metal Ions (Perturbers) Relative to a Naphthalene Chormophore

Introduction

Since the first report of crown ethers by C.J. Pederson in 1967,[1] interest in synthetic multidentate ligands has continually increased. It is amusing to note that the discovery was accidental. Pederson was originally trying to react mono-THP-catechol with 2,2'-bis(chloroethyl)ether. It was the unprotected bis-phenol which gave rise to dibenzo-18-crown-6.



The details of this discovery have been published.[2] Since the original discovery by Pederson, many crown ethers have been made and studied, and several reviews have appeared.[3]

The crown ethers usually have the repeating subunit $(-CH_2-CH_2-O-)_n$. If the ethyleneoxy unit is lengthened by one carbon, the resulting propyleneoxy unit gives rise to a macrocycle which has nowhere near the complexing ability of the ethyleneoxy crown ethers. This difference is

attributed to conformational changes which alter complexation ability.

Crown ethers have been useful in synthetic organic chemistry, due to their ability to solvate cations, especially in a non-polar solvent. Some of the better known examples of this are solubilization of potassium permanganate in benzene ("purple benzene"),[4] solubilization of potassium fluoride in acetonitrile or benzene to form a "naked" fluorine anion,[5] and solubiliztion of potassium superoxide in dimethyl sulfoxide to give a reagent capable of performing nucleophilic displacement on alkyl halides (or other good leaving groups such as tosylate) to yield alcohols.[6] The use of crown ethers to promote base-catalyzed elimination reactions has been reviewed recently.[7] Crown ethers have even been used to solubilize rose bengal, a sensitizer in the photoaddition of singlet oxygen to carbon-carbon double bonds.[8]

Crown ethers have been used as protective groups for aryl diazonium salts.[9] Cram and Cram have described the use of crown ethers as complexing agents for a wide variety of cations ("Host-Guest Chemistry").[10] Cram *et al.* have used resolved chiral crown ethers to select cations on the basis of their absolute configuration.[11]

Crown ethers are well suited for the study of interaction between the complexed cation and functional groups attached to the crown ring. The Sousa group has recently reported on the interaction of the naphthalene system and cations complexed by crowns 3, 6, and 9.[12-16] Some of the studies have focused on the response on naphthalene photoexcited states to complexed and therefore oriented alkali metal cations.[12-14] Other work has investigated field induced π-polarization of naphthalene by an oriented positive monopole (complexed cation) using ^{13}C NMR.[15,16] X-ray studies of 6 and complexed 6,[17] and complexed 3[18]

(all of which are described in Chapter 2) have given some indication of crown conformation as has the ^{13}C NMR work.

An interesting conformational effect has also been seen in the 1,5-naphtho crowns (8 and 9). The ethyleneoxy strand in 9 rotates freely around the naphthalene moiety, whereas the barrier for rotation in 8 is very high.

Results and Discussion

Crown ethers 1 through 11 were designed with the specific intent of being able to probe naphthalene from a variety of different directions (see Figure 1). These crown ethers also allow proximity effects to be seen by altering the length of the ethyleneoxy strand, and moving the cation (preturber) closer or further away.

There are many examples in the literature of crown ethers and macrocyclic polyethers with bis(methylene)benzene (benzylic) subunits.[19] A template effect, which was first reported by Greene,[20] was also observed in the preparation of crown ethers derived from the 1,2-bis(bromomethyl)benzene subunit.[19c] These crowns were prepared using 1,2-bis(bromomethyl)benzene, the appropriate polyethylene glycol, and a suitable metal alkoxide (one which will maximize the template effect based on crown ring size and cation size). The absolute yields of these crowns varied between 1% and 53%, with yields maximized for cation size being 31% to 53%. The yields for these and other benzylic-type crowns are usually substantially lower when 1,2-bis(hydroxymethyl)benzene and the appropriate polyethylene glycol ditosylate are used. Phenolic crown ethers, however, often sucessfully use the ditosylate method with high yields of ring closure, but this is presumably due to the increased

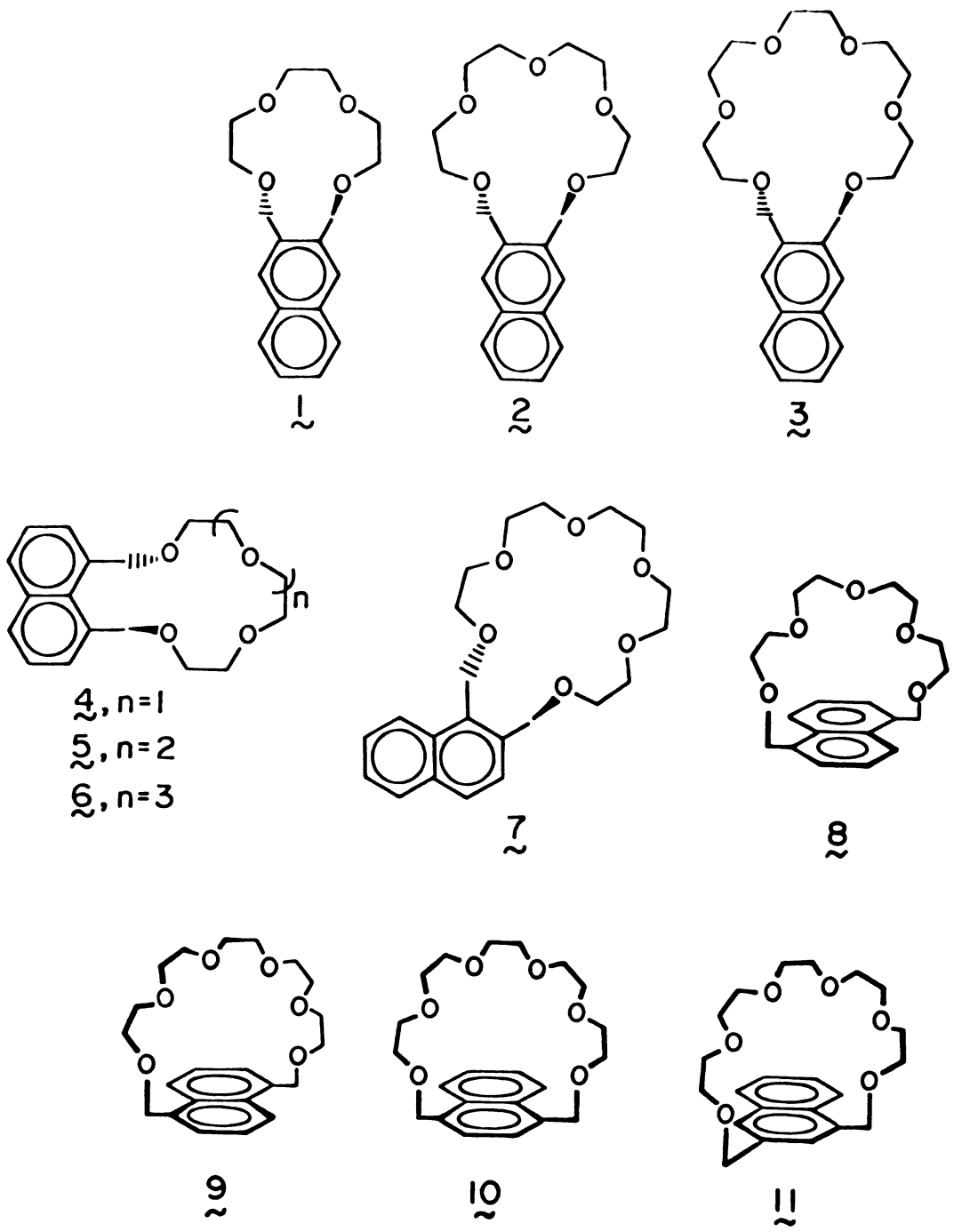
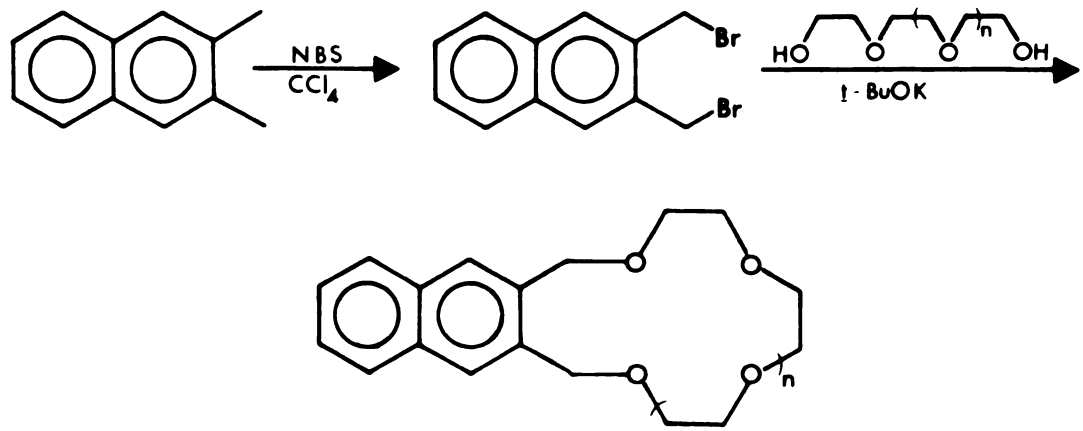


Figure 1. Synthesized naphthalene crown ethers, compounds 1 through 11.

nucleophilicity of the phenoxide over the benzylic alkoxide.

The first synthesis of crowns 3 and 6 used the appropriate bis(hydroxymethyl)naphthalene and pentaethylene glycol ditosylate. These two were stirred together at room temperature with two equivalents of potassium t-butoxide in tetrahydrofuran with ten percent dimethylformamide. The yields of 3 and 6 after chromatography and careful recrystallization were only 11% and 8%, respectively. The bis(hydroxymethyl)naphthalenes were prepared by displacement with sodium acetate on the appropriate bis(bromomethyl)naphthalene to give the corresponding bis(acetoxymethyl)naphthalene, followed by basic hydrolysis to the bis(hydroxymethyl)naphthalene. The use of bis(hydroxymethyl)naphthalenes and the appropriate polyethylene glycol ditosylate not only gave poor yields for crown ring formation reactions, but in all cases except the 1,8-derivatives represented two more steps for preparation of the bis(hydroxymethyl)naphthalenes.

A much higher yield crown ring closure reaction for 3 and 6 involved the addition of an equimolar mixture of the appropriate bis(halomethyl)naphthalene and pentaethylene glycol in dry tetrahydrofuran to a stirred refluxing slurry of potassium t-butoxide in tetrahydrofuran.

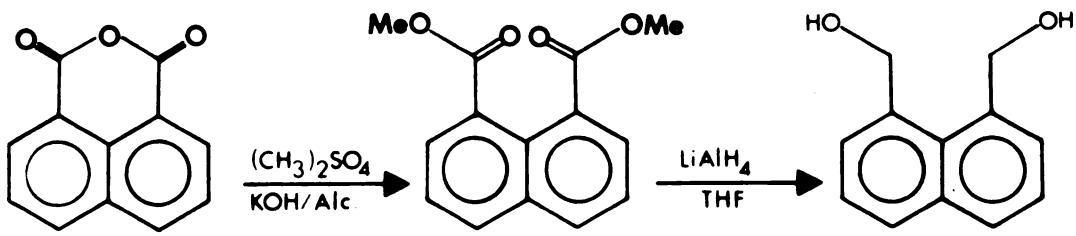


The yields of 3 and 6 after workup, alumina chromatography, and careful recrystallization were 36% and 38% respectively. The other crown forming reaction yields using the appropriate bis(bromomethyl)naphthalene and polyethylene glycol were: 1, 15%; 2, 19%; 4, 20%; 5, 7%; 8, 11%; 9, 14%; 10, 9% and 11, 16%. Crown 7 was synthesized in 4% yield from 1-chloromethyl-2(bromomethyl)naphthalene, which in turn was prepared from 1-chloromethyl-2-methyl naphthalene.

The method of preparation of the bis(bromomethyl)naphthalenes used N-bromosuccinimide in carbon tetrachloride with catalysis by a sunlamp, which produced both light and heat. Although both light and heat were tried independently, neither gave the reproducible results that the sun lamp gave, indicating that both heat and light are probably needed for this reaction. A previous reaction used in preparation of the dibromide, which involved adding benzoyl peroxide to N-bromosuccinimide in refluxing carbon tetrachloride yielded unpredictable results when this author tried it. One time the reaction gave 1,4-dibromo-2,3-dimethylnaphthalene from 2,3-dimethylnaphthalene, instead of the desired product, 2,3-bis(bromomethyl)naphthalene. The N-bromosuccinimide must

be recrystallized,[21] dried *in vacuo*, and stored in a dry dessicator. Use of N-bromosuccinimide not so treated gave poor yields of brominated product, and required long induction periods.

Preparation of 1,8-*bis*(bromomethyl)naphthalene was by a different method, due to the price of 1,8-dimethylnaphthalene (about $80/g in 1976, currently not commercially available). Instead, 1,8-naphthalic anhydride was used.



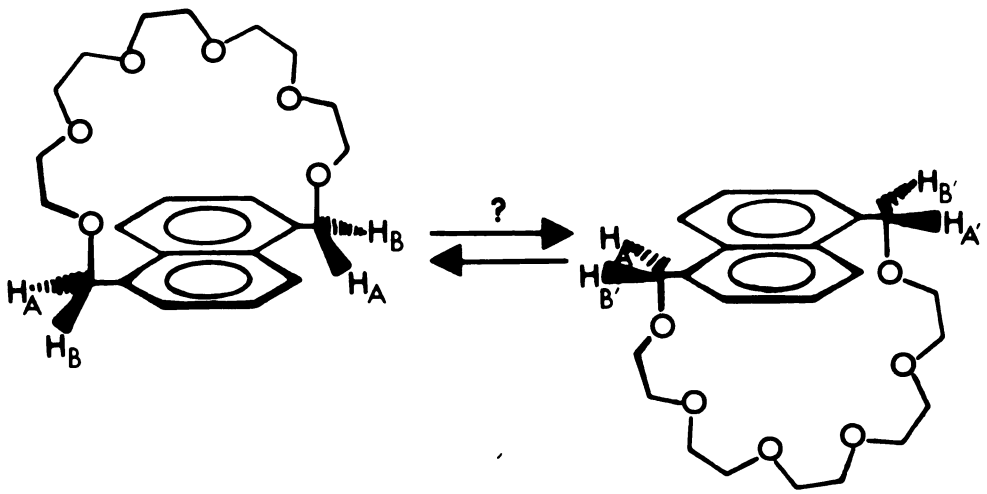
Although 1,8-naphthalic anhydride has been reduced directly to 1,8-*bis*(hydroxymethyl)naphthalene,[22] this procedure was found to give very poor yields. Instead, the anhydride was converted to a diester derivative, using the procedure of Geissman and Morris.[23] This involved a methylation using alcoholic potassium hydroxide and dimethyl sulfate. The yield was about 90%. The 1,8-*bis*(methoxycarbonyl)naphthalene was reduced to the diol in quantitative yield using lithium aluminum hydride.[24] The diol gave 1,8-*bis*(bromomethyl)naphthalene in about 60% yield from the diol using phosphorous tribromide in benzene.[22]

Most of the crowns pictured are likely to exist in solution as mixtures of rapidly interconverting enantiomeric conformations. An x-ray structure determination of 6[17] shows it to prefer chiral conformations in the solid state, as do 3[18] and 6[17] when complexed with potassium thiocyanate. As indicated above, the 1,5-crowns (8 and 9) are particularly interesting since interconversion of enantiomeric

conformations requires the ethyleneoxy strand to stretch past the naphthalene ring and through an achiral intermediate.

The Corey-Pauling-Koltun (CPK) model of crown 9 allows the six oxygen ethyleneoxy strand to slip past the edge of the naphthalene system without much difficulty. Even the CPK model of crown 8 allows its five oxygen ethyleneoxy strand to slip around to the other face of the naphthalene, but just barely. If the CPK model sizes reflect behavior at room temperature, the ethyleneoxy strand of crown 8 should be sweeping around the naphthalene faces slowly, but measureably. Crown 9 might be expected to be "skipping" the strand rapidly. In both crowns 8 and 9, the models show that interconversion of enantiomeric conformations requires that the ethyleneoxy strand free any previously complexed cation. The polyethyleneoxy strand would in effect be wiped free of ions bound by more than two crown oxygens as it passes the edge of the naphthalene ring. Therefore, complexed ions might be expected to slow the turning of the ethyleneoxy strand if the rate of ion decomplexaton is slower than the rate of rope skipping.

Experimental evidence of the extent of equilibraton of the enantiomeric conformations of crowns 8 and 9 is given by the ^1H NMR signal(s) of the naphthylic hydrogens (H_A and H_B below).



When the ethyleneoxy strand is over a face of the naphthalene ring, one hydrogen (H_A) on each naphthalene carbon is directed in the general direction of the peri hydrogen, and the other (H_B) is directed out away from the naphthalene system. Rope skipping would interchange the situations of the A and B hydrogens.

The ^{1}H NMR spectrum of the six oxygen 1,5-crown (9) shows a sharp singlet in the naphthylic region at room temperature. Assuming that H_A and H_B have different chemical shifts (see below), the ethyleneoxy strand is slipping past the naphthalene ring rapidly, as expected from inspection of CPK models. Since the naphthylic protons are diasteriotopic in all conformations except the achiral intermediate described above, one should be able to see two different protons in the ^{1}H NMR. High resolution low temperature spectra of 9 confirm that the interconversion of enantiomeric conformations is very rapid on the NMR time scale. Figure 2 shows the low temperature ^{1}H NMR spectra of 9 from -74 °C to -149 °C, with the coalescence temperature being -134 °C (139 K). The separation between the two peaks in the non-coalesced spectrum (-150 °C) is 178 Hz.

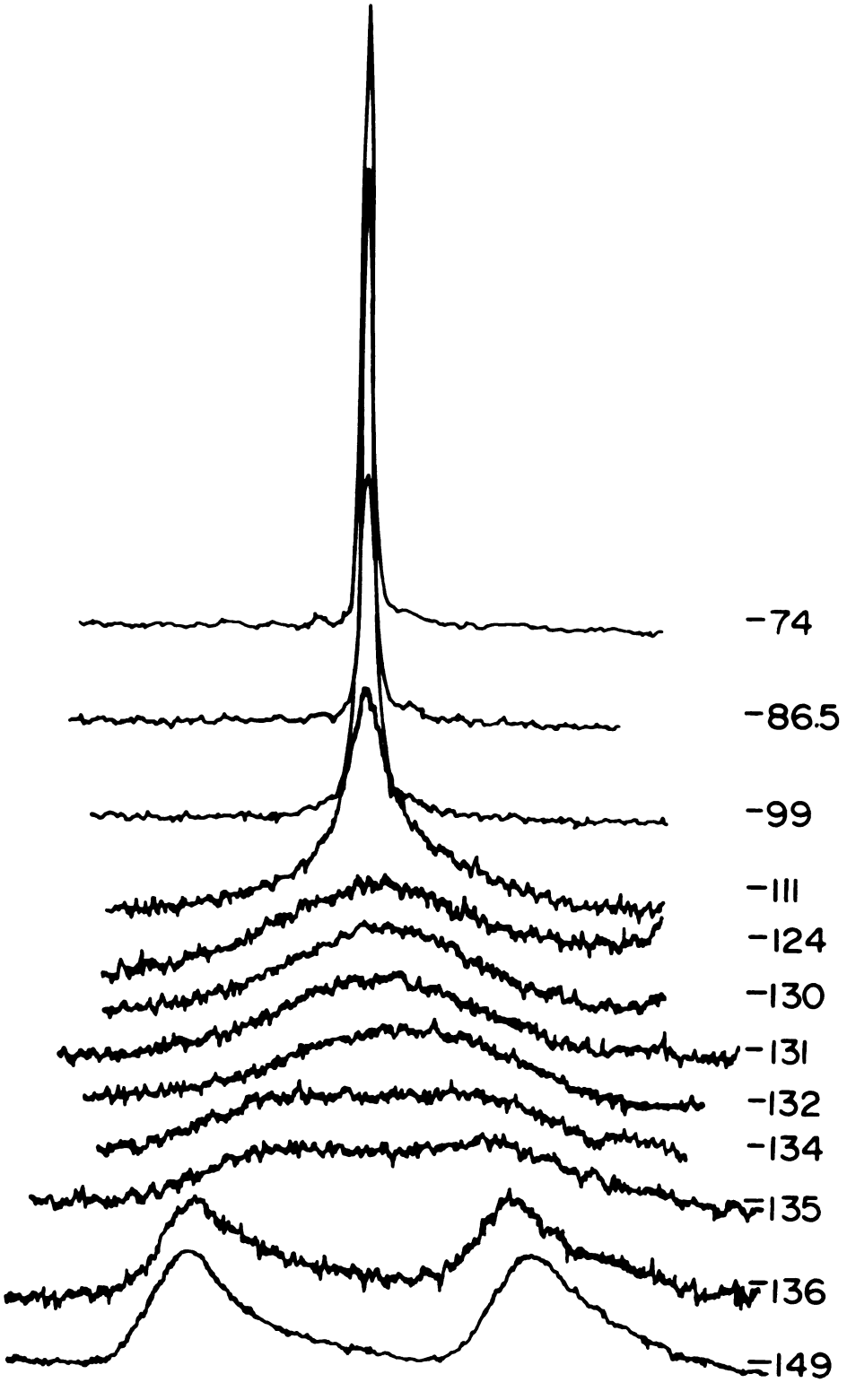


Figure 2. Low temperature ^{1}H NMR spectra of 1,5-naphtho-22-crown-6 (9).

We wanted to find the free energy of activation ($\Delta G^{\ddagger}$) about the sp^2-sp^3 carbon-carbon bond in this system. At coalescence,

$$2\pi\tau(\nu_A-\nu_B) = \sqrt{2}$$

or

$$\tau = \sqrt{2} / (2\pi)(\nu_A-\nu_B)$$

where

τ = the period (or lifetime) of the exchanging system at coalescence

$\nu_A-\nu_B$ = the maximum difference in Hz between peak A and peak B, i.e. the separation between the two peaks in the non coalesced spectrum, before the movement inwards towards coalescence is started.

Since[25]

$$k = (\underline{\underline{k}}/h)(T)(e^{-\Delta G^{\ddagger}/RT})$$

where

k = exchange rate at coalescence = $1/2\tau$

$\underline{\underline{k}} = 1.380 \times 10^{-16}$ erg deg^{-1}

$h = 6.625 \times 10^{-27}$ erg sec

T = temperature (K)

$\Delta G^{\ddagger}$ = free energy of activation for rotation

$R = 1.987$ cal deg^{-1} mol^{-1}

Rearranging, we get

$$\Delta G^{\ddagger} = -RT\ln[(k/T)(h/\underline{\underline{k}})]$$

and since

$$k = 1/2\tau = (\pi)(\nu_A-\nu_B)/\sqrt{2}$$

the final expression for $\Delta G^{\ddagger}$ is

$$\Delta G^{\ddagger} = -RT\ln[(\nu_A-\nu_B)(\pi h)/(T\underline{\underline{k}}\sqrt{2})] \qquad (1)$$

$\Delta G^{\ddagger}$ for 9, using equation (1) , is 6.2 Kcal. The free energy of rotation about the C2-C3 bond in butane is 4 to 6 Kcal, so the rotation of the ethyleneoxy strand around the naphthalene moiety is extremely facile.

Alkali metal salts, which are known to be complexed with 9 from ^{13}C NMR and photophysical measurements,[14] do not appear to slow the rate of crown ring rotation at temperatures above -80 °C. A saturated solution of potassium chloride in d_6-acetone at -80 °C shows no beginning of decoalescence. Judging from ^{13}C NMR experiments in alcohol at room temperature showing complexation of 9 with this salt,[16] and the fact that lower temperatures increase the complexation constant of this particular crown[14], the cation should be complexed under the conditions of the experiment. If decoalescence were starting to take place, one would see a shrinking and widening of the naphthalene proton peak. Unfortunately, the system could not be taken to lower temperatures, since the solubility of the salt was already marginal in acetone. At -150 °C, the crown ether is marginally soluble in dichlorodifluoromethane.

In contrast to crown 9, crown 8 with a shorter ethyleneoxy strand shows two diastereotopic protons at room temperature (25 °C). The five oxygen 1,5-crown (8) has an AB quartet in the naphthylic region of its room temperature NMR spectrum indicating that its equilibration is even slower than predicted from CPK model work. The high temperature ^{1}H NMR spectra of 8 (Figure 3) shows no coalescence to be taking place at up to 160 °C. The line broadening at this temperature is probably not real, since the sample could not spin in the heated NMR probe past 55 °C. The

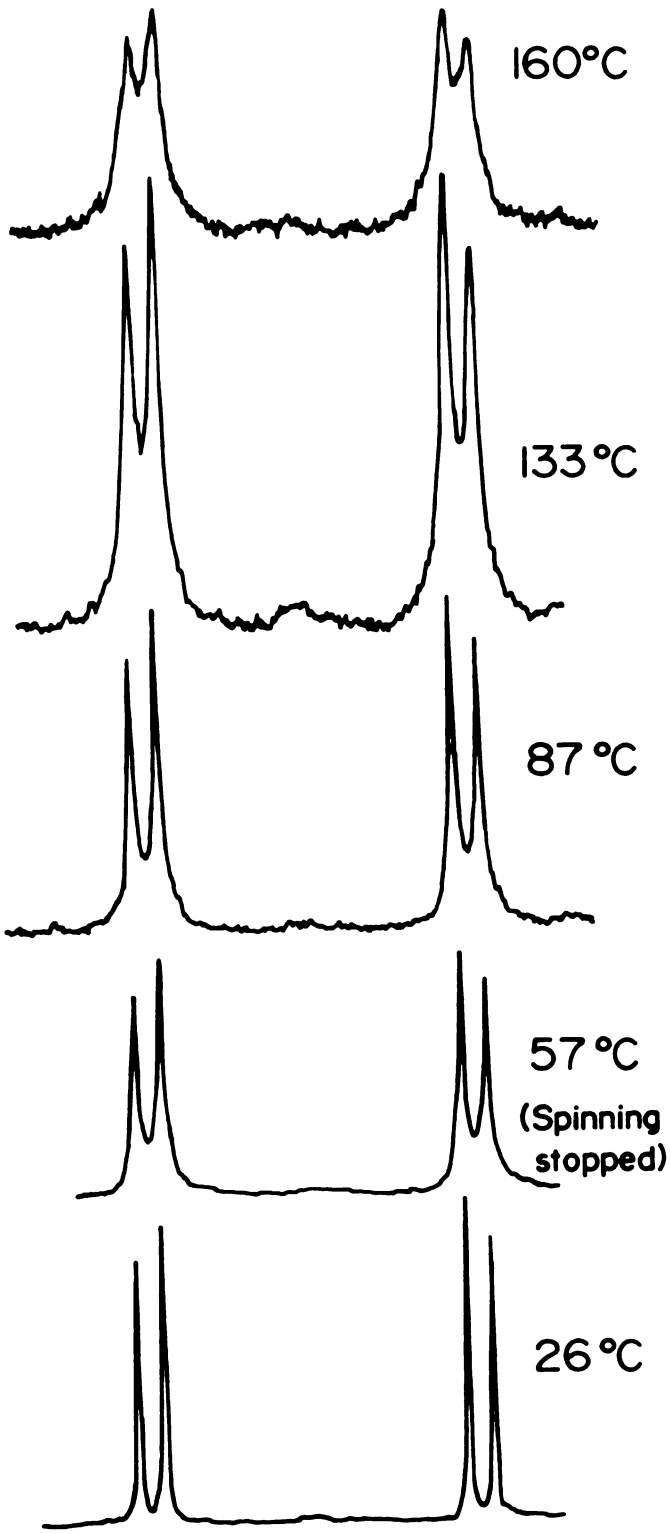


Figure 3. High temperature ^{1}H NMR specta of 1,5-naphtho-19-crown-5 (8).

non-spin conditions will tend to slightly broaden the line. The spearation between peaks of the two diasterotopic protons is 158 Hz. This implies that the free energy of activation for rotation in 8 is greater than 21 Kcal, making interconversion much more difficult than in 9. Inspection of Corey-Pauling-Koltan models for 8 was very misleading, since interconversion of enantiomeric forms of 8 appears to be only moderately hindered.

There are several other crown ethers which the Sousa group has contemplated making. These crowns involve probing a chromophore from not just one direction, but from several at the same time. Three such crowns are 12, 13, and 14 (see Figure 4). Although crowns 12, 13, and 14 have not been synthesized, some work in preparing the immediate precursors to crowns 12 and 14 has been done. The preparation of 1,4,5,8-tetrakis(bromomethyl)naphthalene, the starting material for crown 12, is analogous to that for the preparation of 1,8-bis(bromomethyl)naphthalene but starts instead from commercially available 1,4,5,8-naphthalene carboxylic anhydride.

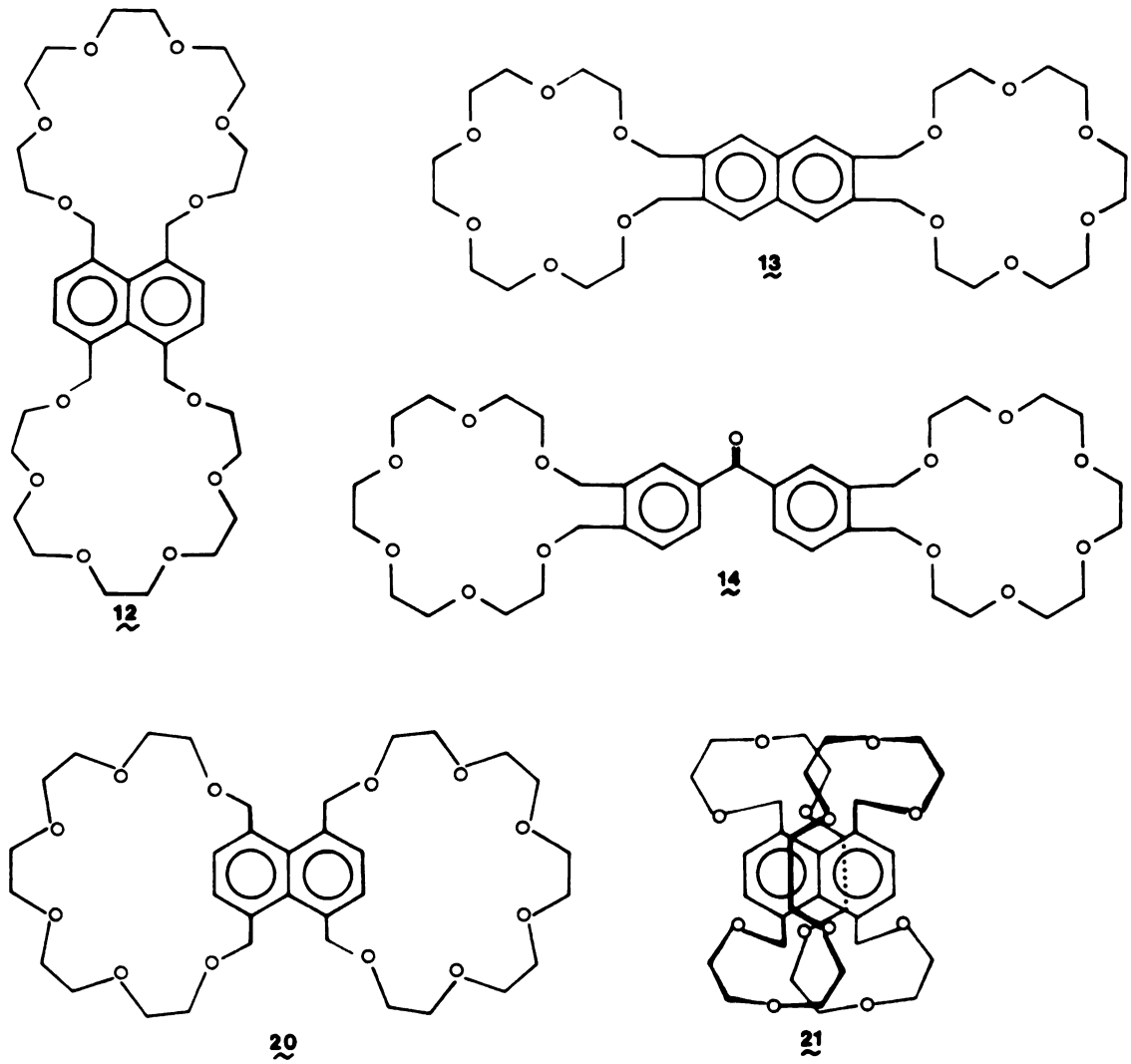
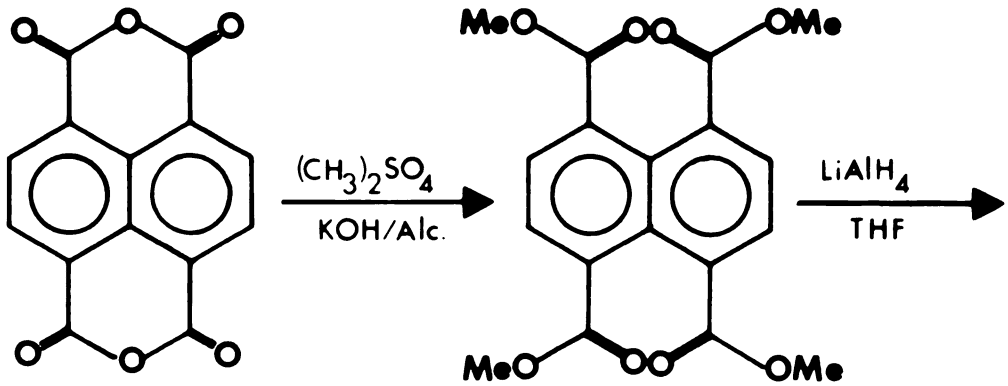
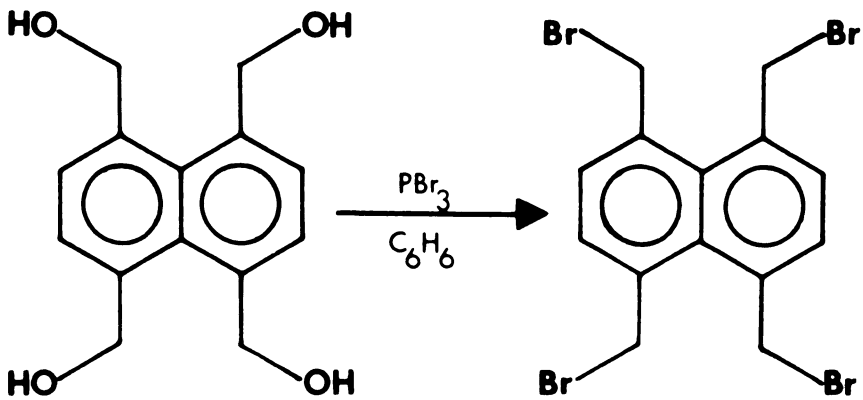


Figure 4. Proposed crown ethers 12, 13, 14, 20, and 21.

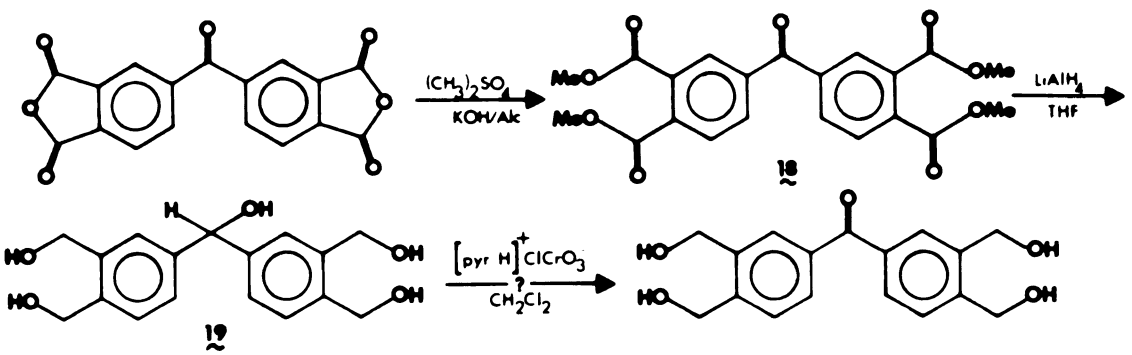


15

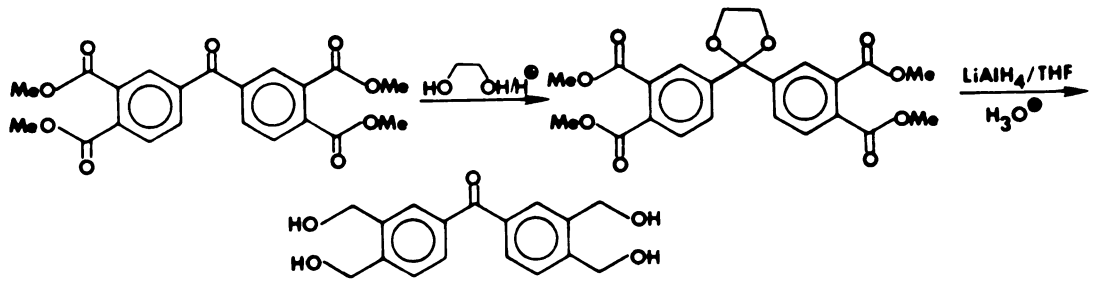


16 17

For crown 14, BDTA[24] was converted to the tetraester and reduced to give a pentaol. This pentaol can probably be selectively oxidized to give 3,3',4,4'-tetrakis(hydroxymethyl)benzophenone. In a preliminary experiment, oxidation of the pentaol with 1.1 equivalents of pyridinium chlorochromate yielded a product which produced an infrared peak at 1660 cm^{-1} (compare with the carbonyl in benzophenone at 1665 cm^{-1}), and no peak near 1690 cm^{-1} (compare with the carbonyl in benzaldehyde). This indicates oxidation of the middle hydroxyl group occurs preferentially to those on the ends of the molecule.



Another approach to this tetraol would be to first protect the ketone carbonyl, and then reduce the ester functionalities.



Preliminary experiments done show that the reaction of 3,3',4,4'-tetrakis(methoxycarbonyl)benzophenone with ethylene glycol and a trace of acid gave an equivalent of water in a Dean-Stark trap, and a solid product of new melting point. This route is probably preferential to the selective oxidation. Although no work on crown 13 has been done, it should be possible to make the tetrabromide from the known 2,3,6,7-tetramethylnaphthalene[27] via N-bromosuccinimide bromination. A sample of 1,4,5,8-tetramethylnaphthalene was successfully brominated to give 1,4,5,8-tetrakis(bromomethyl)naphthalene, which was identical to the sample previously prepared.[28] The 2,3,6,7-system should be easier to brominate, since it is not as sterically hindered.

The problem with crowns 12, 13, and possibly 14 is that a single product will not be obtained when the crown is prepared. Although 12 should be the major product when 1,4,5,8-tetrakis(bromomethyl)-naphthalene is treated with the appropriate polyethylene glycol, there are two other possible products, 20 and 21 (see Figure 4). This mixture of three crowns may be very difficult to separate. Crown 21 exists as two discrete enantiomers. These crowns should present interesting problems for the future.

EXPERIMENTAL

General. All melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. The ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer with deuterochloroform (1538.2 Hz) as an internal standard. The ^{1}H NMR spectra were taken on a Varian T-60 spectrometer with tetramethylsilane and an internal standard, except high resolution spectra, which were taken on a Bruker WH-180 multinuclear spectrometer, with a 10 mm proton insert. Low temperature spectra (<-90°C) were taken with 10 mg of crown dissolved in 3 mL dichlorodifluoromethane with 0.3 mL deuteroacetone as a lock solvent, and 0.1 μL tetramethylsilane as an internal standard. High temperature spectra (>35°C) were taken with 10 mg of crown dissolved in 3 mL d_6-dimethylsulfoxide with 0.1 μL tetramethylsilane as an internal standard. The mass spectra were taken on a Hitachi Perkin-Elmer RMU-6D spectrometer. Tetrahydrofuran was distilled from potassium benzophenone ketyl immediately before use. All reactions were done under nitrogen. Microanalyses were performed by Chemalytics, Inc., Tempe, Arizona, or Instranal Laboratory, Rensselaer, N.Y.

General Procedure for the Synthesis of bis(bromomethyl)naphthalenes. Dimethyl naphthalene (10.0 g, 64.0 mmol) and recrystallized N-bromosuccinimide[19] (46.0 g, 258 mmol) in 250 mL of carbon tetrachloride was irradiated with a 200 watt sun lamp. The reaction was greater than 90% complete (^{1}H NMR) in less than 30 min after noticable conversion of the N-bromosuccinimide to succinimide started. The induction period was

highly variable. The mixture was filtered, and the succinimide was extracted with hot carbon tetrachloride. Some of the dibromides were exceedingly soluble in carbon tetrachloride (e.g. the 2,3-bis(bromomethyl)naphthalene), but others (e.g. 1,4 and 1,5) required multiple extractions to withdraw all of the brominated product from the succinimide. The combined filtrate and extracts were evaporated to give 72-81% yield of the dibromide. The dibromides could be recrystallized from benzene - petroleum ether to remove traces of mono-brominated and starting material.

Preparation of 2,3-bis(bromomethyl)naphthalene. Prepared as described above, 81% yield; m.p. 145-146°C; ^{1}H NMR ($CDCl_3$) δ 4.77 (s, 4 H), 7.15-7.7 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 30.88, 127.08, 127.60, 130.63, 133.19, 133.66.

Preparation of 1,4-bis(bromomethyl)naphthalene. Prepared as described above, 72% yield; mp 190-191°C; ^{1}H NMR ($CDCl_3$) δ 4.83 (s, 4 H), 7.3-8.1 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 31.05, 124.50, 126.76, 127.14, 131.53, 134.85.

Preparation of 1,5-bis(bromomethyl)naphthalene. Prepared as described above, 78% yield; mp 213.5-214°C; ^{1}H NMR ($CDCl_3$) δ 4.87 (s, 4 H), 7.1-8.3 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 31.46, 125.29, 125.94, 128.03, 134.08.

Preparation of 1,3-bis(bromomethyl)naphthalene. Prepared as described above, 76% yield; mp 116-116.5°C; ^{1}H NMR ($CDCl_3$) δ 4.50 (s, 2 H), 4.77 (s, 2 H), 7.2-8.1 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 30.86, 33.10, 123.53, 126.65, 127.06, 128.29, 128.75, 129.25, 130.51, 133.68, 134.11, 134.46.

Preparation of 1-chloromethyl-2-(bromomethyl)naphthalene. Prepared as described above, except that 1-chloromethyl-2-methylnaphthalene was used, 78% yield; mp 130-131.5°C; ^{1}H NMR ($CDCl_3$) δ 4.83 (s, 2 H), 5.08 (s, 2 H), 7.08-8.07 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 30.52, 37.99, 123.48, 126.47, 127.21, 127.49, 128.59, 129.93, 131.50, 131.65, 133.60, 134.45.

Preparation of 1,8-bis(methoxycarbonyl)naphthalene. The dimethyl ester of 1,8-naphthalene dicarboxylic acid was prepared by the method of Geissman and Morris[23] from the 1,8-naphthalic anhydride (Aldrich). Spectral data were as follows: ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 6H), 7.2-8.0 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 51.77, 125.01, 129.55, 129.94, 132.17, 134.03, 168.94.

Preparation of 1,8-bis(hydroxymethyl)naphthalene. To 40.0 g (0.164 mol, 2 equiv) 1,8-bis(methoxycarbonyl)naphthalene in 1 L THF was cautiously added 20.0 g (0.528 mol, 3.2 equiv) lithium aluminum hydride (Alfa-Ventron) under a dry nitrogen atmosphere. The lithium aluminum hydride was added at such a rate that reflux was not vigorous. The reaction was allowed to stir for 8 H. Water (20 mL), 15% sodium hydroxide (20 mL), and then water again (60 mL) were added over a 2 h period.[24] Initial addition of water should be slow, and the nitrogen flow should be fast. The resulting white granular precipitate was filtered and washed with an additional 250 mL THF. The solvent was removed from the filtrate under reduced pressure, and the resulting solid recrystallized from methanol, 98% yield; m.p. 156-157 °C; ^{1}H NMR ($CDCl_3$) δ 3.30 (s, 1H, disappears with D_2O), 5.13 (s, 2H), 7.25-7.90 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 63.80, 124.96, 129.10, 130.15, 135.18, 138.54.

Preparation of 1,8-bis(bromomethyl)naphthalene. 1,8-Bis(hydroxymethyl)-naphthalene was brominated by the method of Bergman and Szmuszkovicz[22], to give 1,8-bis(bromomethyl)-naphthalene: mp 130-131°C; ^{1}H NMR ($CDCl_3$) δ 5.22 (s,4 H), 7.20-7.80 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 35.43, 123.91, 127.27, 130.11, 131.26, 131.63, 134.30.

General Procedure for the Synthesis of the Crowns. A solution of the appropriate polyethylene glycol (10 mmol) and bis(halomethyl)-naphthalene (10 mmol) in 150 mL dry THF was added dropwise to a refluxing tetrahydrofuran slurry of potassium t-butoxide (2.36 g, 21 mmol in 500 mL THF) over a six h period under a dry nitrogen atmosphere. The slurry was stirred at reflux another four h before filtration through a diatomatious earth pad, and subsequent washing of the solid with tetrahydrofuran. Solvent was removed from the filtrate under vacuum, and the resulting yellow oil was chromatographed on a quartz column with alumina (400 g, Fisher neutral alumina with Lumilux[29] added) eluted with dichloromethane-methanol (200:1). The first band eluted which was observable on the column using a 375 nm lamp gave a yellow-brown oil. Some of the fractions of this band crystallize from ether-pentane, and can be recrystallized from cyclohexane except as otherwise noted.

Preparation of 2,3-naphtho-14-crown-4 (1). Prepared as above except that lithium t-butoxide (1.67 g, 21 mmol) and triethylene glycol (1.44g, 10 mmol) were used: (460 mg, 15.2%); mp 86.0-88.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 4 H), 3.73 (s, 8 H), 4.87 (s, 4 H), 7.13-7.68 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.27, 70.00, 71.37, 71.46, 125.72, 127.46, 132.83,

134.89; IR($CHCl_3$) cm^{-1} 3000, 2850 (s), 1550, 1450, 1350, 1300, 1250, 1125 (s), 1025 (w), 975, 925, 900, 875, 800; m/e 302.

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.77; H, 7.40.

Preparation of 2,3-naphtho-17-crown-5 (2). Prepared as above except that lithium t-butoxide (1.67 g, 21 mmol) and tetraethylene glycol (1.67 g, 10 mmol) were used: 652 mg (18.8%); mp 51.0-53.0 °C; ^1H NMR ($CDCl_3$) δ 3.58 (s, 10 H), 3.70 (s, 10 H), 4.8 (s, 4H), 7.15-7.73 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.69, 70.43, 70.71, 70.96, 71.14, 125.71, 126.85, 127.44, 132.63, 134.69; IR ($CDCl_3$) cm^{-1} 2850 (s), 1550, 1450, 1350, 1300, 1250 (w), 1100 (s), 980, 950, 890, 810 (s); m/e 346.

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.58; H, 7.36.

Preparation of 2,3-naphtho-20-crown-6 (3). Prepared as above except that pentaethylene glycol (2.39 g, 10 mmol) was used: 1.39 g (35.6%); mp 58.0-58.5 °C; ^1H NMR ($CDCl_3$) δ 3.63 (s, 12 H), 3.68 (s, 8H), 4.78 (s, 4H), 7.13-7.77 (br.m, 6H); ^{13}C NMR ($CDCl_3$) δ 69.80, 70.67, 71.31, 125.72, 127.35, 127.57, 132.63, 134.55; IR ($CHCl_3$) cm^{-1} 3000, 2850-2025 (s), 1470 (w), 1450 (w), 1350, 1075-1150 (s); m/e 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.65; H, 7.89.

Preparation of 1,8-naphtho-15-crown-4 (4). Prepared as above except that lithium t-butoxide (1.67 g, 21 mmol) and triethylene glycol (1.44 g, 10 mmol) were used: 619 mg (20.5%); mp 77.0-77.5 °C; ^1H NMR ($CDCl_3$) δ 3.62 (s, 4 H), 3.80 (s, 8 H), 5.17 (s, 4 H), 7.28-7.77 (br.m, 6 H);

^{13}C NMR ($CDCl_3$) δ 69.74, 70.19, 71.09, 73.13, 124.79, 128.17, 129.43, 134.74, 135.33; IR ($CHCl_3$) cm^{-1} 3010, 2860 (s), 1600 (w), 1450, 1350, 1290, 1240, 1100, 1000 (w), 960, 940, 875, 800 (s); m/e 302.

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.72; H, 7.47.

Preparation of 1,8-naphtho-18-crown-5 (5). Prepared as above except that lithium t-butoxide (1.67 g, 21 mmol) and tetraethylene glycol (1.94 g, 10 mmol) were used; 239 mg (6.9%); mp 69.5-70.0 °C; ^1H NMR ($CDCl_3$) δ 3.60 (s, 10 H), 3.72 (s, 10 H), 5.03 (s, 4 H), 7.22-7.70 (br.m., 6 H); ^{13}C NMR ($CDCl_3$) δ 70.00, 70.19, 70.66, 77.16, 124.73, 129.01, 129.68, 130.69, 134.21; IR ($CHCl_3$) cm^{-1} 3000, 2850, 1720 (w), 1600 (w), 1450, 1350, 1300, 1250 (w), 1100 (s), 1000, 940 (w), 880, 800 (s); m/e 346.

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.49; H, 7.47.

Preparation of 1,8-naphtho-21-crown-6 (6). Prepared as above except that pentaethylene glycol (2.39 g, 10 mmol) was used: 1.50 g (38.4%); mp 53.5-55.5 °C; ^1H NMR ($CDCl_3$) δ 3.73 (s, 12 H), 3.78 (s, 8 H), 5.17 (s, 4 H), 7.35-7.87 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.30, 70.43, 70.58, 124.62, 129.90, 130.19, 131.11, 133.91, 135.51; IR ($CHCl_3$) cm^{-1} 3050 (w), 1460, 1350, 1125 (s), 1090 (s), 840, 820; m/e 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.77; H, 7.79.

Preparation of 1,2-naphtho-20-crown-6 (7). Prepared as above except that pentaethylene glycol (2.39 g, 10 mmol) and 1-chloromethyl-2-(bromomethyl)naphthalene (2.70 g, 10 mmol) were used: 172 mg (4.4%); mp

58.0-58.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.62 (s, 12 H), 3.65 (s, 8 H), 4.44 (s, 2 H), 5.05 (s, 2 H), 7.33-8.22 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 124.69, 125.49, 126.16, 127.23, 127.89, 128.11, 128.47, 132.16, 133.16, 133.39, 135.06; IR ($CDCl_3$) cm^{-1} 3000, 2860 (s), 1460, 1450, 1350, 1300, 1250, 1100 (s), 815; m/e 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.84; H, 7.79.

Preparation of 1,5-naphtho-19-crown-5 (8). Prepared as above except that tetraethylene glycol (1.94 g, 10 mmol) and lithium t-butoxide (1.67 g, 21 mmol) were used: 391 mg (11.3% after molecular distillation (110°C at 0.05 mm Hg)); ^{1}H NMR ($CDCl_3$) δ 3.35 (s, 2H), 3.42 (s, 2H), 3.45 (s, 2H), 3.52 (s, 2H), 4.83 (dd, 4H, J_{AB}=12 Hz, d separated by 1.00 ppm), 7.1-7.4 (br.m, 4H), 7.7-8.1 (br.m, 2H); ^{13}C NMR ($CDCl_3$) δ 68.87, 69.53, 69.76, 69.96, 71.81, 124.77, 125.33, 127.25, 132.35, 134.07; IR (neat) cm^{-1} 3075 (w), 3050 (w), 3025 (w), 1750, 1710 (w), 1600 (w), 1540, 1460, 1360, 1300, 1250, 1110 (s), 1050, 950, 875, 800(s); m/e 346.

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.73; H, 7.61.

Preparation of 1,5-naphtho-22-crown-6 (9). Prepared as above except that pentaethylene glycol (2.39 g, 10 mmol) was used; 544 mg (14.2%) yield; mp 55.0-56.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.08 (s, 4 H), 3.25 (s, 8 H), 3.52 (s, 8 H), 4.70 (s, 4h), 7.37-8.10 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 68.75, 69.69, 70.00, 70.21, 71.64, 124.90, 126.68, 132.00, 134.04; IR ($CHCl_3$) cm^{-1} 2975, 2945 (s), 2900 (s), 2865 (s), 1500, 1405, 1290, 1175 (s), 1110, 1035, 825; m/e 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67, H, 7.74. Found: C, 67.87;

H, 7.71.

Preparation of 1,4-naphtho-22-crown-6 (10). Prepared as above except that pentaethylene glycol (2.39 g, 10 mmol) was used; 359 mg (9.2%) yield; mp 71.5-72.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.37 (s, 4 H), 3.42 (s, 8 H), 3.60 (s, 8 H), 4.97 (s, 4h), 7.1-8.2 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.99, 70.46, 70.55, 70.75, 124.07, 125.15, 125.48, 131.40, 133.61; IR ($CHCl_3$) cm^{-1} 2990, 2850 (s), 1600 (w) 1450 (w), 1350, 1300 (w), 1100 (s), 975, 870, 800 (s); m/e 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67, H, 7.74. Found: C, 67.72; H, 7.54.

Prepartion of 1,3-naphtho-21-crown-6 (11). Prepared as above except that pentaethylene glycol (2.39 g, 10 mmol) was used; 632 mg (16.2% after molecular distillation (120°C at 0.05 Hg)); ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 12 H), 3.65 (s, 8 H), 4.63 (s, 2 H), 4.97 (s, 2 H), 7.30-7.98 (br.m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.21, 69.50, 69.79, 70.09, 70.48, 70.69, 71.13, 73.25, 123.32, 125.71, 125.83, 126.22, 126.58, 126.80, 128.30, 133.41, 134.08, 135.25; IR ($CHCl_3$) cm^{-1} 3000, 2860 (s), 1700, 1450, 1350, 1290, 1240, 1100 (s), 940, 875, 800; m/e 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67, H, 7.74. Found: C, 67.41; H, 7.63.

Preparation of 1,4,5,8-tetrakis(methoxycarbonyl)naphthalene (15). To a solution of 1,4,5,8-naphthalene tetracarboxylic dianhydride (93 g, 0.35 mol) in 670 mL 2.0 N ethanolic KOH was added dimethyl sulfate (373 mL, 3.45 mol) and concurrently 1330 mL 2.0 N ethanolic KOH in a dropwise fashion. The reaction was done at 0 °C, with mechanical stirring, and

under nitrogen. After 12 to 16 hours, the solvent was removed under reduced pressure, and the resulting sludge extracted several times by boiling in methanol and decantation. The methanol was diluted with an equal amount of water, and upon cooling gave 12.3 g crystals, 10% yield; (methoxycarbonyl)naphthalene mp 196-197.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 12H), 7.92 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 52.33, 128.97, 133.16, 168.09; IR (Nujol) cm^{-1} 1715, 1280, 1200, 1160(w), 1110(w), 855, 750, 720; m/e 360.

Preparation of 1,4,5,8-tetrakis(hydroxymethyl)naphthalene (16). To a solution of lithium aluminum hydride (30.0 g, 0.79 mol) in 750 mL THF under nitrogen was added tetraester 15 (71.6 g, 0.199 mol) in 750 mL THF in a dropwise fashion over a 2 hour period. After 12 hours additional stirring, water (30 mL), 15% NaOH (30 mL), and water (90 mL) were added. After 4 additional hours of stirring, the pure white mixture was filtered, the solvent removed under reduced pressure, and the resulting solid, recrystallized in methanol and water, to give 12.8 g of a light brown solid, 26% yield; mp 130-132 °C; ^{1}H NMR (d_6-DMSO) δ 3.30 (s, 4H, exchangeable with D_2O), 5.00 (s,8H), 7.43 (s, 4H); ^{13}C NMR (CD_3OD) δ 64.30, 127.32, 182.21, 188.70; IR (Nujol) cm^{-1} 3300, 3200, 1460, 1375, 1295(w), 1055, 100, 845(w); m/e 248.

Preparation of 1,4,5,8-tetrakis(bromomethyl)naphthalene (17). To a 70 °C solution of 16 (2,5 g, 10 mmol) in 300 mL benzene containing 0.2 mL pyridine was added phosphorous tribromide (3.2 mL, 20 mmol) at such a rate that the temperature of the reaction did not exceed 74 °C. After an additional 2 hours at 55 °C, followed by cooling, the solution was washed with water (3 x 100 mL), then washed with saturated bicarbonate solution (2 x 100 mL), and the benzene layer dried over magnesium

sulfate. After removal of the solvent under reduced pressure, the residue was recrystallized from benzene-petroleum ether to give 250 mg 17 as a white solid, 5% yield; mp 107-109 °C; ^{1}H NMR (CCl_4) δ 4.77 (s, 8H), 7.17 (s, 4H); m/e - see Figure 5.

Preparation of 3,4,3',4'-tetrakis(methoxycarbonyl)benzophenone (18). To a solution of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (93.0 g, 0.29 mol) in 2.0 N ethanolic KOH (670 mL) was added dimethyl sulfate (373 mL, 3.45 mol) and concurrently 2.0 N ethanolic KOH (1330 mL) in a dropwise fashion. The reaction was done at 0 °C, with mechanical stirring, and under nitrogen. After 12 to 16 hours, the solution was filtered, warmed, and water added until the solution just started to turn milky. After cooling, 62.1 g of crystalline 18 were collected, 52% yield; mp 84-86 °C; ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 1H), 3.90 (s, 1H), 7.6-8.3 (br.m, 1H); ^{13}C NMR ($CDCl_3$) δ 59.00, 130.35, 131.87, 132.41, 136.19, 138.63, 166.64, 167.43, 193.09; IR (Nujol) cm^{-1} 1740(s), 1660, 1480(w), 1395(w), 1280(s), 1260, 1240, 1120, 1060, 990(w), 940; m/e 414.

Preparation of 3,4,3',4'-tetrakis(hydroxymethyl)benzhydrol (19). To a solution of lithium aluminum hydride (30.0 g, 0.79 mol) in 750 mL THF under nitrogen was added tetraester 18 (40.9 g, 99 mmol) in 750 mL THF in a dropwise fashion. The tetraester was added at such a rate that a steady reflux was maintained. After addition was complete, the solution was gently refluxed for 12 hours. Water (30 mL), 15 % NaOH (30 mL), and water (90 mL) were then slowly added. After 4 hours of stirring, the pure white mixture was filtered, and the filtrate concentrated under reduced pressure, to give 23.8 g solid 19, 79% yield (note: on one of the runs, 19 was held by the lithium salts. It was necessary to grind

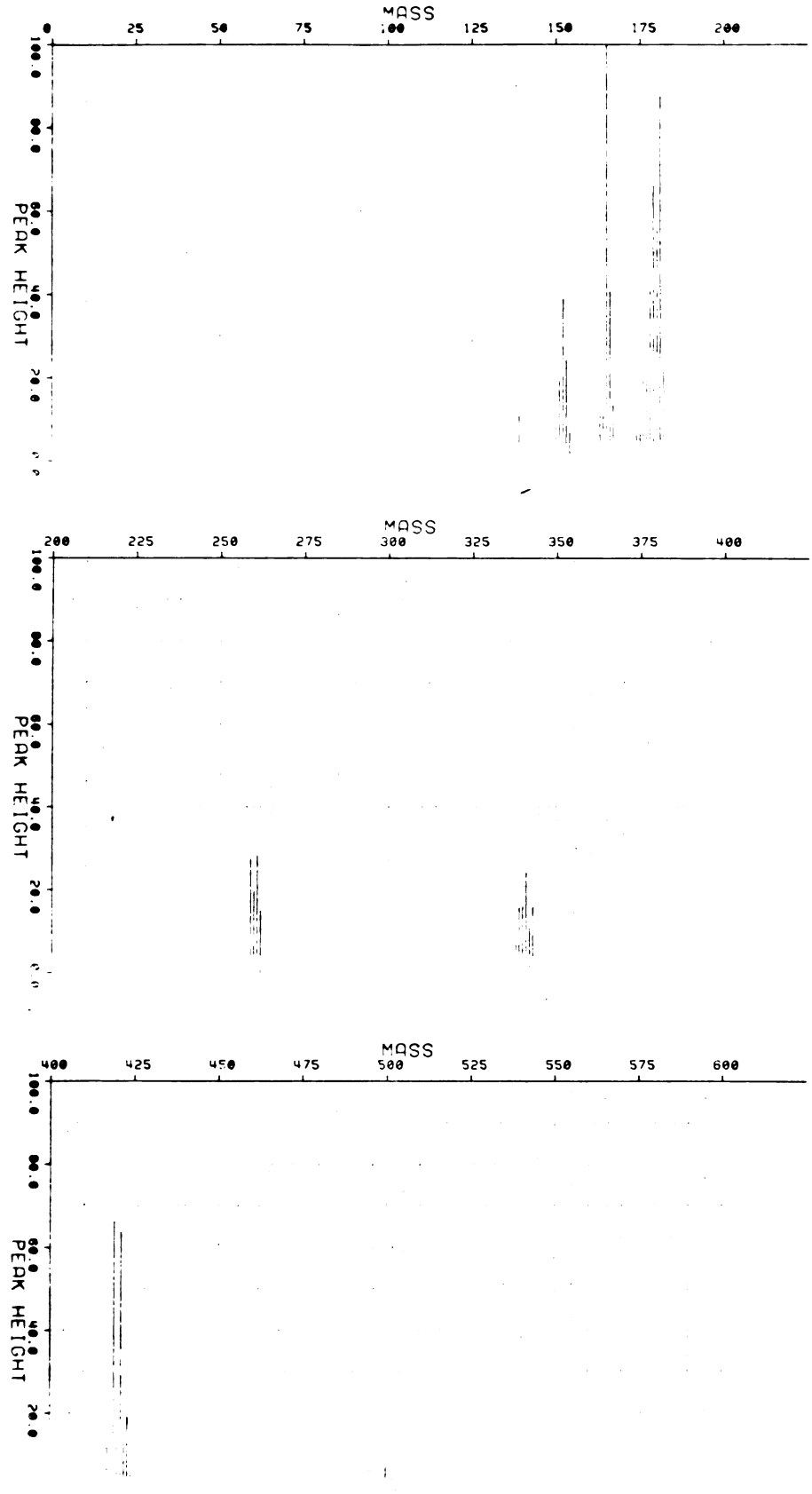


Figure 5. Mass spectrum of 1,4,5,8-tetrakis(bromomethyl)naphthalene (17).

the salts and continuously extract with THF to free 19 from the salts); mp 150-152 °C; ^{1}H NMR (CD_3OD, external TMS) δ 4.23 (s, 4H), 4.37 (s, 4H), 4.0-4.8 (br.m, 5H, dissappear with D_2O), 5.37 (s, 1H), 6.7-7.2 (br.m, 6H); ^{13}C NMR (d_6-DMSO) δ 60.54, 60.69, 74.55, 124.59, 125.11, 126.95, 137.83, 139.25, 144.33; IR (Nujol) cm^{-1} 3000-3500 (s), 1150 (w), 1115 (w), 1040, 1025, 990; m/e 304.

Chapter 2

Solid State Structure of Three Crown Ethers

Introduction

Interest in the crystal structures of macrocyclic polyethers has increased in recent years, as evidenced by the large number of structures done on synthetic and natural macrocycles.[30] The interest in these compounds centers about their ability to surround many different cations. This usually involves a planar coordination geometry for the smaller crowns (e.g. the complex of sodium bromide and dibenzo-18-crown-6) and a cage for the larger crowns and crypts (e.g. the potassium iodide complex with dibenzo-30-crown-10).[31] The sorts of information which can be derived from these structures includes the following:

1) The type of the coordination which occurs between the ligand and the cation can be elucidated by investigation of such factors as size of cation, ligand size, and solvent effects.

2) Conformational changes which are necessary for a free ligand to complex different sized cations can be examined. This can be striking. In order for 30-crown-10 to form a complex with potassium thiocyanate, only four bonds need to be twisted.[32]

3) The actual size of the cavity in the free ligand can be determined, which can give an accurate estimate of complexation ability.

4) One can examine the interaction between molecules of solvent and the cation, as well as the overall effect that this cation solvation has on the ligand complexation by the crown ligand.

5) The effect which counterions have on the packing of the unit cell

as well as general symmetry of the molecule.

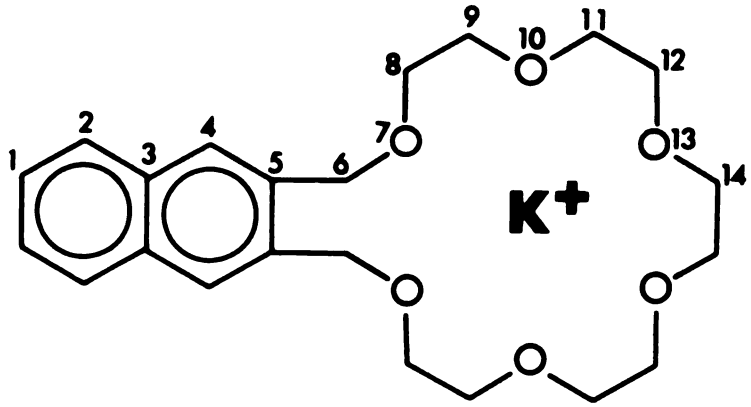
This section of the dissertation will discuss three structures which have been determined, and will focus on their similarities to, and differences from, those already in the literature. The relevence of these structures to some of the other work which has been undertaken in the L.R. Sousa group will also be discussed.

Results and Discussion

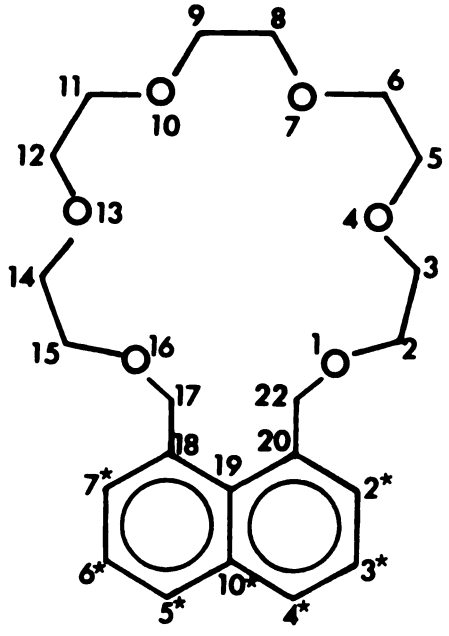
The crystal structure determination of the potassium thiocyanate complex of 2,3-naphtho-20-crown-6 (22) was undertaken because it seemed likely[15a,33] that the conformation of the crystalline complex would closely resemble the most probable conformation(s) in a solution or glass. The numbering scheme for 22 is shown in Figure 6.[34]

A major structural feature is the twofold axis present in the molecule. The potassium ion lies on this twofold rotation axis. The thiocyanate ion is disordered and lies accross the twofold axis, while the naphtho-crown ligand is also related, one half to the other, by this axis.

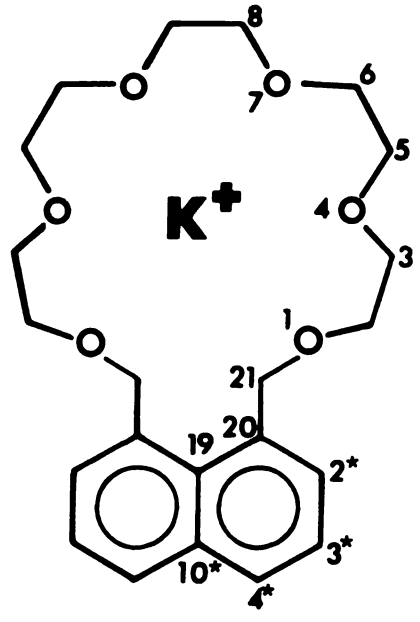
The six crown ether oxygen atoms, which all coordinate to the potassium ion, lie within ±0.35 Å of the best plane containing the oxygen atoms and the potassium ion, as well as the twofold rotation axis. The potasium ion is 6.97 Å from the center of the naphthalene ring (midpoint of the C3-C3^a bond), and 4.52 Å from the end (midpoint of the C5-C5^a bond) of the naphthalene ring. The potassium to oxygen distances average 2.80 Å and the oxygen-potassium-oxygen angles are close to 60, 120, and 180° as expected. The C-O and C-C distances in the crown portion of the ligand average 1.42 and 1.48 Å, while the C-O-C



22



6



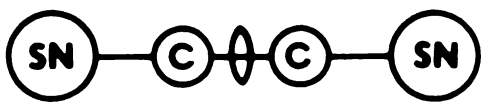
23

Figure 6. The numbering schemes used for 2,3-naphtho-20-crown-6 complexed with KSCN (20), 1,8-naphtho-21-crown-6 uncomplexed (6) and complexed with KSCN (21).

and O-C-C angles average 114.0° and 109.2°, respectively. Complete bond distances and angles for all non-hydrogen atoms are listed in Table 1. The torsion angles for O-C-C-O and C-O-C-C average 64.4° and 175.8° respectively, in good agreement with previously published crown structures.[35] The torsion angles for all non-hydrogen atoms are listed in Table 2.

The naphthalene portion of the molecule is planar, with all ten carbon atoms within ±0.004 Å of a plane which also contains the potassium ion. The naphthylic carbon atom (C6), which is bonded to naphthalene, lies 0.07 Å from this plane. The C-C distances in the aromatic ring average 1.389 Å and the C-C-C angles 120.0°. The naphthalene plane is rotated 51° about the twofold axis from the plane of the six oxygen atoms of the crown portion of the ligand. The results of the least-squares planes calculations are listed in Table 3. Figure 7 shows the molecule with the naphthalene plane parallel to the plane of the page. Figure 8 shows the molecule with the crown ether oxygen plane parallel to the plane of the page.

There do not appear to be any strong intermolecular interactions observed in the packing of the complex in the crystal lattice. The disordered thiocyanate ion lies between two potassium ions, but the ends of the thiocyanate do not point towards the potassium ions. Figure 9 shows the packing diagram as viewed along (0 0 1). The model which was used for the disordered thiocyanate was the following:



It uses a composite sulfur and nitrogen atom, and a carbon atom placed

Table 1

Interatomic distances (Å) and angles (°)

for 2,3-naphtho-20-crown-6

NS -C15	1.054(8)	NS -C15-NS	173.6(7)
NS -C15[a]	1.652(9)	C1[a]-C1 -C2	115.4(4)
O7 -C6	1.424(5)	C1 -C2 -C3	122.3(4)
O7 -C8	1.411(4)	C2 -C3 -C3[a]	118.1(5)
O10-C9	1.413(5)	C3[a]-C3 -C4	117.3(2)
O10-C11	1.415(5)	C3 -C4 -C5	124.4(3)
O13-C12	1.412(5)	C4 -C5 -C5[a]	118.3(4)
O13-C14	1.420(5)	C4 -C5 -C6	120.0(4)
C1 -C1[a]	1.392(9)	C5[a]-C5 -C6	121.6(2)
C1 -C2	1.356(6)	C5 -C6 -O7	114.3(3)
C2 -C3	1.396(6)	C6 -O7 -C8	115.4(4)
C3 -C3[a]	1.419(7)	O7 -C8 -C9	107.9(3)
C3 -C4	1.412(5)	C8 -C9 -O10	109.9(3)
C4 -C5	1.351(5)	C9 -O10-C11	113.5(4)
C5 -C5[a]	1.437(7)	O10-C11-C12	109.5(3)
C5 -C6	1.504(6)	C11-C12-O13	108.8(4)
C8 -C9	1.479(6)	C12-O13-C14	113.0(4)
C11-C12	1.493(7)	O13-C14-C14[a]	109.7(4)
C14-C14[a]	1.467(10)	C2 -C3 -C4	124.6(4)
K -O7	2.733(3)	O7 - K -O7[a]	66.31(5)
K -O10	2.884(2)	O7 - K -O10	57.45(7)
K -O13	2.796(3)	O7 - K -O10[a]	121.89(10)
		O7 - K -O13	118.41(9)
		O7 - K -O13[a]	165.50(11)
		O10- K -O10[a]	179.33(6)
		O10- K -O13	60.97(8)
		O10- K -O13[a]	119.70(10)
		O13- K -O13[a]	60.83(5)

Symmetry code - (a) represents an atom at 1-x, y, 3/2-z

Table 2

Torsion angles (°)

for the potassium thiocyanate complex of 2,3-naphtho-20-crown-6

$C2^a$-$C1^a$- C1 -C2	- 0.9
$C1^a$-C1 - C2 -C3	1.0
C1 -C2 - C3 -$C3^a$	- 1.0
C1 -C2 - C3 -C4	-180.0
C2 -C3 -$C3^a$ -$C2^a$	1.0
C2 -C3 -$C3^a$ -$C4^a$	180.0
C4 -C3 -$C3^a$ -$C4^a$	- 1.0
C2 -C3 - C4 -C5	179.9
$C3^a$-C3 - C4 -C5	1.0
C3 -C4 - C5 -$C5^a$	- 0.8
C3 -C4 - C5 -C6	-177.1
C4 -C5 -$C5^a$ -$C4^a$	0.7
C4 -C5 -$C5^a$ -$C6^a$	176.9
C6 -C5 -$C5^a$ -$C6^a$	- 6.9
C4 -C5 - C6 -O7	-129.3
$C5^a$-C5 - C6 -O7	54.6
C5 -C6 - O7 -C8	90.2
C6 -O7 - C8 -C9	172.4
O7 -C8 - C9 -O10	- 56.0
C8 -C9 -O10 -C11	-175.8
C9 -O10-C11 -C12	-173.6
O10-C11-C12 -O13	71.8
C11-C12-O13 -C14	179.8
C12-O13-C14 -$C14^a$	-179.0
O13-C14-$C14^a$-$O13^a$	- 66.4

Symmetry code - (a) represents an atom at 1-x, y, 3/2-z

Table 3
Least squares planes
for the potassium thiocyanate complex of 2,3-naphtho-20-crown-6

Plane 1. The ten naphthalene carbon atoms

$-12.367*x + 0.000*y + 7.017*z - 0.921 = 0.000$

Plane 2. The six crown ether oxygen atoms

$-0.187*x + 0.000*y + 7.809*z + 5.763 = 0.000$

	------ Distance (Å) ------	
Atom	to plane 1	to plane 2
K	0.000	0.000
C1	-0.004	
C2	0.002	
C3	-0.004	
C4	0.003	
C5	-0.002	
C6	0.072	1.221
O7		0.332
O10		-0.001
O13		-0.352

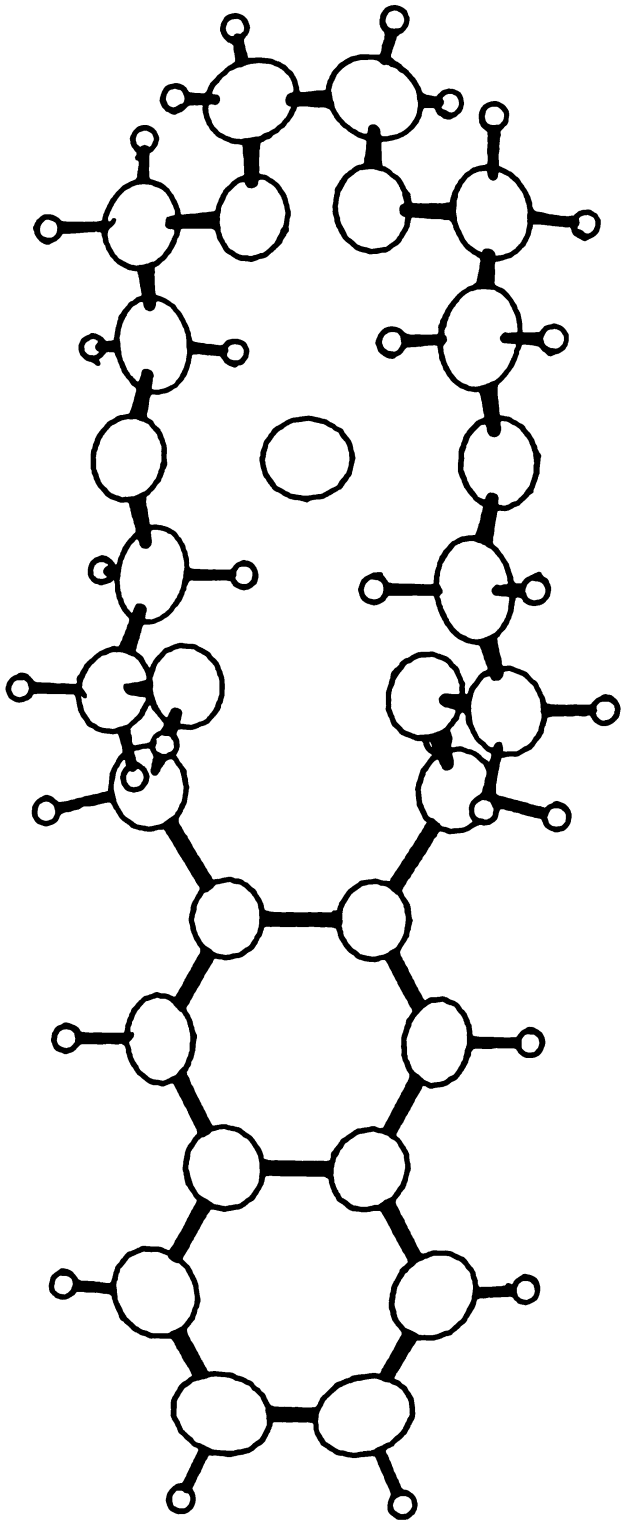


Figure 7. The potassium thiocyanate complex of 2,3-naphtho-20-crown-6 viewed with naphthalene in the plane of the page.

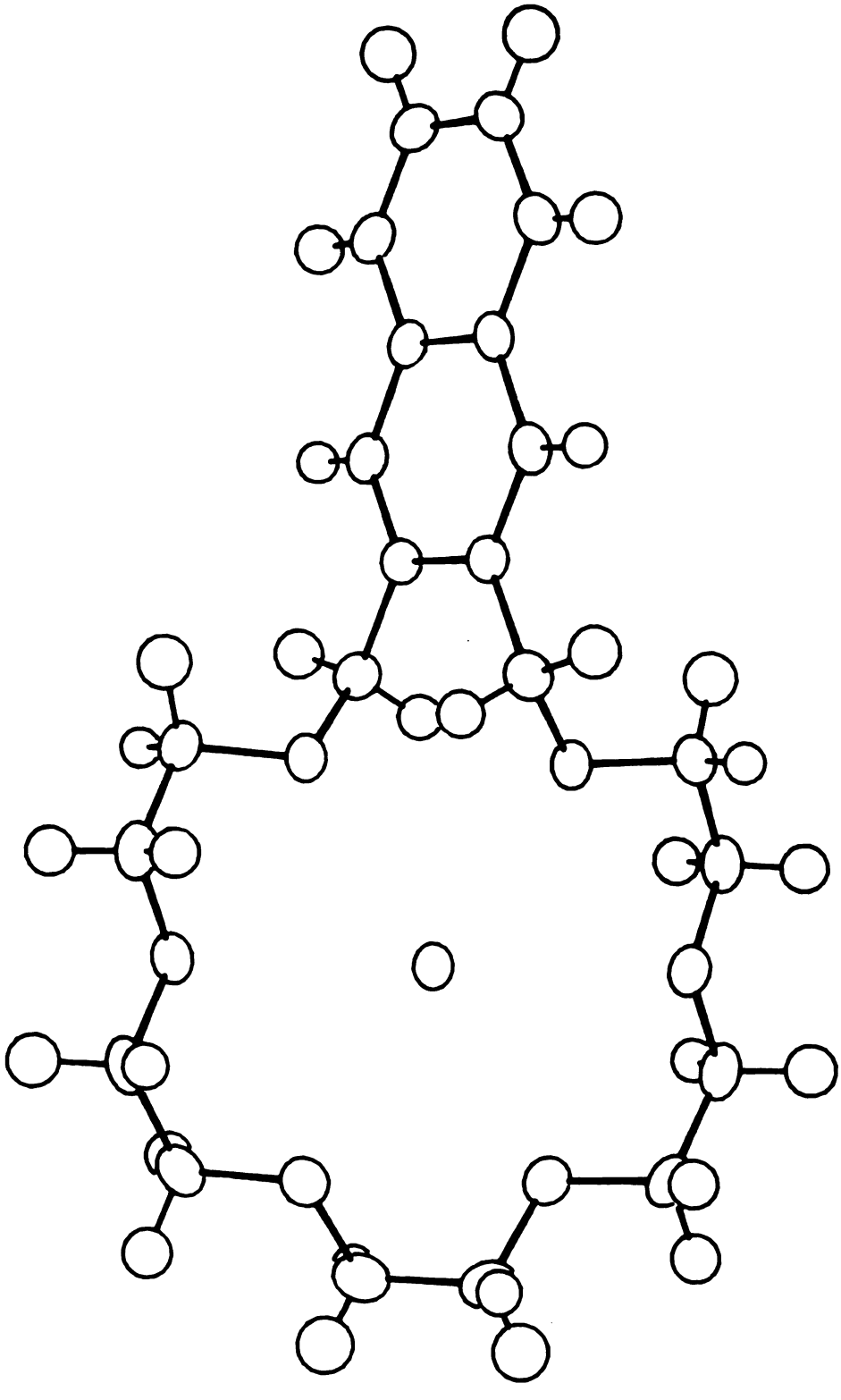


Figure 8. The potassium thiocyanate complex of 2,3-naphtho-20-crown-6 viewed with the six crown ether oxygen atoms in the plane of the page.

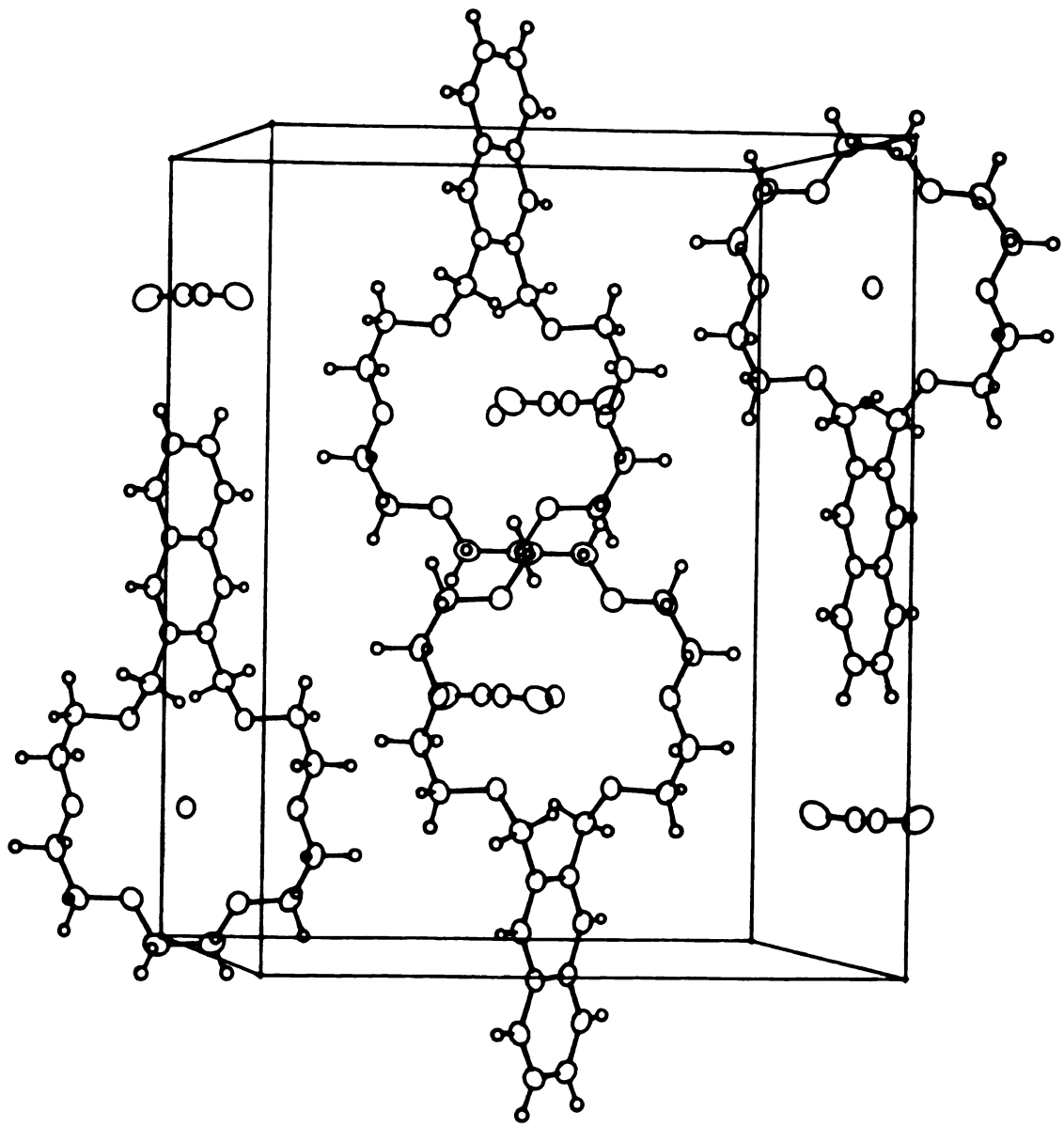


Figure 9. Packing diagram for the potassium thiocyanate complex of 2,3-naphtho-20-crown-6 viewed along (0 0 1).

at half occupancy about the twofold axis. The model used for the thiocyanate fits fairly well. The final difference map showed no residual electron density of any significance, indicating no incorrectly placed or missing atoms.

The crystal structure determinations of 1,8-naphtho-21-crown-6 (6) and the potassium thiocyanate complex of 1,8-naphtho-21-crown-6 (23) were undertaken for much the same purposes as for 22. However, we were also interested in comparing the free ligand 6 to its complex 23 and observing the conformational changes which took place. These conformational changes have been noted elsewhere.[15a,16] The numbering scheme used for 6 and 23 is shown in Figure 6.

The structure of 6 shows a very rigid naphthalene system, while the crown ether hangs slightly to one side. There is no molecular symmetry present as there is in structures 22 and 23.

The six crown ether oxygen atoms of 6 lie within ±0.57 Å of a plane. These six oxygen atoms are not as planar as those in 22, owing to freedom from constraints placed on the molecule when it is complexed. The C-O and C-C distances in the crown portion of 6 average 1.421 Å and 1.506 Å, respectively, while the C-O-C and O-C-C angles average 112.35° and 109.55°, respectively. Complete bond distances and angles for all non-hydrogen atoms are listed in Table 4. The torsion angles for O-C-C-O average 74.95 for four of the dihedral angles. O10-C11-C12-O13 is, however, 179.13°. This deviates significantly from the expected 60°, and indicates a significant conformational change from that of highly symmetrical 23 The C-O-C-C torsion angles also show a deviation, with eight of the angles averaging 173.13°, but with C6-O7-C8-C9 and C8-C9-O10-C11 being 73.74° and 89.79°, respectively. The torsion angles for

Table 4

Interatomic distances (Å) and angles (°)

for 1,8-naphtho-21-crown-6

O1	-C2	1.427(7)	C21	- O1 -C2	109.57(47)
C2	-C3	1.517(7)	O1	- C2 -C3	109.00(40)
C3	-C4	1.419(7)	C2	- C3 -O4	108.05(42)
O4	-C5	1.441(6)	C3	- O4 -C5	112.05(44)
C5	-C6	1.503(8)	O4	- C5 -C6	106.29(39)
C6	-O7	1.398(7)	C5	- C6 -O7	110.79(48)
O7	-C8	1.420(8)	C6	- O7 -C8	113.71(63)
C8	-C9	1.530(10)	O7	- C8 -C9	114.14(41)
C9	-O10	1.425(8)	C8	- C9 -O10	111.41(69)
O10	-C11	1.416(7)	C9	-O10 -C11	114.66(48)
C11	-C12	1.496(9)	O10	-C11 -C12	105.87(41)
C12	-O13	1.418(7)	C11	-C12 -O13	109.41(39)
O13	-C14	1.426(7)	C12	-O13 -C14	112.00(45)
C14	-C15	1.486(10)	O13	-C14 -C15	109.66(39)
C15	-O16	1.420(7)	C14	-C15 -O16	109.85(58)
O16	-C17	1.417(6)	C15	-O16 -C17	112.13(62)
C17	-C18	1.509(8)	O16	-C17 -C18	110.10(42)
C18	-C19	1.428(8)	C17	-C18 -C19	124.69(43)
C19	-C20	1.451(7)	C18	-C19 -C20	127.13(47)
C20	-C21	1.498(7)	C19	-C20 -C21	121.78(47)
C21	-O1	1.434(6)	C20	-C21 -O1	109.87(36)
C20	-C2*	1.360(8)	C20	-C19 -C10*	115.54(49)
C2*	-C3*	1.399(9)	C21	-C20 -C2*	118.56(43)
C3*	-C4*	1.359(9)	C20	-C2* -C3*	123.58(47)
C4*	-C10*	1.400(9)	C2*	-C3* -C4*	118.76(55)
C10*	-C19	1.446(8)	C3*	-C4* -C10*	120.83(58)
C10*	-C5*	1.420(9)	C4*	-C10*-C19	121.52(46)
C5*	-C6*	1.342(11)	C5*	-C10*-C19	119.50(58)

Table 4 (cont'd)

C6* -C7*	1.396(11)	C4* -C10*-C5*	118.95(57)
C7* -C18	1.370(8)	C10*-C19 -C18	117.33(41)
		C10*-C5* -C6*	121.17(71)
		C5* -C6* -C7*	119.80(59)
		C6* -C7* -C18	122.56(57)
		C7* -C18 -C17	115.68(48)
		C7* -C18 -C19	119.63(52)

all non-hydrogen atoms are listed in Table 5.

The naphthalene portion of the molecule is planar, with the largest deviation from planarity being C3* at 0.034 Å. This is not quite as planar as the naphthalene portion of 22, but 1,8-disubstituted naphthalenes are known to deviate from planarity. Table 6 shows a comparison of some different 1,8-substituted naphthalenes. The naphthylic carbon atoms of 6 are bent out of the plane by an average of 0.060 Å. Overall, the naphthalene carbon atoms of 6 (largest out of plane distortion is 0.034 Å) are significantly twisted compared to dimethyl naphthalene (largest out of plane distortion is 0.012 Å), but not as badly bent out of the plane as are those in 1,8-bis(bromomethyl)naphthalene (largest out of plane distortion is 0.068 Å). Table 7 shows the least squares planes for 6. The angle between the two least-squares planes is 55°. The C-C distances in the aromatic ring average 1.397 Å and the C-C-C angles 120.04°. Figure 10 shows 6 with the naphthalene plane parallel to the plane of the paper. Figure 11 shows the molecule with the crown ether oxygen plane parallel to the plane of the paper. Figure 12 shows the packing diagram as viewed along (0 1 0).

The structure of 23 is much like that of 22(they are both in the same space group), but 23 is much less well behaved (see experimental). The R factor for 23 is high, as is the goodness of fit. This should be kept in mind when evaluating the results of the structure determination of 23. Again, the twofold axis is a major structural feature. The potassium ion lies on this twofold rotation axis, and is 5.33 Å from C19, 4.87 Å from C20, and 6.08 Å from the center (midpoint of the C19-C10* bond) of the naphthalene ring. The thiocyanate ion also lies

Table 5
Torsion angles (°)
for 1,8-naphtho-21-crown-6

O1 - C2 - C3 -O4	- 86.0
O1 -C21 -C20 -C19	175.2
O1 -C21 -C20 -C2*	- 5.8
C2 - O1 -C21 -C20	169.5
C2 - C3 - O4 -C5	-169.2
C3 - C2 - O1 -C21	176.2
C3 - O4 - C5 -C6	173.4
O4 - C5 - C6 -O7	- 69.3
C5 - C6 - O7 -C8	170.9
C6 - O7 - C8 -C9	- 73.7
O7 - C8 - C9 -O10	- 72.2
C8 - C9 -O10 -C11	89.8
C9 -O10 -C11 -C12	178.4
O10-C11 -C12 -O13	179.2
C11-C12 -O13 -C14	174.1
C12-O13 -C14 -C15	168.7
O13-C14 -C15 -O16	72.2
C14-C15 -O16 -C17	-171.9
C15-O16 -C17 -C18	178.3
O16-C17 -C18 -C19	- 79.9
O16-C17 -C18 -C7*	100.0
C17-C18 -C19 -C20	1.4
C17-C18 -C19 -C10*	-179.2
C17-C18 -C7* -C6*	178.8
C18-C19 -C20 -C21	1.6
C18-C19 -C20 -C2*	-177.5
C18-C19 -C10*-C4*	178.2
C18-C19 -C10*-C5*	0.1

Table 5 (cont'd)

C18-C7* -C6* -C5*	0.6
C19-C18 -C7* -C6*	- 1.3
C19-C20 -C2* -C3*	- 1.1
C19-C10*-C4* -C3*	- 0.7
C19-C10*-C5* -C6*	- 0.8
C20-C19 -C18 -C7*	-178.5
C20-C19 -C10*-C4*	- 2.3
C20-C19 -C10*-C5*	179.6

Table 6

Comparison of some 1,8-substituted naphthalene derivatives, and the amount of out of plane distortion by the naphthalene carbons.

Compound	Largest out of plane dispalcement by one of the naphthalene carbons	Average out of plane displacement of all ten naphthalene carbons	Absolute magnitude of displacement for C11	C12	Ref.
1,8-dimethylnaphthalene	0.012(C-4)	0.006	0.001	0.0015	36
1,8-bis(bromomethyl)-naphthalene	0.068(C-1)	0.036	0.229	0.188	37
1,3,6,8-tetra-tert-butyl-naphthalene	0.29 (C-1)	0.18	1.22	1.22	38
6	0.034(C3*)	0.013	0.056	0.064	
23	0.079(C20)	0.040	0.379	0.379	

Table 7

Least squares planes

for 1,8-naphtho-21-crown-6

Plane 1. The ten naphthalene carbon atoms

10.271*x + 3.547*y - 3.639*z + 10.596 = 0.000

Plane 2. The six crown ether oxygen atoms

-3.554*x + 4.409*y + 4.414*z + 1.884 = 0.000

	------ Distance (Å) ------	
Atom	to plane 1	to plane 2
C18	0.020	
C19	-0.004	
C20	-0.028	
C2*	0.002	
C3*	0.034	
C4*	-0.007	
C5*	-0.008	
C6*	0.001	
C7*	0.009	
C10*	0.019	
C17	0.056	0.452
C21	-0.064	-0.248
O1		-0.342
O4		0.057
O7		0.405
O10		-0.570
O13		0.350
O16		0.100

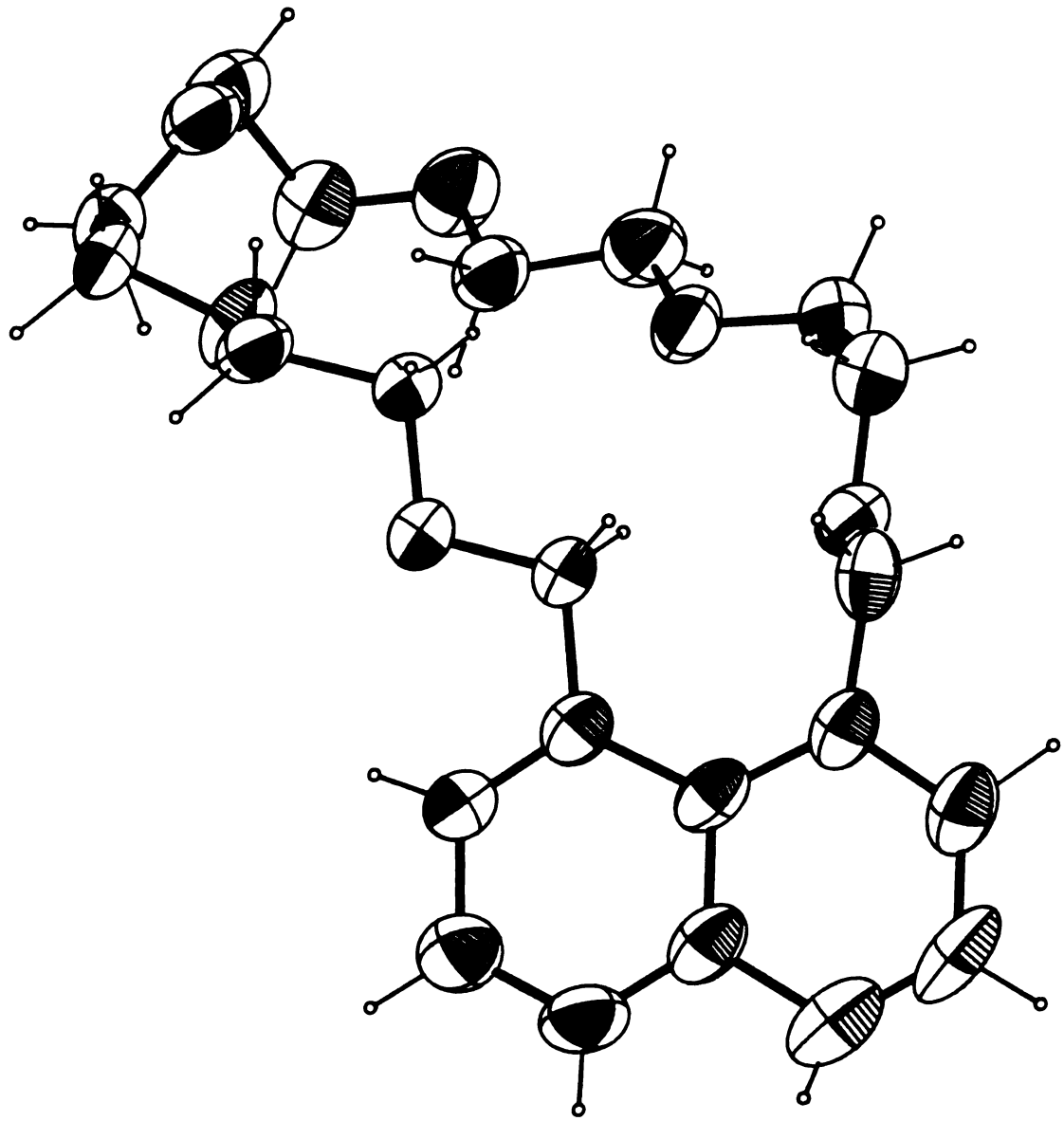


Figure 10. 1,8-naphtho-21-crown-6 viewed with naphthalene in the plane of the page.

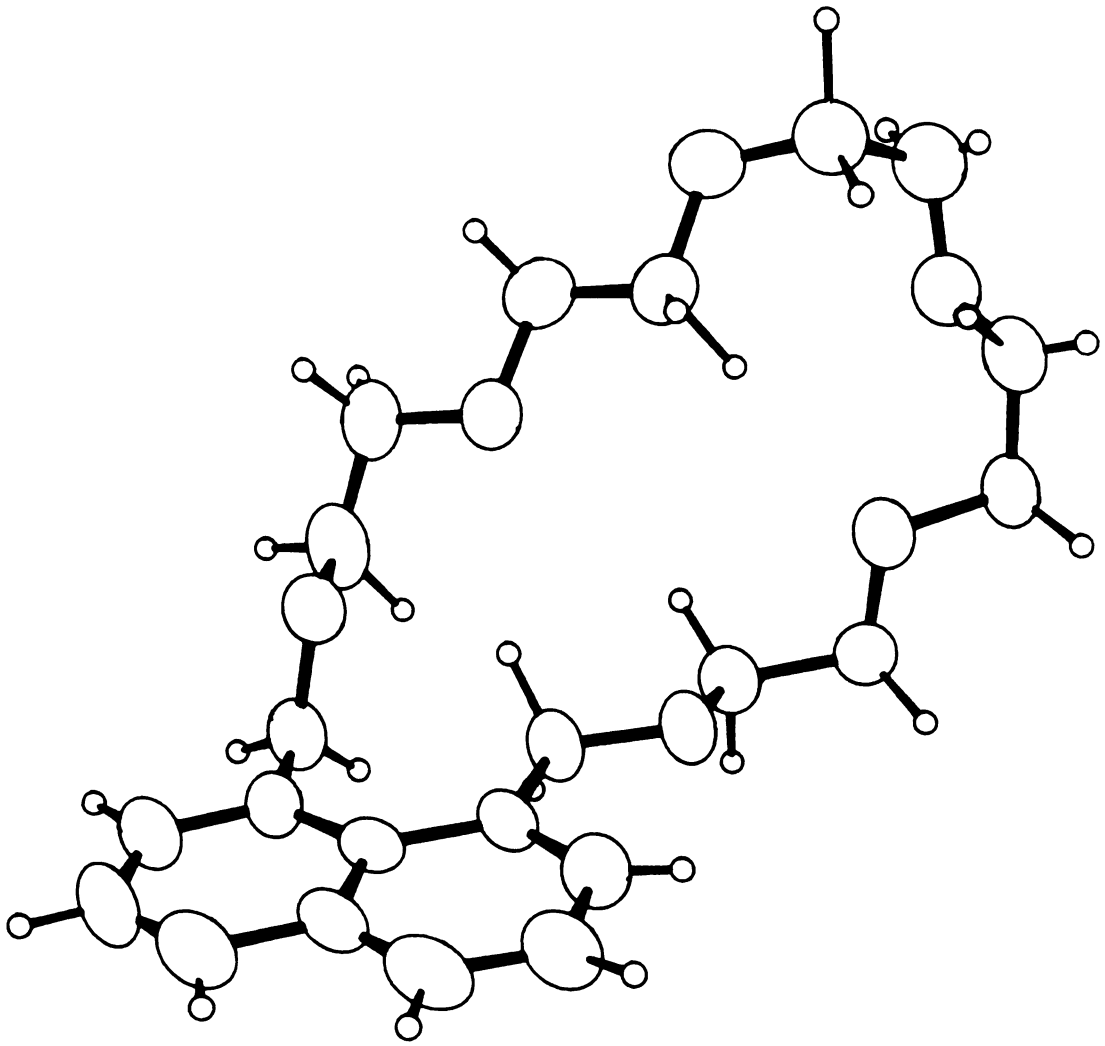


Figure 11. 1,8-naphtho-21-crown-6 viewed with the six crown ether oxygen atoms in the plane of the page.

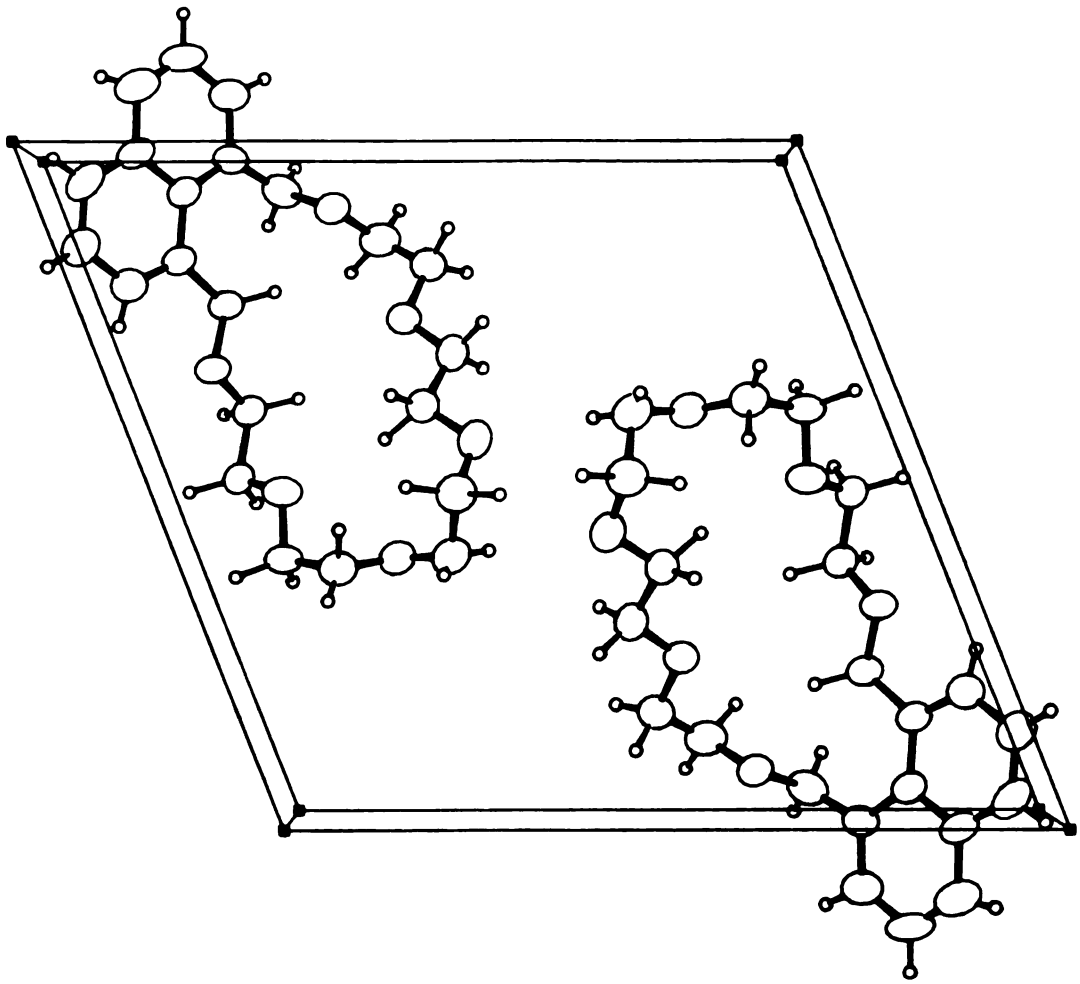


Figure 12. Packing diagram of 1,8-naphtho-21-crown-6 viewed along (0 1 0).

accross this axis, but it was found that the carbon of the thiocyanate refines best (or at least as well) when placed on the twofold axis. The naphtho-crown ligand is related, one half to the other, by this axis, with atoms C10* and C20 lying on the axis.

The six crown ether oxygen atoms, all coordinated to the potassium ion, lie within ±0.38 Å of the best plane of the six oxygen atoms and the potassium ion, as well as the twofold rotation axis. The potassium to oxygen distances average 2.84 Å and the oxygen-potassium-oxygen angles are close to 60°, 120°, and 180° as expected. The C-O and C-C distances in the crown portion of the ligand average 1.415 Å and 1.488 Å, while the C-O-C and O-C-C angles average 113.56° and 108.59°. Complete bond distances and angles for all non-hydrogen atoms are listed in Table 8. The torsion angles for O-C-C-O and C-O-C-C average 67.6° and 175.9° respectively. Once again, these values are in good agreement with published crown structures. The torsion angles for all non-hydrogen atoms are listed in Table 9.

The naphthalene portion of the molecule is still moderately planar, with the largest deviation from planarity being 0.079 Å (C20). The potassium ion and twofold axis are also contained in this plane. The naphthylic carbon atom (C21), which is bonded directly to naphthalene, lie 0.379 Å from this plane. Again, this number should be put in perspective by the uncertainty in 23. The C-C distances in the aromatic ring average 1.386 Å, and the C-C-C angles 120.39°. The naphthalene plane is rotated 39° about the twofold axis from the plane of the six oxygen atoms of the crown protion of the ligand. The results of the least-squares planes calculations are listed in Table 10. Figure 13 shows 3 with the naphthalene plane parallel to the plane of the page.

Table 8
Interatomic distances (Å) and angles (°)
for 1,8-naphtho-21-crown-6

S -C	1.767(12)	S - C -N	160.10(2.19)
N -C	0.913(27)	S - C -S[a]	173.56(1.44)
S -N	2.644(32)	C21- O1 -C2	114.68(84)
S -N	0.955(23)	O1 - C2 -C3	107.57(67)
C21-O1	1.427(9)	C2 - C3 -O4	108.23(66)
O1 -C2	1.412(9)	C3 - O4 -C5	114.14(103)
C2 -C3	1.491(13)	O4 - C5 -C6	109.88(87)
C3 -O4	1.410(10)	C5 - C6 -O7	108.13(77)
O4 -C5	1.418(13)	C6 - O7 -C8	111.86(86)
C5 -C6	1.475(16)	O7 - C8 -C8[a]	109.12(72)
C6 -O7	1.426(12)	C20-C19 -C20[a]	126.74(52)
O7 -C8	1.411(11)	C19-C20 -C21	123.78(68)
C8 -C8[a]	1.506(24)	C20-C21 -O1	115.40(56)
C19-C20	1.429(10)	C21-C20 -C2*	116.98(83)
C20-C21	1.511(12)	C20-C2* -C3*	122.67(105)
C20-C2*	1.365(12)	C20-C19 -C10*	116.63(66)
C2*-C3*	1.400(15)	C2*-C3* -C4*	119.67(137)
C3*-C4*	1.317(17)	C3*-C4* -C10*	121.53(145)
C4*-C10*	1.391(15)	C4*-C10*-C4*[a]	119.26(64)
C19-C10*	1.442(18)	C4*-C10*-C19	120.37(74)
K -O1	2.824(6)	C19-C20 -C2*	118.84(99)
K -O4	2.888(6)	O1 - K -O1[a]	67.04(12)
K -O7	2.813(6)	O1 - K -O4	57.86(18)
		O1 - K -O7	117.92(23)
		O4 - K -O4[a]	178.41(15)
		O4 - K -O7	60.11(20)
		O7 - K -O7[a]	60.77(14)

Symmetry code - (a) represents an atom at 1-x, y, 3/2-z

Table 9

Torsion angles (°)

for the potassium thiocyanate complex of 1,8-naphtho-21-crown-6

C19 -C5*-C4*-C3*	1.7
C19 -C20-C21-O1	- 85.0
C19 -C20-C2*-C3*	- 2.4
C5* -C19-C20-C21	-166.8
C5* -C19-C20-C2*	5.8
C5* -C4*-C3*-C2*	2.0
O1 -C2 -C3 -O4	64.9
O1 -C21-C20-C2*	102.3
O4 -C5 -C6 -O7	- 70.2
C2 -O1 -C21-C20	- 80.7
C2 -C3 -O4 -C5	175.6
C3 -O4 -C5 -C6	-178.6
C3 -C2 -O1 -C21	-171.1
C5 -C6 -O7 -C8	177.6
C21 -C20-C2*-C3*	170.6
C20 -C19-C5*-C4*	- 5.6
C20 -C2*-C3*-C4*	- 1.7
C6 -O7 -C8[a]-C8	177.4
C21 -C20-C19-C20[a]	13.2
C20 -C19-C5*-C4*[a]	174.4
C20[a]-C19-C5*-C4*[a]	- 5.6
C20[a]-C19-C5*-C4*	174.4
C20[a]-C19-C20-C2*	-174.2
C4*[a]-C5*-C4*-C3*	-178.3
O7 -C8 -C8 -O7[a]	67.4

Symmetry code - (a) represents an atom at 1-x, y, 3/2-z

Table 10

Least squares planes

for the potassium thiocyanate complex of 1,8-naphtho-21-crown-6

Plane 1. The ten naphthalene carbon atoms

$-11.319*x + 0.000*y + 7.235*z - 3.851 = 0.000$

Plane 2. The six crown ether oxygen atoms

$-0.367*x + 0.000*y + 0.970*z + 1.754 = 0.000$

	------ Distance (Å) ------	
Atom	to plane 1	to plane 2
K	0.000	0.000
C19	0.000	0.000
C5*	0.000	0.000
C4*	0.042	
C3*	0.050	
C2*	-0.028	
C20	-0.079	
C21	-0.379	-1.218
O1		-0.289
O4		-0.026
O7		0.377
C(SCN)	0.000	0.000

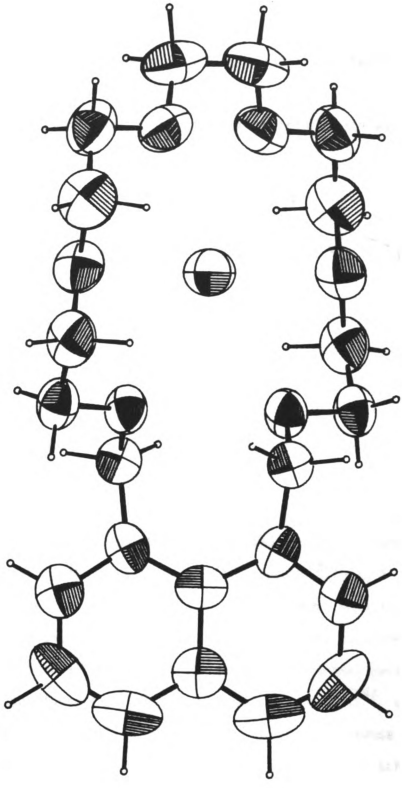
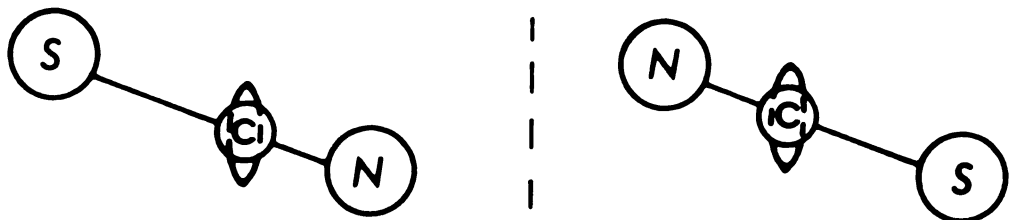


Figure 13. The potassium thiocyanate complex of 1,8-naphtho-21-crown-6 viewed with naphthalene in the plane of the page.

Figure 14 shows the compound with the plane defined by the six crown ether oxygen atoms parallel to the plane of the page.

The thiocyanate is again disordered, and lies between two potassium atoms. Figure 15 shows the packing diagram as viewed along (0 0 1). The model which was used for the disordered thiocyanate was the following:



superimposed on

The sulfur and nitrogen were placed at half occupancy, as was the carbon which is on the twofold axis. The model for the thiocyanate used in 22 was tried, but did not fit as well. This model was the simplest to which we could adequately fit the data. It is possible that there is more disorder about the twofold axis, since some of the atoms have fairly large thermal parameters.

The C-C distances in the crown ether portion of both 22 and 23 are fairly short. It has been observed that the C-C bond lengths in crown ethers are fairly short compared to the expected[39] 1.537 Å or 1.523 Å measured for gas phase dioxane.[40] Although several investigators have attributed the shorter than normal C-C bond lengths to inadequate treatment of thermal motion in refinement of positional parameters,[41] Truter has concluded that the bond lengths may be real.[42] Goldberg has done several studies on crowns at low temperature to reduce thermal motion effects. In addition, he has also used weighting schemes in the refinement of his data to attempt to correct for the thermal motion. In all instances, he continued to calculate the shorter bond lengths.[43]

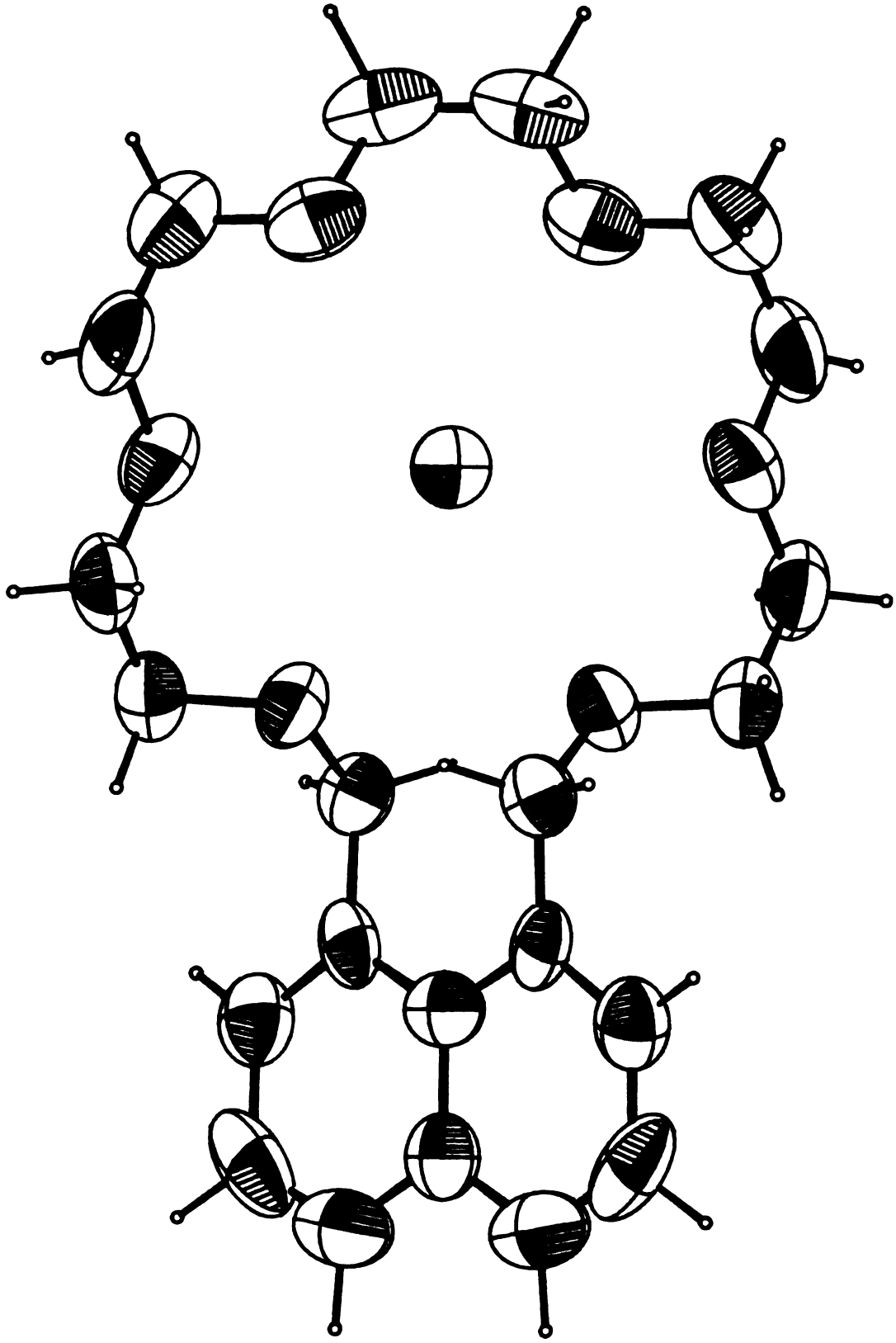


Figure 14. The potassium thiocyanate complex of 1,8-naphtho-21-crown-6 viewed with the six crown ether oxygen atoms in the plane of the page.

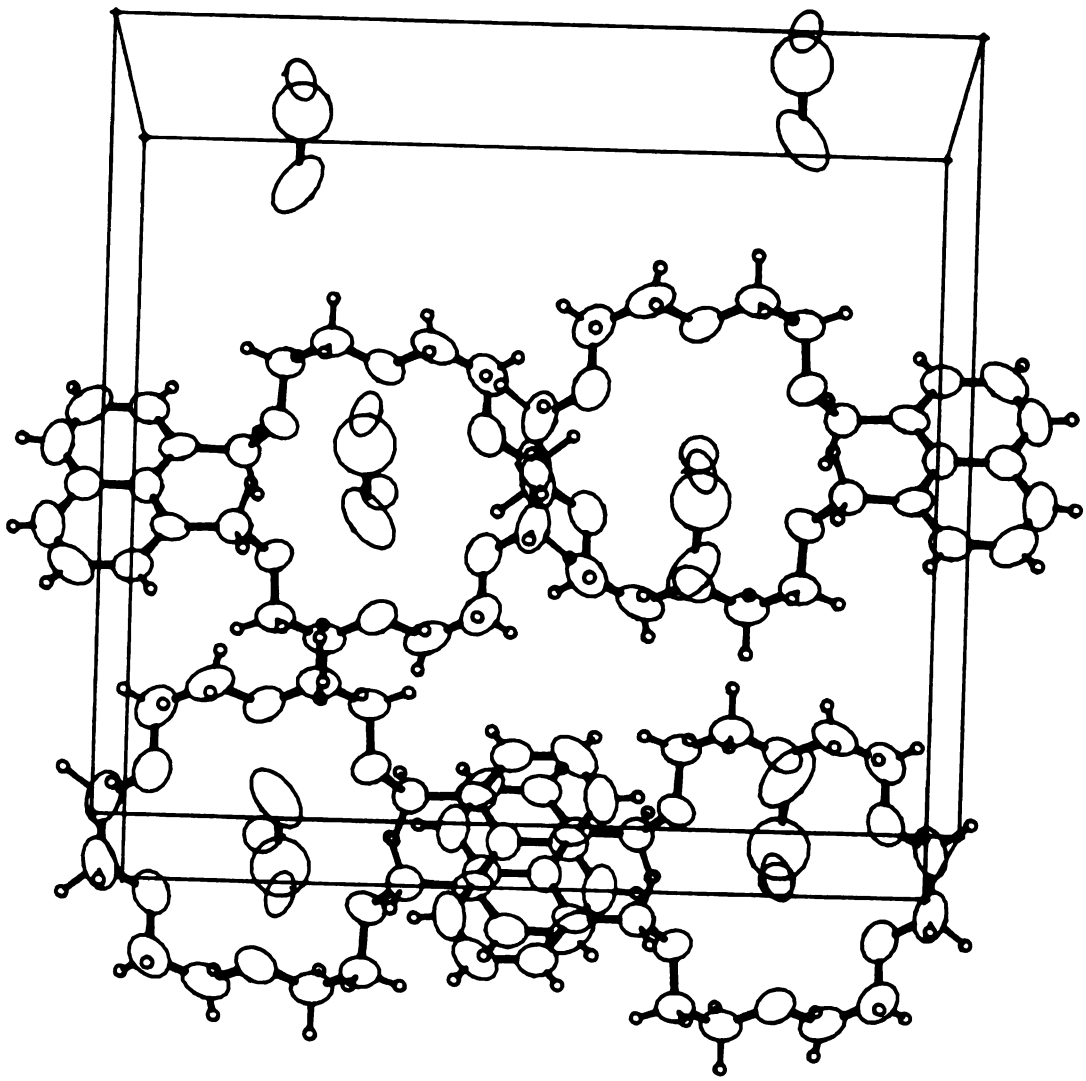


Figure 15. Packing diagram for the potassium thiocyanate complex of 1,8-naphtho-21-crown-6 viewed along (0 0 1).

The C-C distances for 22 and 23 are about 0.02 Å shorter than most crown structures, while 6 is fairly normal.

Apparently, the metal ion has a fair amount to do with determining the conformation of the crown ether in the crystalline state, as evidenced by the difference in symmetry between 6 and 23. The crystal structure of 1,5-naphtho-22-crown-6 complexed with either cesium thiocyanate or potassium thiocyanate was not done, because suitable crystals of this complex could not be obtained. The conformational differences between the free and complexed ligand would be interesting, since the 1,5-naphtho-22-crown-6 has more severely restricted motion.

EXPERIMENTAL

General. 2,3-Naphtho-20-crown-6 and 1,8-naphtho-21-crown-6 were prepared as described earlier in this thesis. Both 22 and 23 were prepared by addition of equimolal amounts of potassium thiocyanate dissolved in a miniumum of methanol, and crown dissolved in several mL of ethyl acetate. This mixture was refluxed until all traces of solid were gone, and was then allowed to cool. The free ligand 6 was recrystallized from cyclohexane.

The crystal dimensions are listed in Table 11. The space groups were determined by the diffraction conditions noted in Table 11. Diffraction data were measured with a Picker FACS-I automated diffractometer using zirconium filtered MoKα radiation. The cell parameters were determined by a least-squares fit of the angular settings of reflections in the range $35° \leq 2\Theta \leq 40°$ and are shown in Table 11. The $\alpha_1 - \alpha_2$ doublet was clearly resolved for 22 and 23, and was not recorded for 2 (λ for MoKα = 0.70926 Å). The unique reflections in the $+h+k\pm\ell$ region were calculated by $\Theta - 2\Theta$ scans [$1.0°(2\Theta)\ min^{-1}$] with three standard reflections measured after every 50 data to scale the data. The data were reduced and standard deviations calculated as a function of counting statistics.[44] The least-squares refinement weights were calculated from the standard deviations of the structure factors by

$$\underline{\text{weight}} = 1 / (\sigma^2 + (0.02F)^2).$$

Extinction corrections were applied as noted in Table 12. Densities were confirmed by a pycnometer.

Table 11

Diffraction data, collection data, and cell parameters.

	* 22	* 6	* 23 *
crystal dimensions (mm)	.1 x .25 x .3	.25 x .25 x .50	.12 x .37 x .43
μ for MoKα (cm^{-1})	2.841	0.536	2.86
diffraction conditions	*hkℓ: h+k=2n*	*0k0: k=2n*	*hℓk: h+k=2n*
	h0ℓ: ℓ=2n		*h0ℓ: ℓ=2n*
possible space groups	C/c, Cc	P21, P21/m	C/c, Cc
reflections (cell parmeters)	13	15	16
2θ range (cell parmeters)	35° - 39°	35° - 40°	35° - 40°
Data collection			
temperature	23.5-25.4 °C	26.8-28.6 °C	24.0 °C
scan range (2θ)	to 50°	to 55°	to 55°
backgrounds (each, seconds)	10	20	20
total unique reflections	2247	2653	2891
number observed/cutoff(σ)	1265/1	1413/2	1598/2
Cell parameters			
a	17.416(4)	15.865(6)	15.698(6)
b	18.772(3)	4.654(1)	20.543(6)
c	7.995(1)	14.954(3)	8.274(2)
β	105.36(2)	111.66(2)	109.98(2)
d_x ($g\ cm^{-3}$)	1.285	1.264	1.292

Table 12

Final results from refinement of 6, 22, and 23.

	22	6	23
R	0.056	0.056	0.123
R (all data)	0.131	0.121	0.204
R_2	0.051	0.056	0.095
G.O.F.	1.30	1.32	1.68
average shift-error (non-H)	0.01	0.10	0.02
maximum shift-error (non-H)	0.13	0.51	0.12

$R = (\Sigma|Fo - Fc|)/\Sigma Fo$

$R_2 = \{[\Sigma w(Fo - Fc)^2]/\Sigma w(Fo)_2\}^{\frac{1}{2}}$

$G.O.F. = [\Sigma w(Fo - Fc)/(\#\text{ of reflections} - \#\text{ of parameters})]^{\frac{1}{2}}$

Structure Solution and Refinement. The crystal structures were solved with MULTAN.[45] Other programs used in this study included ORTEP,[46] the entire system of Allan Zalkin's programs,[47] and programs written and / or modified locally. A CDC 6500 computer was used.

The structures were refined to convergence by a full-matrix least-squares calculation. The final results are listed in Table 12. The average and maximum shift to error ratios are also listed in Table 12. Final difference maps showed no indication of incorrectly placed or missing atoms. The scattering factors of Doyle and Turner[48] were used for the non-hydrogen atoms, while those of Stewart, Davidson, and Simpson[49] were used for the hydrogen atoms. The anomalous scattering factors of Cromer and Liberman[50] were used for the non-hydrogen atoms, and anomalous scattering factors of zero were assumed for hydrogen. The atomic parameters for all three structures have either been published[18] or will be shortly.[17]

Chapter 3

Crown Ether Modified Systems Designed to Probe Intramolecular Energy Transfer (Preliminary Studies)

Introduction

Energy transfer is generally thought of as a transfer of energy from an excited molecule to some other species; this energy can be in the form of vibrational, translational, or rotational energy. Without energy transfer, photosynthesis could not be nearly as efficient as it is, if it could even take place at all. Many biological systems are affected by energy transfer, and the effect which metal ions play in preturbing these systems is just beginning to be studied.

The first observation of energy transfer was made by Cario and Frank in 1922 when they noted that a mixture of mercury and thallium vapor, when irradiated with light from the mercury resonance line, showed emission spectra characteristic of both elements.[51] Since the thallium atoms do not absorb the exciting light, they can get excited only indirectly by transfer of energy from the mercury atoms. This simple system laid the groundwork for work with more complex systems involving energy transfer. We are interested mainly in systems which deal with intramolecular energy transfer.[52]

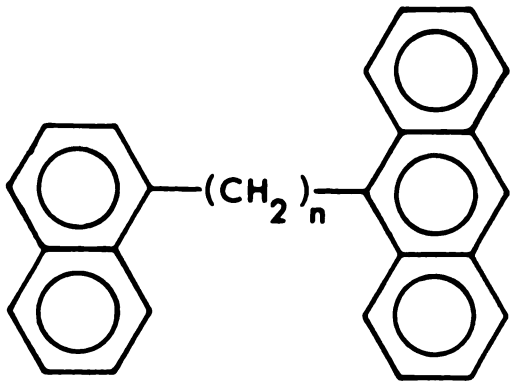
The first complete study done on an intramolecular system was by Schnepp and Levy in 1962.[53] A mixture of 9-methylanthracene and 1-methylnaphthalene, upon irradiation with light appropriately filtered to excite both the anthracene and the naphthalene, showed two fluorescence spectra, one characteristic of naphthalene, the other of anthracene.

When solutions of compounds 24, 25, and 26 were irradiated through this same filter, only anthracene fluorescence could be detected, indicating the presence of an energy transfer process.

24, n=1

25, n=2

26, n=3

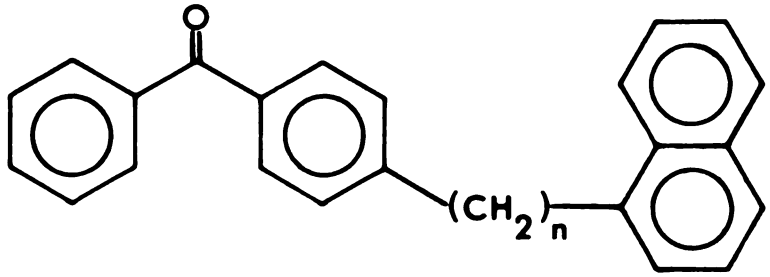


Lamola et al.[54] describe a system which uses benzophenone and naphthalene as the chromophores in an intramolecular energy transfer study (compounds 27, 28, and 29).

27, n=1

28, n=2

29, n=3



Again, the absorption spectra of an equimolar mixture of 4-methylbenzophenone and 1-methylnaphthalene had the same absorption as compounds 27, 28, and 29. The only emission of a sample of 4-methylbenzophenone and 1-methylnaphthalene, irradiated at 366 nm, was phosphorescence of the 4-methylbenzophenone (366 nm selectively excites the benzophenone). This indicates little, if any, intermolecular energy transfer at the concentrations used. The phosphoresence of 27, 28, and 29 are nearly identical to that of 1-methylnaphthalene, even when just the benzophenone chromophore (366 nm) is excited. This can be readily understood by looking at Figure 16. Light absorbed by the naphthalene

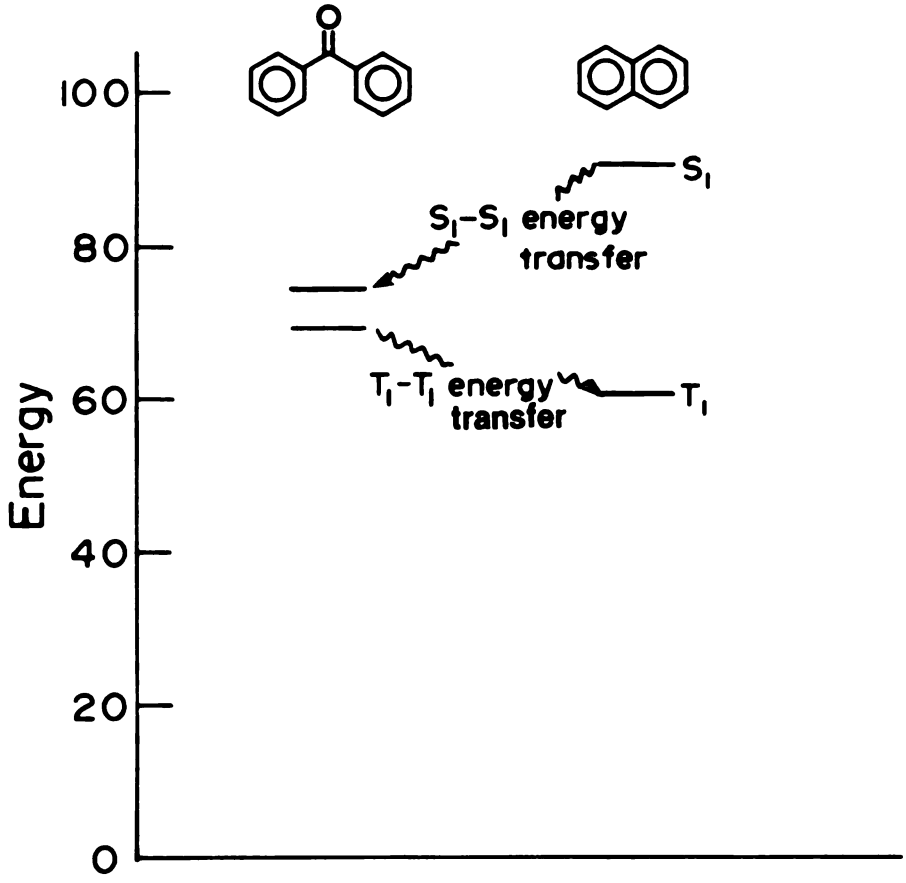
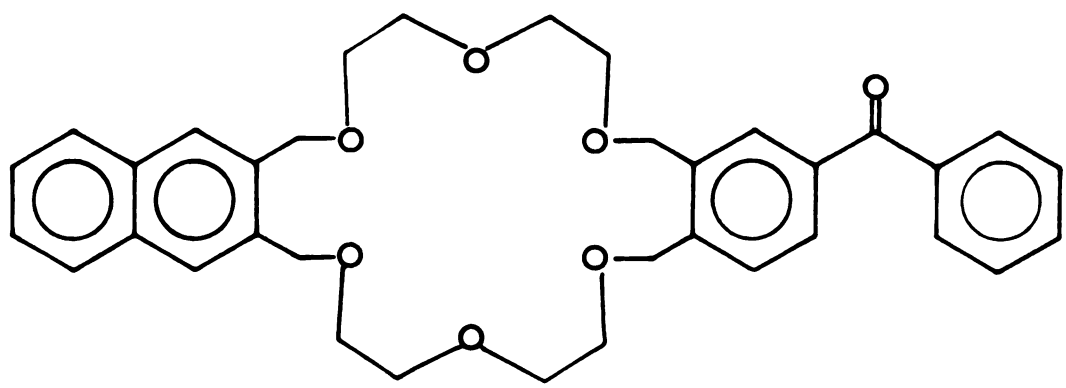


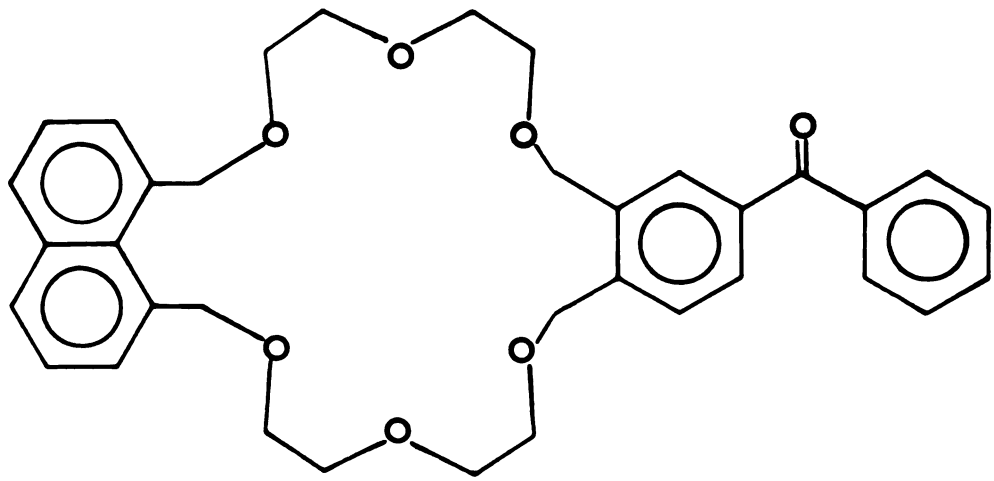
Figure 16. Energy levels of the first excited states of naphthalene and benzophenone.

chromophore (313 nm) excites the naphthalene to its ^1S state, which transfers energy to the ^1S state of benzophenone (singlet-singlet energy transfer, a process which in this case, the authors claim to be 90%, 75%, and 85% efficient for compounds 27, 28, and 29 respectively). Benzophenone readily intersystem crosses to the ^1T state ($\Phi_{ISC}>0.99$), which then transfers triplet energy to the naphthalene chromophore with 100% efficiency.

This leads directly into our systems, compounds 30 and 31. Notice that compound 30 has an important modification to the system of Lamola et al., which adds the possibility of using a metal ion complexed by the crown to accept energy transfer from the donor to the acceptor.



30



31

A metal ion complexed to either 3 of 6 is known to preturb the emission and possibly the electronic structure of the naphthalene moiety.[12,14] Experimental evidence concerning the role of metal and non-metal cations on energy transfer is not available, despite the importance of energy transfer in living systems, where ions may play an important role. The expected conformational effect of a metal ion on crowns 30 and 31 from inspection of CPK models is to flatten out the molecule through complexation, whereas the non-complexed crown may prefer a folded conformation. If compound 30 (or 31) transfers triplet energy from the benzophenone to the naphthalene with almost total efficiency, this could be used to study the triplet behavior of naphthalene with almost all of the triplet state populated, and almost none of the singlet state populated, something which can't be achieved directly for naphthalene. The effect of concentration of perturber may also be interesting. At high concentrations of crown compared to to preturber, large cation preturbers could complex with two crowns, and thus act as a template for intermolecular energy transfer. The effect

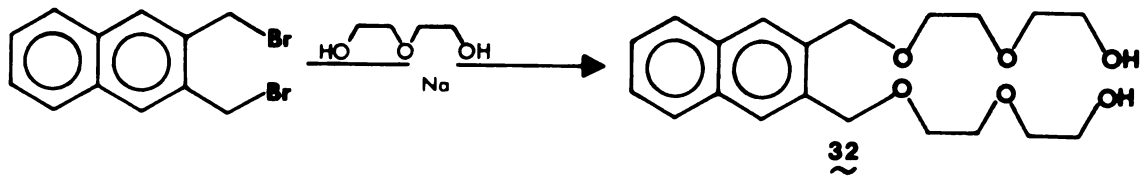
of a third chromophore held between benzophenone and naphthalene (held by attachment to a primary ammonium cation) would also be interesting.

Results and Dicussion

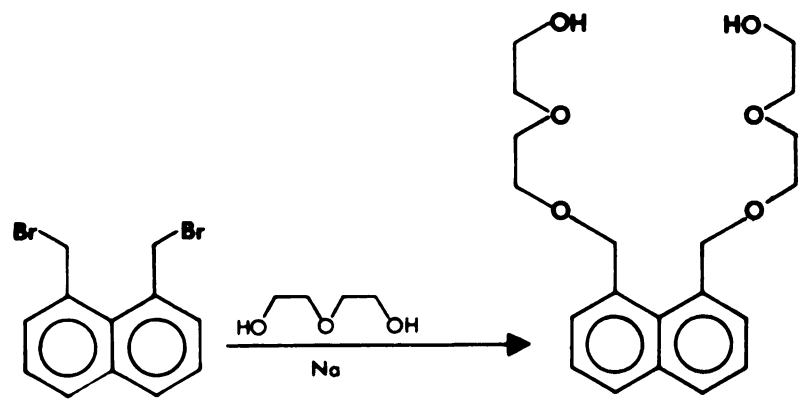
Synthesis of crowns 30 and 31 proved to be a non trivial task. The synthetic approach taken to these crowns was to attach "arms" (ethyleneoxy strands with a free hydroxyl) at one end, and then to form the crown by joining the "two-armed" naphthalene to the 3,4-bis(bromomethyl)benzophenone moiety.

Originally, the "two armed" naphthalene was to be made from displacement of the chloride in protected (tetrahydropyranyl ether) 2-(2'-chloroethoxy) ethanol by the alkoxide formed from the appropriate bis(hydroxymethyl)naphthalene and potassium t-butoxide. In the case of 2,3-bis(hydroxymethyl)naphthalene (made from hydrolysis of the bis-acetate, which was in turn made from the dibromide), this gave poor yields (less than 20%) of the two-armed material, some one-armed material, and mostly starting material. The reaction of 1,8-bis(hydroxymethyl)naphthalene with protected 2-(2'-chloroethyl) ethanol gave only poor yields of one-armed material, and no two-armed material. Presumably, this is due to the larger steric crowding in the 1,8-disubstituted naphthalene system.

An easier and better method involved formation of the sodium alkoxide of diethylene glycol with sodium, and then adding the appropriate bis(bromomethyl)naphthalene in a small amount of THF and diethylene glycol to the refluxing slurry of the alkoxide. This method gives good yields of the two-armed naphthalene in both the 2,3- and 1,8-systems.



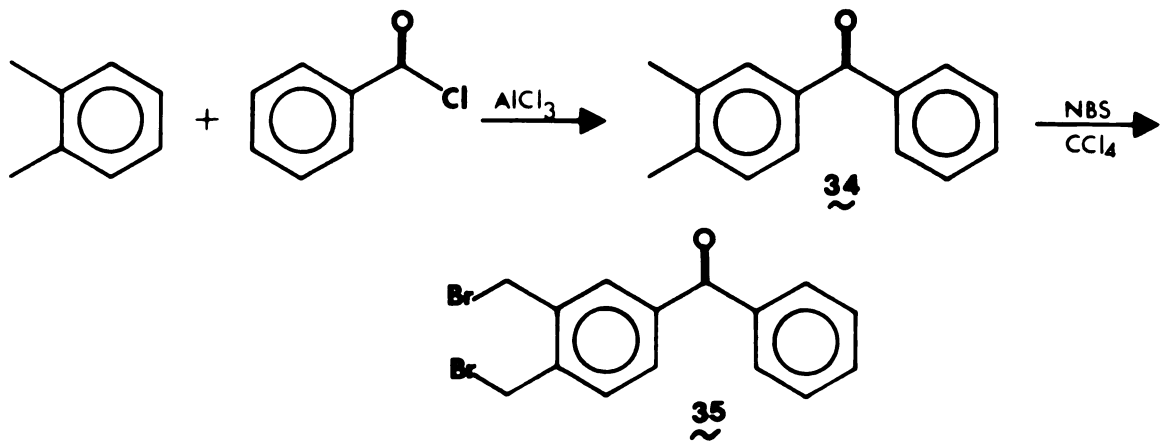
32



33

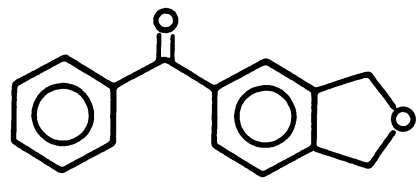
The small amount of one-armed material formed is separated by chromatography on silica gel, as is the naphtho-crown-3, which is the other undesired (!) side product (confirmed by spectral data).

The other side of the molecule, 3,4-bis(bromomethyl)benzophenone (35), is formed by NBS bromination of 3,4-dimethylbenzophenone (34), which in turn is made by Friedel-Crafts acylation of o-xylene with benzoyl chloride.



34 35

Although 3,4-bis(bromomethyl)benzophenone appears to be a solid, it can not be isolated as such from the reaction mixture. The reaction mixture from NBS bromination of 34 is about 75% (^{1}H NMR) pure 35. Attempted purification on alumina gives the solid cyclic ether 36 in poor yield.



36

The rest of the material appears to irreversably bind to the alumina, although more 36 does bleed off the column with time. This reaction of alumina with 1,2-bis(halomethyl)arenes is known.[55] A pure sample (greater than 95%) of 35 can be obtained by refluxing 36 in aqueous HBr, although 35 is still a waxy solid (mp is 42-46 °C). 35 was used 75% pure for the synthesis of 30 and 31. The crowns 30 and 31 were made as in chapter 1 from 32 and 35 (to give 30) and 33 and 35 (to give 31) in low yield.

Figures 17-20 show emission specra of crown 30 (Figures 17, 18) and crown 31 (Figures 19, 20). Figures 21 and 22 show excitation spectra of

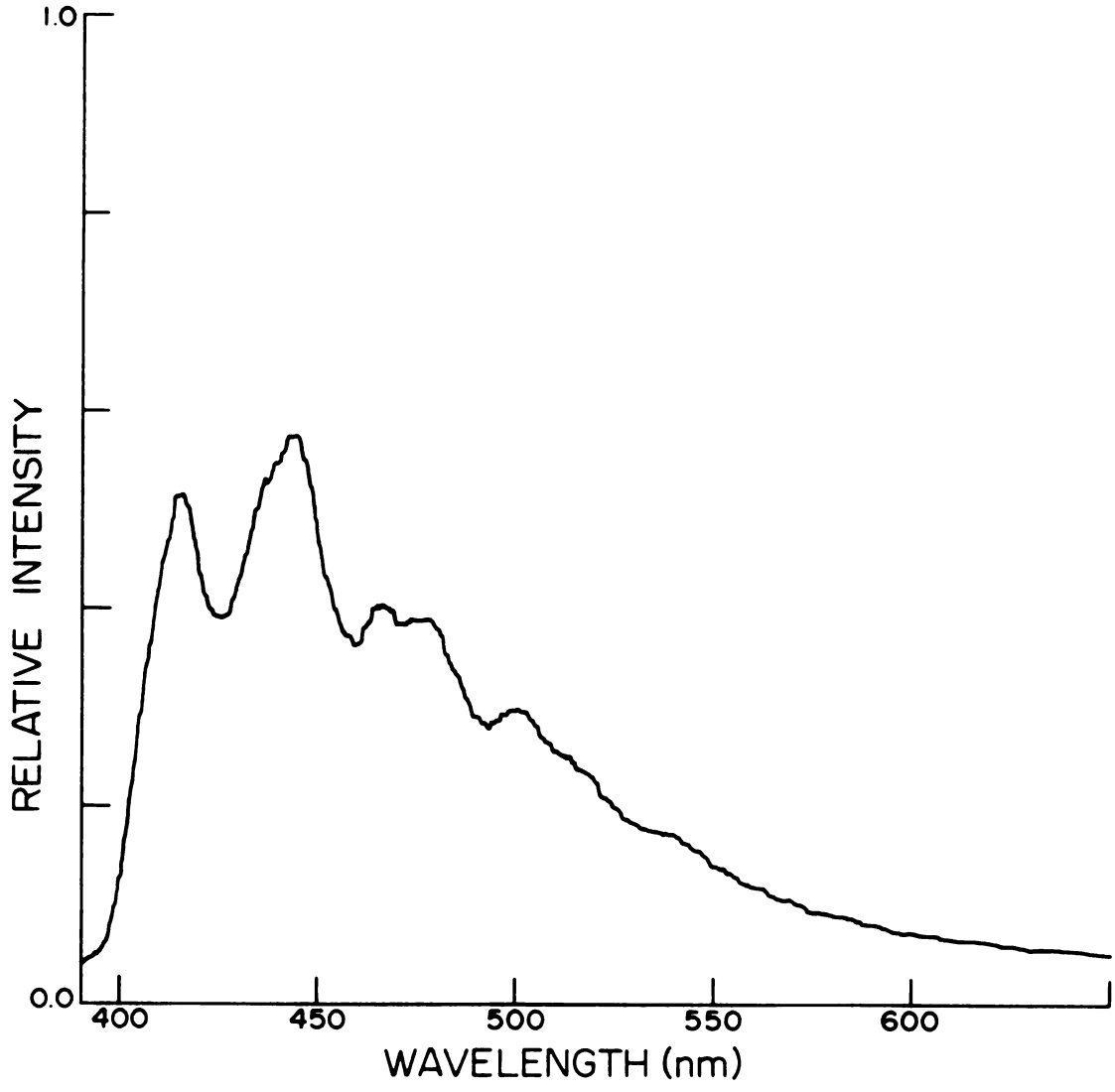


Figure 17. Phosphorescence spectra of crown 30. Excitation is at 307 nm. Concentration is 1.0×10^{-4} M.

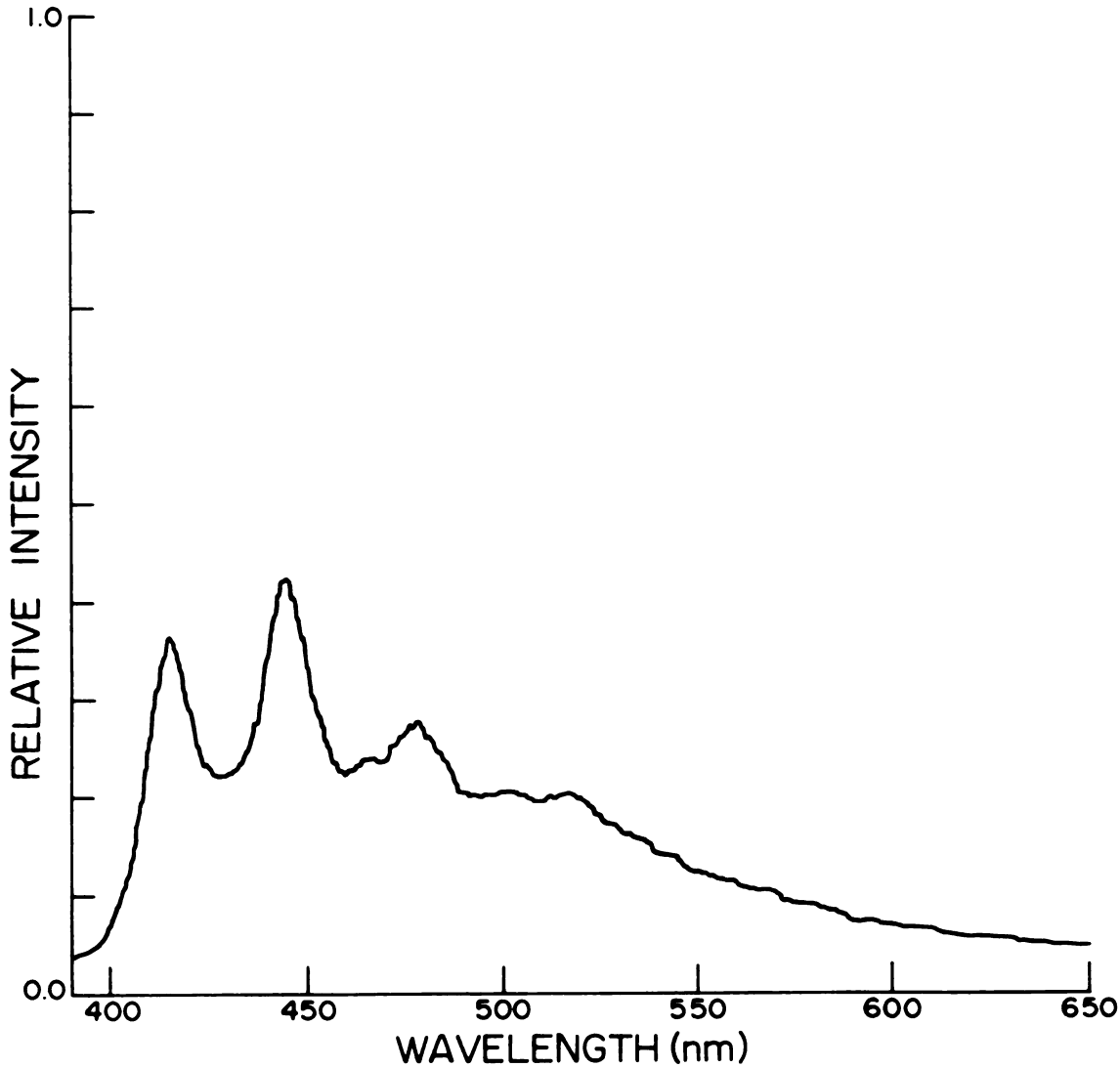


Figure 18. Phosphorescence spectra of crown 30. Excitation is at 350 nm. Concentration is 1.0×10^{-4} M.

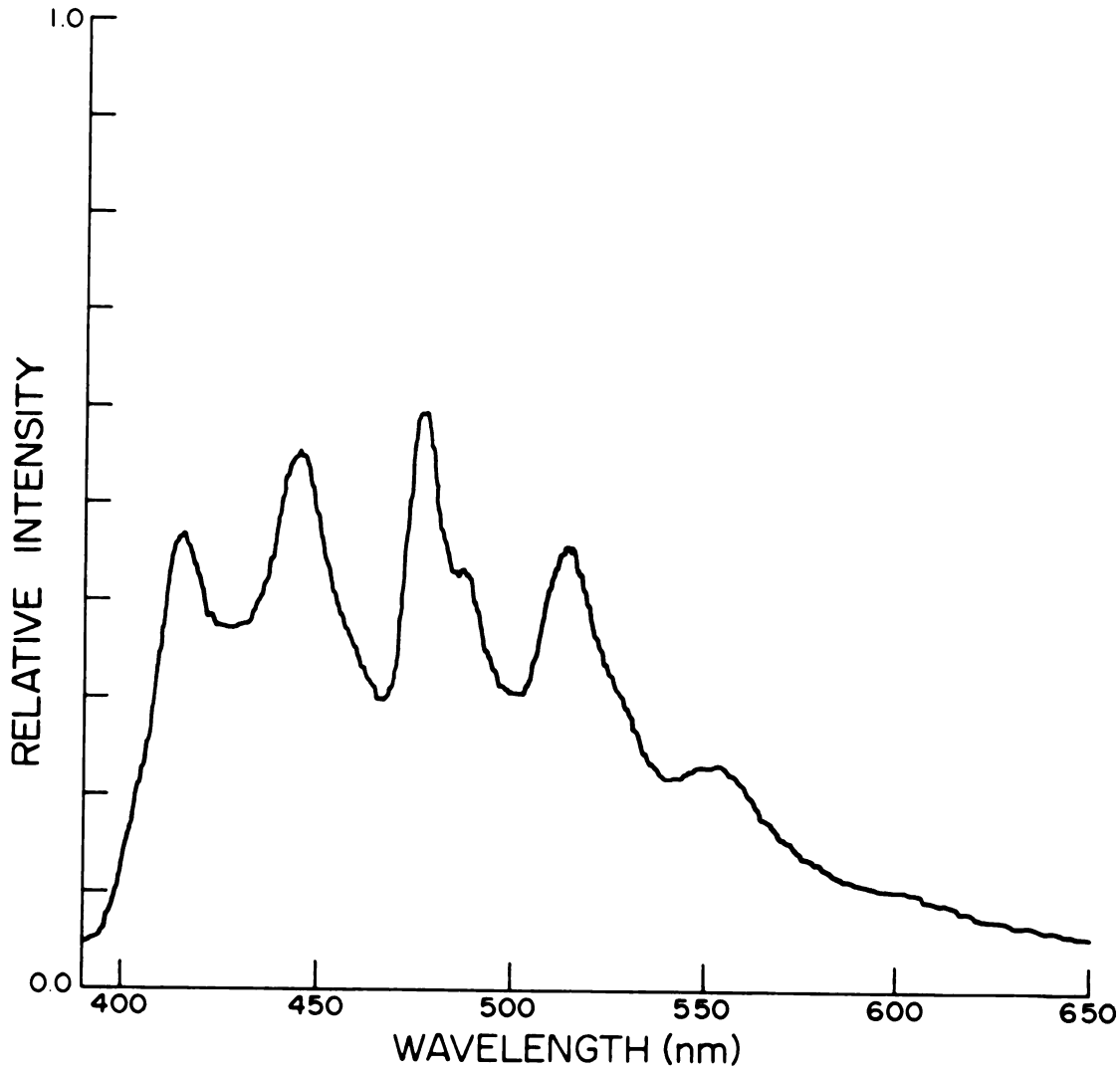


Figure 19. Phosphorescence spectra of crown 31. Excitation is at 307 nm. Concentration is 1.0 x 10-4 M.

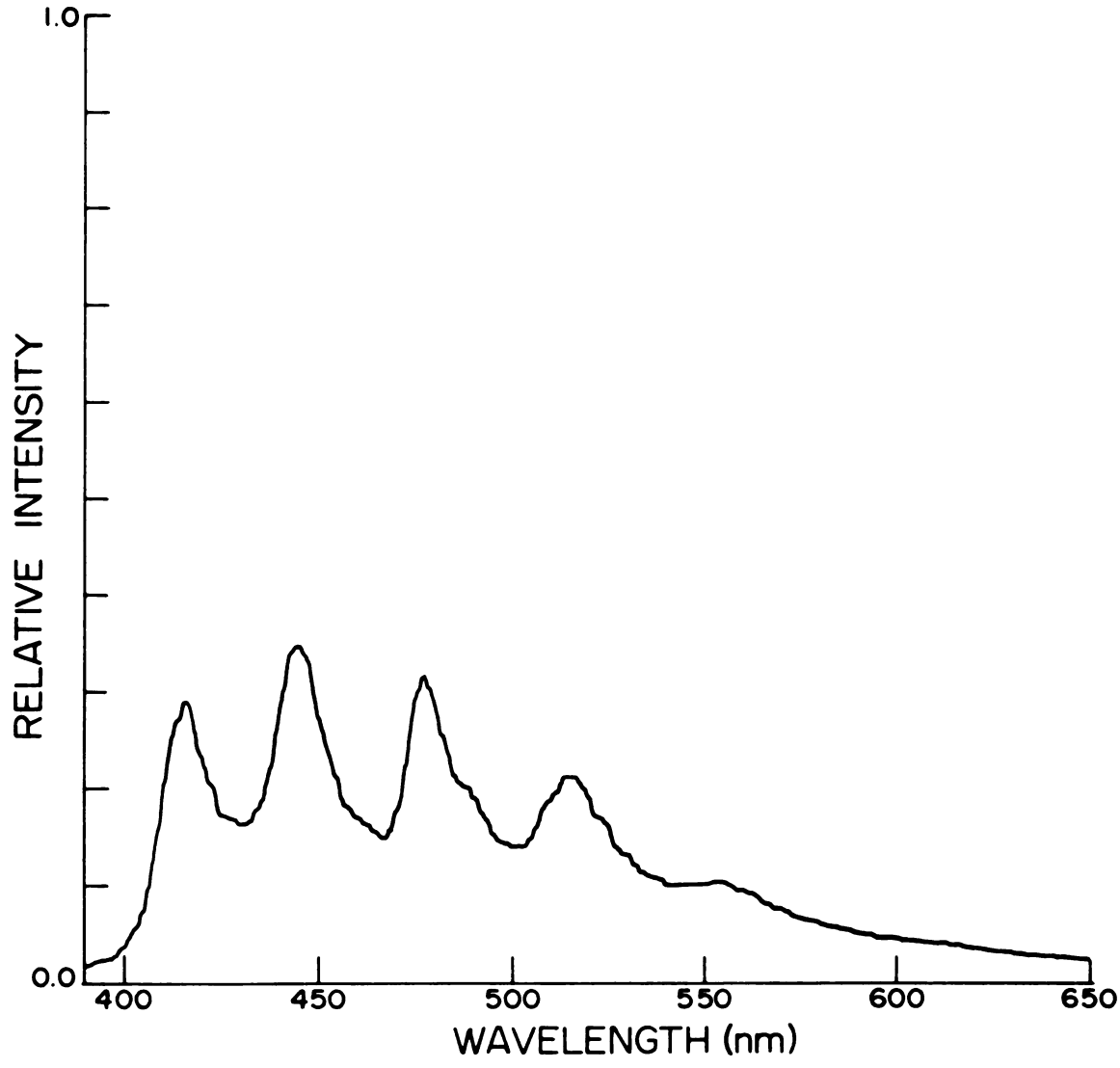


Figure 20. Phosphorescence spectra of crown 31. Excitation is at 350 nm. Concentration is 1.0 x 10^{-4} M.

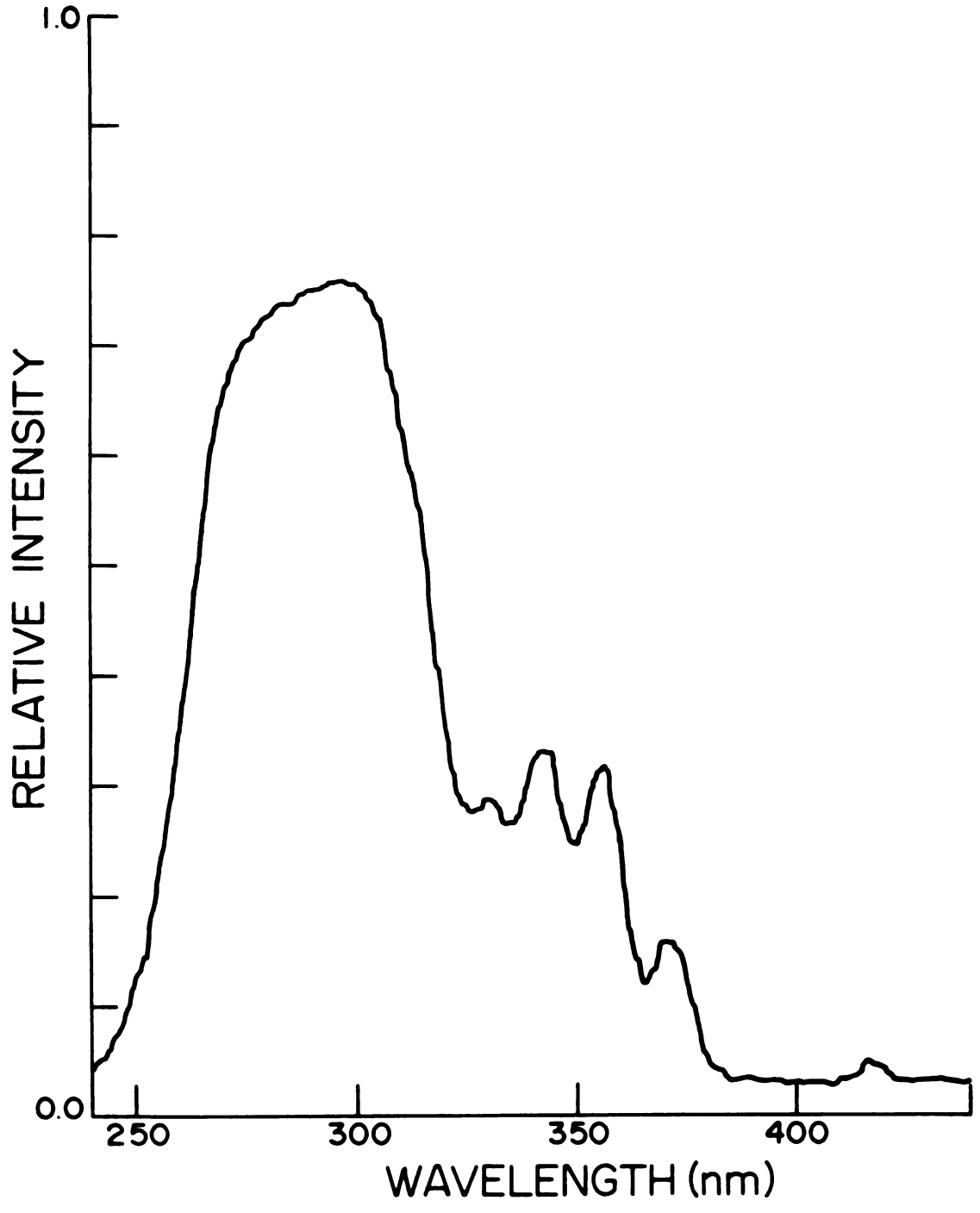


Figure 21. Excitation spectra of crown 31, observing at 415 nm. Concentration is 1.0×10^{-4} M.

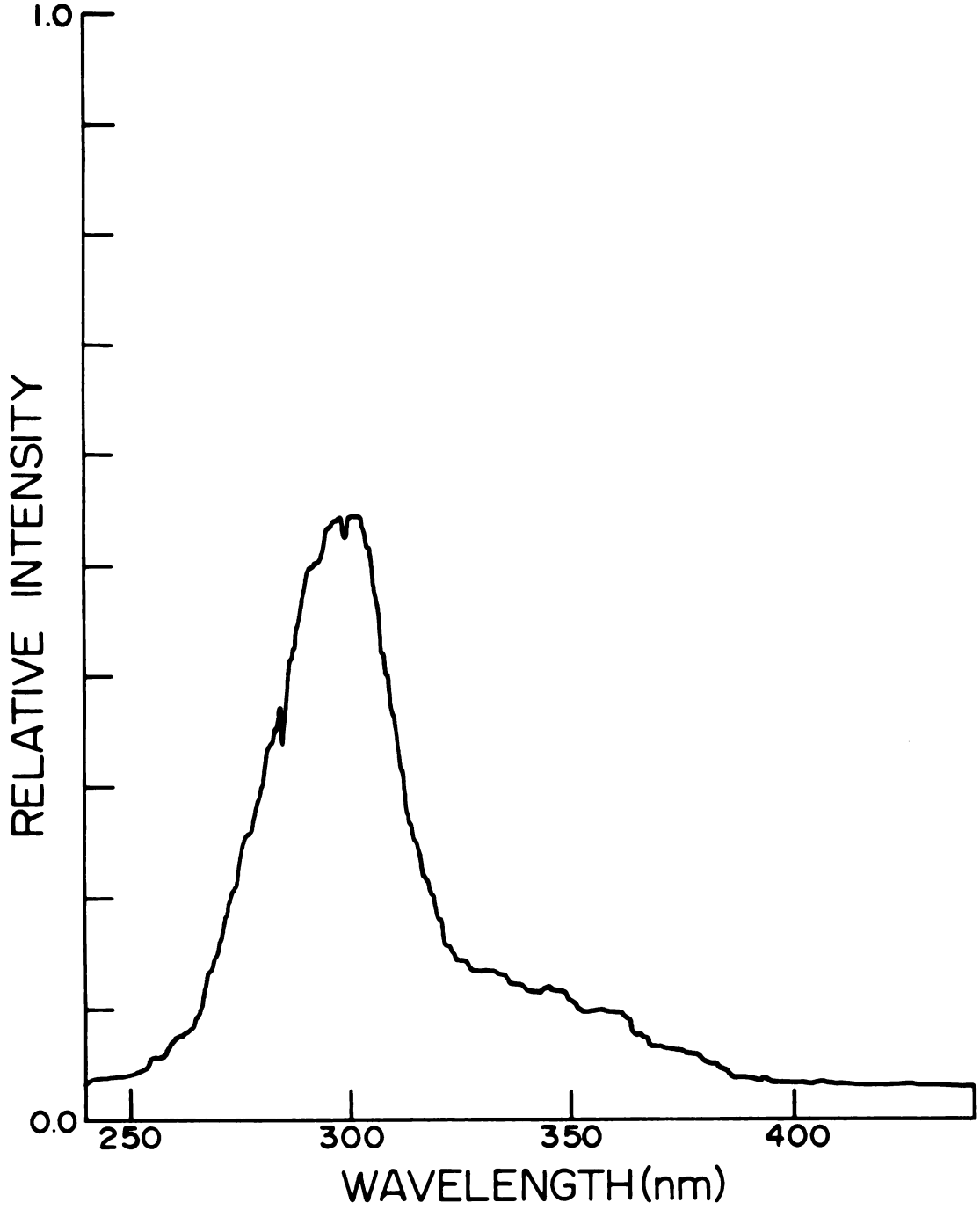


Figure 22. Excitation spectra of crown 31, observing at 560 nm. Concentration is 1.0×10^{-4} M.

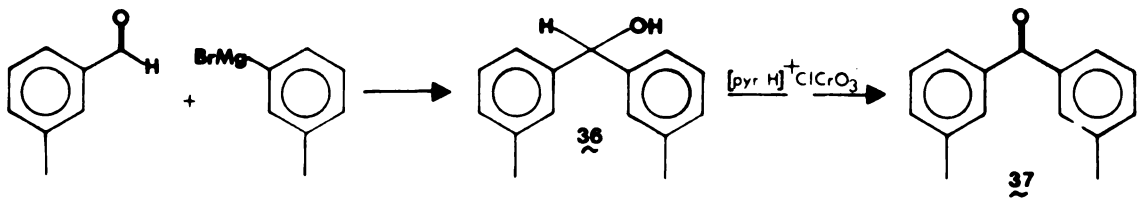
31. From these spectra (taken at 77 K in uncracked ethanol glasses), as well as others which are not reproduced here,[56] some qualitative statements can be made about energy transfer in these systems. Exciting at 350 nm (energy into benzophenone), a little naphthalene phosphorescence is observed, but not much. This is true for both 30 and 31. The naphthalene phosphorescence involves energy transfer from the benzophenone triplet (B_T) to the naphthalene triplet (N_T). These preliminary experiments indicate between 40% and 10% energy transfer. CPK models of 30 and 31 show that the distance between the centers of the two chromophores is between 14.5 to 15.5 Å in both crowns. This compares very well with the system of Keller and Dolby,[57] where the two identical chromophores are separated by about 15 Å, and the B_T to N_T energy transfer was about 20%.

If naphthalene singlet (N_S) to benzophenone singlet (B_S) energy transfer occurs, it is not a dominant process. When exciting at 307 nm (energy into naphthalene, and some into benzophenone), there is some benzophenone phosphorescence. However, this could be from minimal excitation of benzophenone. Still, one can't rule out 20-30% energy transfer on the basis of these spectra, although nothing in these results requires that N_S to B_S energy transfer is occuring.

From the room temperature U.V. spectra of 30 and 31, it can be seen that no eximer absorption is present. The crowns which have been placed inbetween the naphthalene and benzophenone chromophores have not greatly changed these energy transfer systems from those already reported. Also, there appears to be no big orientation effect since the energy transfer behavior of 30 is much like that of 31, and the fluorescence and naphthalene phosphorescence spectra for 30 and 31 resemble the

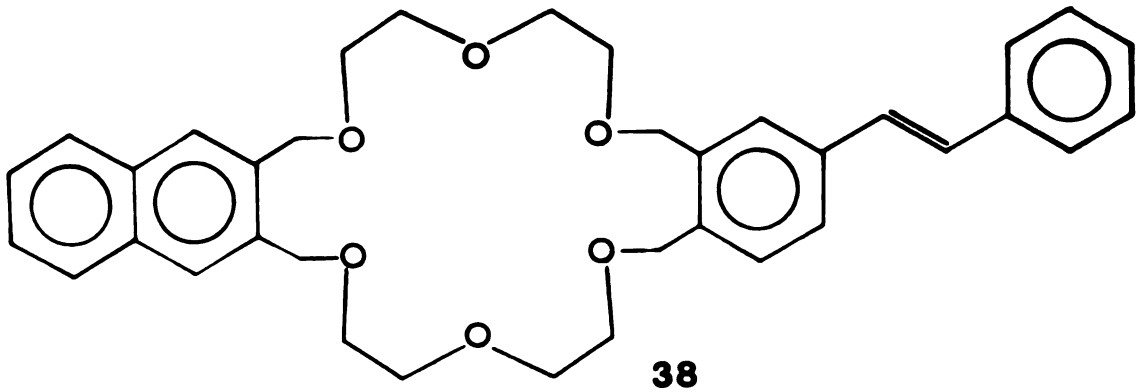
fluorescence and phosphorescence spectra for 3 and 6 respectively.[14]

Preliminary experiments with 31 and potassium, sodium, and cesium salts shows little, if any, effect of the alkali metal cation on the shape of the spectra, but may be affecting the quantum yields of fluorescence and phosphorescence. A detailed study as was done for 3 and 6[14] would be the only way to determine the exact extent to which the quantum yields are being affected. There are a variety of different crowns that could be made along the same lines as crowns 30 and 31. In addition to 2,3- and 1,8- orientation on naphthalene (x and y) one could also use a 1,5- orientation (z). In addition to 3,4- orientation on benzophenone (end), one could approach the carbonyl from another direction with either 4,4'- or 3,3'- orientation. The precursor to the 4,4'- system, 4,4'-dimethylbenzophenone is commercially available (Eastman), and the synthesis of 3,3'-dimethyl benzophenone (37) is outlined below.



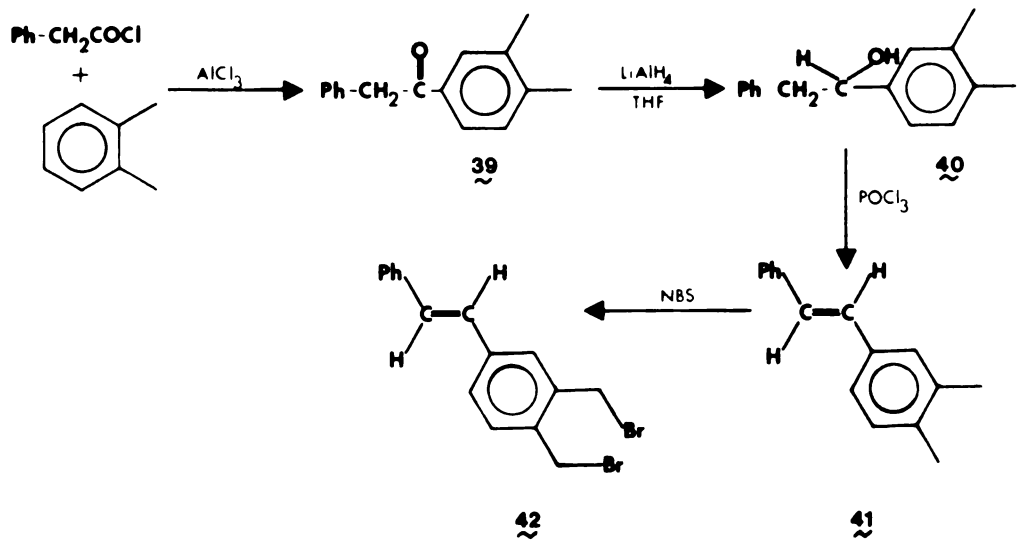
Another chromophore which would be interesting in an energy transfer system (as well as by itself) is stilbene. In an energy transfer system, energy transfer to the triplet state of stilbene would isomerize the double bond in stilbene, with a known yield of

isomerization.[58] Energy transfer might then be readily observeable by ^{1}H NMR. An example of such a crown would be 38.



38

To make the precursor for the stilbene chromophore, o-xylene was acylated with phenylacetylchloride. The carbonyl in the resulting desoxybenzoin (39) was reduced with lithium aluminium hydride, and eliminated with phosphorous oxychloride to give 3,4-dimethyl stilbene (41). Compound 41 was brominated in the usual manner to give dibromide 42 without bromination of the stilbene double bond.



39 40 41 42

An interesting project for the future would be to make crowns 30 and 31 with one less ethyleneoxy subunit on each arm of the crown. The resulting crowns, although possessing smaller cavities, might give larger amounts of energy transfer, since the chromophores are closer to each other.

EXPERIMENTAL

General. Fluorescence and phosphorescence spectra were taken on a Hitachi / Perkin-Elmer Spectrophotometer Model MPF-44A. Ultraviolet spectra were taken on a Varian Instruments Cary 219 spectrophotometer. Ethanol (95%) was donated by Dr. Jim Larsen, and its purification has been described in FULL detail.[14] Ether was distilled from sodium benzophenone ketyl immediately before use. Pyridine was stored over potassium hydroxide for at least one week prior to use. Mass spectra of crowns 30 and 31 were chemical ionization spectra taken on a Finnigan 4000 gc/ms with data system. All other instrumentation and procedures were as described in earlier portions of this dissertation.

Preparation of 2,3-bis(7-hydroxy-2,5-dioxaheptyl)naphthalene (32). To diethylene glycol (100 mL) was added freshly cut sodium (4.6 g, 200 mmol). The reaction is sluggish at first, but becomes quite vigorous and should be controlled with either a temperature bath or a condenser, in addition to sweeping nitrogen through the system. After solution of the sodium, the mixture was brought to reflux. 2,3-Bis(bromomethyl)naphthalene (3.14 g, 10 mmol) in THF (20 mL) was added in a dropwise fashion over a 3 h period. After an additional 3 - 6 h, the mixture was filtered, and the solvent removed by vacuum distillation. The resulting oil is taken up in dichloromethane (300 mL), washed with water (3 x 200 mL), dried over sodium sulfate, and the solvent removed under reduced pressure. This oil is then chromatographed on silica gel (c.a. 300 g). Subsequent elution with

dichloromethane gives a small crystalline fraction (2,3-naphtho-11-crown-3 ?), and a small amount of "one-armed" naphthalene. Elution with 0.5% methanol in dichloromethane gives a pure fraction of 32, 3.0 g (83%); ^{1}H NMR ($CDCl_3$) δ 3.35 (br.s, 16 H), 4.63 (s, 4H), 5.0-5.4 (br.s, 2H, dissappear with D_2O), 7.2-8.0 (br.m, 6H); ^{13}C NMR ($CDCl_3$) δ 61.27, 69.14, 70.12, 71.04, 72.31, 125.85, 127.28, 127.82, 132.51, 133.88; m/e 364.

Preparation of 1,8-bis(7-hydroxy-2,5-dioxaheptyl)naphthalene (33). Same as the preparation of 32, except that 1,8-bis(bromomethyl)naphthalene (3.14 g, 10 mmol) was used, 3.1 g (86%); ^{1}H NMR ($CDCl_3$) δ 3.1-3.3 (br.s, 2H, disappear with D_2O), 3.60 (s, 16H), 5.10 (s, 4H), 7.2-8.0 (br.m, 6H); m/e 364.

Preparation of 3,4-dimethylbenzophenone (34). To 1 L of o-xylene was added aluminum chloride (65.0 g, 0.487 mol) with stirring. After 10 min, the mixture was cooled to 0 °C, and benzoyl chloride (70.0 g, 58.8 mL, 0.453 mol) was added in a dropwise fashion. After 4 h, the reaction mixture was allowed to warm to room temperature, and stir for an additional 8 h. The mixture was washed with water (3 x 200 mL), the solvent removed under reduced pressure, and the resulting oil distilled at 1 mm. After a small forerun at 65 °C, the main fraction came at 110-120 °C, a clear oil which solidified on standing, 73 g (77%); mp 47-48 °C[59]; ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 6H), 6.9-7.8 (br. m, 8 H); ^{13}C NMR ($CDCl_3$) δ 19.52, 19.76, 127.82, 127.95, 128.12, 129.25, 129.70, 129.87, 130.97, 131.85, 135.13, 136.50, 137.90, 141.71, 201 (approx, foldover); IR (Nujol) cm^{-1} 1660 (s), 1610, 1595, 1575 (w); m/e 210.

Preparation of 3,4-bis(bromomethyl)benzophenone (35). To 3,4-dimethylbenzophenone (34, 10.0 g, 48 mmol) in carbon tetrachloride was added NBS[21] (16.9 g, 95 mmol) and the solution irradiated with a 200 watt sun lamp. After conversion of the NBS to succinimide (about 3 h), the solution was filtered, and the solvent removed under reduced pressure to give an orange oil, which was about 75% pure by ^{1}H NMR; ^{1}H NMR (CCl_4) δ 4.53 (s, 4 H), 6.8-7.8 (br.m, 8H); m/e 368. Attempted purification using an alumina column, with dichloromethane, then 0.5% methanol in dichloromethane gave a white solid (36); mp 87-89 °C; ^{1}H NMR ($CDCl_3$) δ 5.07 (s, 4H), 7.1-7.8 (br.m, 8H); m/e 224.

Preparation of 9,10-(1',2'-(4'-benzoyl)benzo)-20,21-(2',3'-naphtho)-1,4,7,12,15,18-hexaoxacyclodocosane (30). A solution of 3,4-bis(bromomethyl)benzophenone (2.96 g, 5.5 mmol, 75% pure) and 32 (2.0 g, 5.5 mmol) in 150 mL dry THF was added dropwise to a refluxing THF slurry of potassium t-butoxide (1.29 g, 11.5 mmol in 500 mL THF) over a six h period under a dry nitrogen atmosphere. The slurry was stirred at reflux another 4 h before filtration through a diatomatious earth pad, and subsequent washing of the solid with tetrahydrofuran. Solvent was removed from the filtrate under reduced pressure, and the resulting yellow oil was chromatographed on a quartz column with alumina (400 g, Fisher neutral alumina with Lumilux[29] added), and eluted with dichloromethane-methanol (200:1). After a broad band (several inches) which was observable using a 375 nm lamp had eluted, the narrow band after this contained the crown (30). The various cuts of this fraction were of different purity, with the first few cuts being of best purity. Furthur attempts to purify this compound on silica gel, alumina, or by

distillation only gave product of worse purity. The good fractions gave 67 mg of 30 (2%); ^{1}H NMR ($CDCl_3$) δ 3.5-3.8 (br.m, 16 H), 4.66 (s, 2H), 4.76 (s, 2H), 4.80 (s, 4H), 7.1-7.8 (br.m, 14 H); UV (95% ethanol) nm max 332 (ε86,000), 362 (ε17,500), min 308 (ε38,500), 338 (ε10,000), tail 510; m/e see Figure 23.

Preparation of 9,10-(1',2'-(4'-benzoyl)benzo)-20,22-(1',8'-naphtho)-1,4,7,12,15,18-hexaoxacyclotricosane (31). Same as the preparation of 30, except that bis(bromomethyl)benzophenone (5.40 g, 11 mmol, 75% pure) and 33 (4.00 g, 11 mmol) in 150 mL dry THF were used with potassium t-butoxide (2.59g, 23 mmol in 500 mL THF). Similar workup and chromatography gave 112 mg 31 (1.8% yield); ^{1}H NMR ($CDCl_3$) δ 3.6-3.9 (br.m, 16H), 4.63 (s, 2H), 4.72 (s, 2H), 5.02 (s, 2H), 5.05 (s, 2H), 7.1-7.9 (br.m, 14H); UV (95% ethanol) nm max 328 (ε92,200), 358 (ε19,720), min 308 (ε20,500), 338 (ε11,500), tail 510; m/e - see Figure 24.

Preparation of 3,3'-dimethylbenzhydrol (37). To magnesium turnings (0.56 g, 23 mmol) in dry ether (50 mL) was added m-bromotoluene (3.42 g, 20 mmol) at such a rate that vigorous reflux was maintained. After an additional 0.5 h reflux, 3-methylbenzaldehyde (2.40 g, 20 mmol in 20 mL dry ether) was added in a dropwise fashion over a 2 h period, while still refluxing. The reaction mixture was washed with saturated ammonium chloride (2 x 50 mL), water (2 x 50 mL), dried with sodium sulfate, and solvent removed under reduced pressure to give 4.10 g of 36 as on oil (97%); ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 6H), 3.25 (br.s, 1H, disappears with D_2O), 5.38 (s, 1H), 6.8-7.0 (br.s, 8H); ^{13}C NMR ($CDCl_3$) δ 21.05, 75.30, 123.36, 126.91, 127.75, 127.89, 137.50, 143.72; m/e 212.

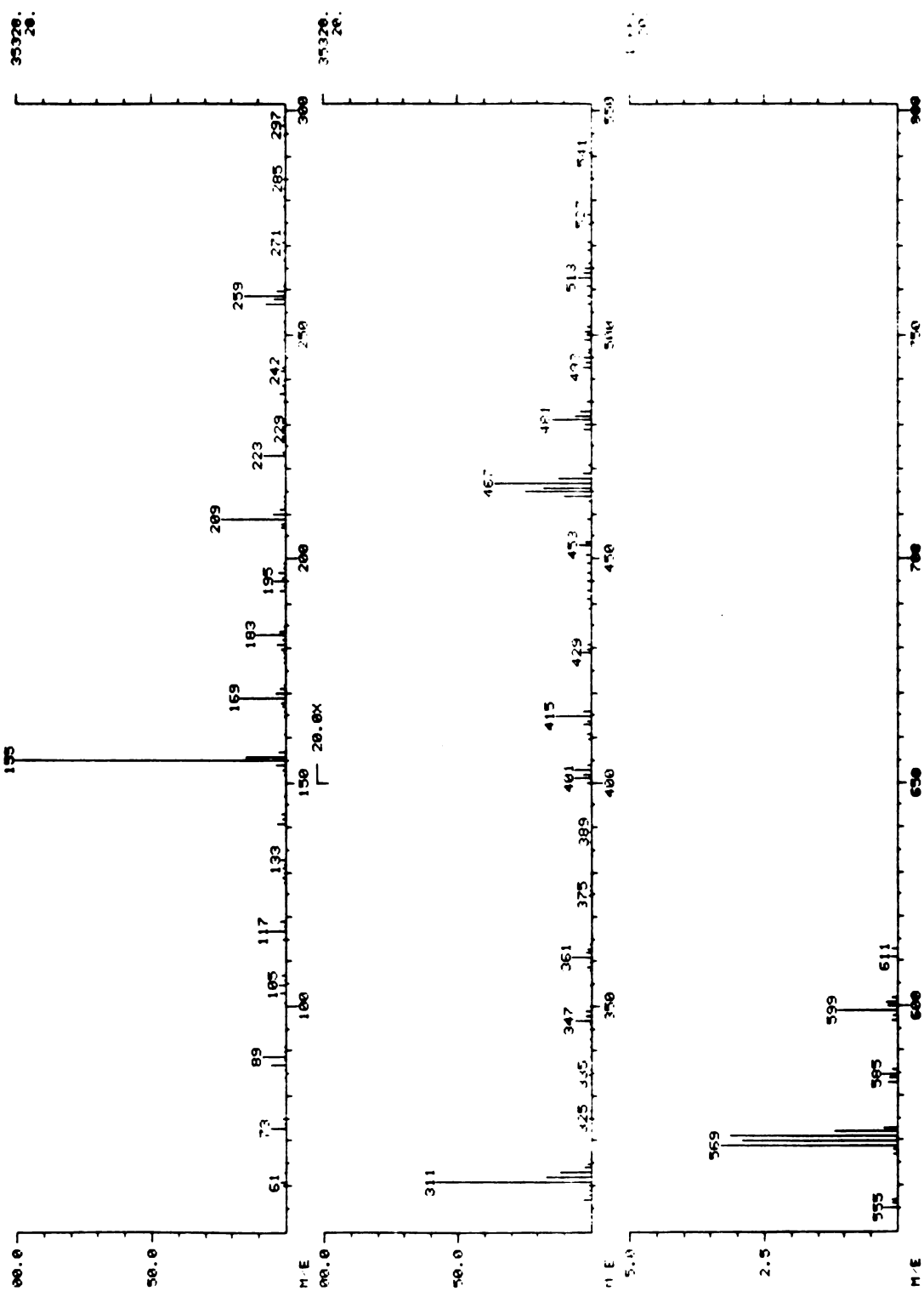


Figure 23. Chemical ionization mass spectrum of crown 30.

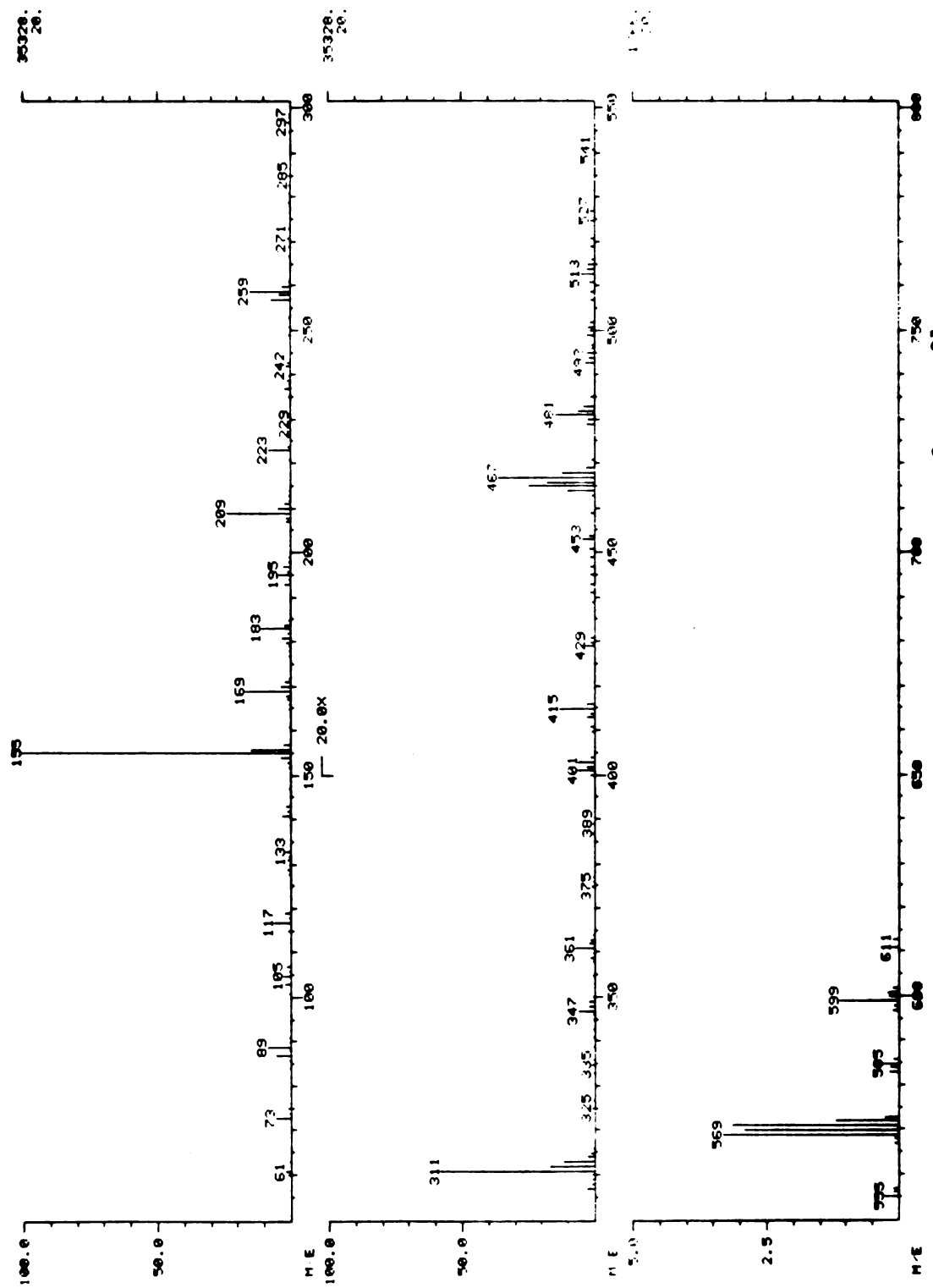


Figure 24. Chemical ionization mass spectrum of crown 31.

Preparation of 3,3'-dimethylbenzophenone (38). To 3,3'-dimethylbenzhydrol (2.12 g, 10 mmol) in methylene chloride (20 mL) was added pyridinium chlorochromate[60] (3.23 g, 15 mmol). The mixture turned black almost immediately. After 2 h, ether (20 mL) was added, and the solution filtered through a florisil plug. Solvent was removed under reduced pressure to give 2.05 g of 37 (98%); ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 6H), 6.9-7.1 (s, 8H); ^{13}C NMR ($CDCl_3$) δ 20.76, 123.19, 126.72, 127.36, 127.58, 137.07, 143.79, 193.89; m/e 210.

Preparation of 3',4'-dimethyldesoxybenzoin (39). To aluminum chloride (140 g, 1.05 mol) in o-xylene (2 L) was slowly added phenylacetyl chloride (140 g, 120 mL, 0.90 mol) in a dropwise fashion at 0 °C. After addition, the reaction mixture was stirred for an additional 8 h at room temperature. The mixture was then washed with water, and the xylene layer was reduced under vacuum. The resulting oil crystallized on standing, and after recrystallization from methanol / water, gave 127 g (63%) of 39; mp 90-91 °C (lit - 95 °C)[61]; ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 6H), 4.13 (s, 2H), 7.0-7.9 (br.m, 8H); ^{13}C NMR ($CDCl_3$) δ 19.43, 19.63, 45.05, 126.13, 126.42, 128.28, 129.16, 129.44, 129.53, 134.34, 134.71, 136.64, 142.33, 194.30; IR (neat) cm^{-1} 1675 (s), 1610, 1595 (w); m/e 224.

Preparation of 2-(3',4'-dimethylphenyl)-1-phenylethanol (40). To lithium aluminum hydride (7.6 g, 0.2 mol, x's) in THF (500 mL) was added 39 (22.4 g, 0.1 mol) in THF (100 mL) in a dropwise fashion. The mixture was allowed to stir for 8 h, after which water (7.6 mL), 15% NaOH (7.6 mL), and water (22.8 mL) were added.[24] After 2 h stirring, the pure white solid is filtered, and the filtrate evaporated under reduced pressure to give 22.5 g (100%) of a slightly yellow oil. An analytical

sample was prepared by molecular distillation (95 °C, 1 mm); ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3H), 2.20 (s, 3H), 3.25 (d, 2H, J=7Hz), 4.88 (t, 1H, J=7Hz), 6.8-7.5 (br.m, 8H); ^{13}C NMR ($CDCl_3$) δ 19.06, 19.40, 45.58, 74.76, 123.08, 123.28, 126.00, 126.92, 127.97, 129.20, 135.23, 136.00, 138.19, 141.23; IR (neat) cm^{-1} 3100-3550 (br.,s), 1605, 1500 (s), 1450 (s); m/e 226.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.75; H, 7.94.

Preparation of 3,4-dimethylstilbene (41). To alcohol 40 (20 g, 88 mmol) in dry pyridine (40 mL) at 0 °C was SLOWLY added phosphorous oxychloride (20 mL, 220 mmol, x's). Solid appears in about 10 min, but the reaction is allowed to stir an additional 8 h. Ice was then cautiously added to the reaction mixture. When the original violence seceeds, water was added to a total volume of 40 mL. The solution is then extracted with ether (2 x 100 mL), the combined ether layers washed with cold HCl (4 x 25 mL), and the ether removed under reduced pressure to give a solid which was recrystallized from ethanol / water, 16.6 g (91%); mp 72-73; ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 6H), 6.92 (s, 2H), 7.0-7.6 (br.m, 8H); ^{13}C NMR ($CDCl_3$) δ 19.37, 19.62, 123.91, 126.25, 127.16, 127.41, 127.68, 128.48, 128.64, 129.83, 134.89, 136.03, 136.53, 137.52; m/e 208.

Preparation of 3,4-bis(bromomethyl)stilbene (42). NBS (3.5 g, 19.7 mmol) and 41 (2.08 g, 10 mmol) in carbon tetrachloride (50 mL) were irradiated using a 200 watt sunlamp for 3 h. Although conversion to 42 is not complete, ^{1}H NMR indicates that the reaction mixture is about 60 % pure 42; ^{1}H NMR (CCl_4, external TMS) δ 4.42 (s, 4H), 6.88 (s, 2H), 7.0-7.5(br.m, 8H).

Chapter 4

Synthesis and Properties of Ferrocene Crown Ethers

Introduction

The discovery of ferrocene (dicyclopentadienyliron) in 1951[62,63] has led to the development of a field of organometallic chemistry, that of the π-metallohydrocarbons. Numerous extensive reviews have appeared.[64]

The general method for the preparation of pentahapto-cyclopentadienyl compounds applies to ferrocene.

$$2\ NaC_5H_5 + FeCl_2 = (h_5\text{-}C_5H_5)_2Fe + 2\ NaCl$$

A useful alternative method for the preparation of this "sandwich" or "Doppelkegel" compound is[64,65]

$$2\ C_5H_6 + 2\ (C_2H_5)_2NH + FeCl_2 = (h_5\text{-}C_5H_5)_2Fe + 2\ (C_2H_5)_2NH_2Cl$$

Ferrocene is an extremely interesting compound in that there is free rotation about the iron-cyclopentadienyl bond(s). This allows us to construct a crown of variable size, which may conform to a variety of different cations. The name we have given to this is the "ratchet" effect. Most ferrocene derivatives, as well as ferrocene, can also be reversably oxidized to give ferrocenium ion, as is the case with the ferrocene crowns.

Results and Discussion

Since 1,1'-bis(bromomethyl)ferrocene may not be a stable compound,[66] it seemed that the only reasonable precursor for ferrocene crowns was 1,1'-bis(hydroxymethyl) ferrocene. To this end, we searched the literature for methods to make this known compound.[67] Unfortunately, the majority of the literature methods were not reproducable, or gave yields drastically different from those reported by the authors.

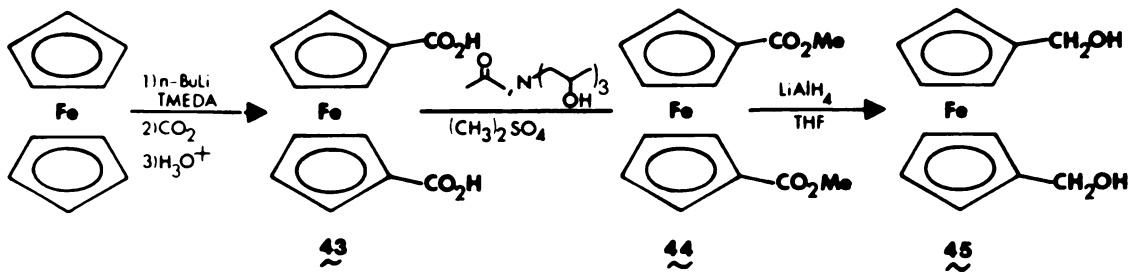
Raush and Ciapenelli[68] report a synthesis of 1,1'-ferrocene dicarboxylic acid which gives high yields (greater than 90%) from ferrocene. The method involves generating the 1,1'-dilithio anion of ferrocene, followed by carboxylation with carbon dioxide. This dilithio anion failed to give 1,1'-bis(hydroxymethyl) ferrocene when treated with gaseous formaldehyde, or solid paraformaldehyde. This dianion gave polymer when treated with ethylene oxide in an attempt of make 1,1'-ferrocene diethanol. The method of Raush and Ciapenelli does form the ferrocene carbon-carbon bond in high yields.

Direct reduction of 1,1'-ferrocene dicarboxylic acid proved to be futile, although this procedure has been reported.[67] Attempts to reduce the diacid with diborane in THF,[69] a reagent which is known for high yield reductions of diacids, failed to give bis(hydroxymethyl)ferrocene, as did direct reduction with lithium aluminum hydride.

The dimethyl ester of 1,1'-ferrocene dicarboxylic acid reduces cleanly and in high yield with lithium aluminum hydride to give 1,1'-bis(hydroxymethyl)ferrocene. A method to get the ester from the acid in high yield was needed. Acidic methanolysis tore apart the ferrocene

structure. Methanolysis of the acid chloride, which was formed by thionyl chloride chlorination on the diacid gave poor yields, and involved a lengthy column.[70] A much higher yield method involved methylation using a potent alkylating agent (dimethyl sulfate) with a weak comercially available base (tris(isopropanol)amine).[71]

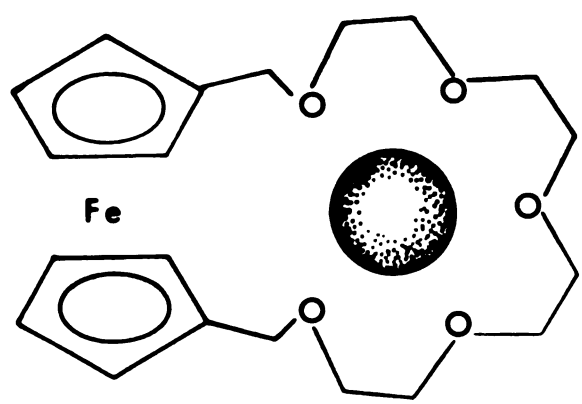
The entire synthesis of 1,1'-bis(hydroxymethyl)ferrocene is outlined below.



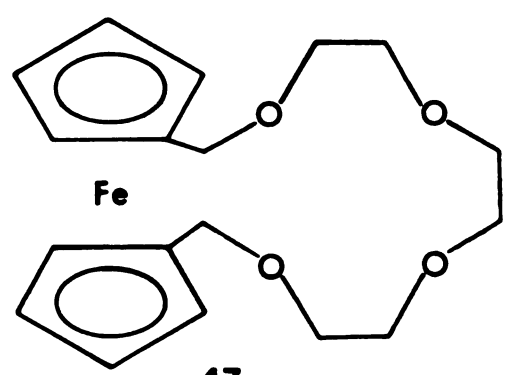
43 44 45

The synthesis is high yield, and has no tricky steps.

The ferrocene crown ethers were formed by standard crown formation reactions, i.e. the reaction of a dialkoxide with the appropriate polyethylene glycol ditosylate. The crown 5 and the crown 4 are shown below, with the crown 5 shown complexed to a cation.



46



47

The ferrocene crowns show a completely reversible oxidation in acetonitrile. Some preliminary experiments with alkali metal cations present during oxidation / reduction (cyclic voltammetry) shows little, if any, effect on the oxidation potential due to the presence of the alkali metal cations. This may be indicative of a very low complexation constant between ferrocene crown and cations.[72] This could be due to either unfavorable iron-alkali metal interactions, or could be due to the fact that the ferrocene crown prefers the 180° anti-prismatic conformation.[73]

An interesting experiment which was not run, but should be, is to see if one can see the two ferrocenylic protons decoalesce into two separate peaks in the low temperature ^{1}H NMR. These two protons are diastereotopic in all conformations but one. From this experiment, one could calculate the free energy of rotation about the cyclopentadienyl-iron-cyclopentadienyl bonds.

EXPERIMENTAL

General. Hexane was refluxed over calcium hydride for at least 24 h, and then distilled from calcium hydride immediately before use. Microanalyses were performed by Spang, Ann Arbor, MI. Ferrocene was purchased from either Aldrich or PCR, Inc. The gel permeation column used to separate polymer from monomer used Enzacryl gel K1, fine (Aldrich) which was swelled in THF for 24 h prior to column packing. All other instrumentation and procedures were as described in earlier portions of this dissertation.

Preparation of 1,1'-ferrocene dicarboxylic acid (43). Prepared by the method of Rausch and Ciappenelli,[68] yield 96%; mp dec over 245 °C (lit.[74] dec over 250 °C); ^{1}H NMR (d_6DMSO) δ 4.0 (br.s, 2H, COOH exchanging with DMSO), 4.40 (s, 4H), 4.65 (s, 4H); ^{13}C NMR (d_6-DMSO) δ 71.34, 72.66, 73.47, 171.13; m/e 274.

Preparation of 1,1'-bis(methoxycarbonyl)ferrocene (44). To 1,1'-ferrocene dicarboxylic acid (15.0 g, 55 mmol) and tris(isopropanol)amine (22.0 g, 115 mmol) in acetone (85 mL) was added dimethyl sulfate (13.8g, 10.4 mL, 100 mmol) and the system refluxed for 3 h. The acetone was evapoarated, the resulting sludge taken up in benzene (200 mL), and washed with water (2 x 100 mL), 0.5 N hydrochloric acid (2 x 50 mL), then dried over magnesium sulfate, and concentrated under reduced pressure. The resulting solid was recrystallized from cyclohexane to give 14.5 g (87%) of crystalline 44; mp 116-118 °C (lit 114-115 °C);[67a] ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 6H), 4.33 (t, 4H, J=2 Hz), 4.75 (t, 4H, J=2

Hz); ^{13}C NMR ($CDCl_3$) δ 51.55, 71.49, 72.48, 72.81, 170.67; m/e 302.

Preparation of 1,1'-bis(hydroxymethyl)ferrocene (45). To lithium aluminum hydride (1.68 g, 44 mmol, 2 fold x's) in THF (100 mL) was added 44 (6.7 g, 22 mmol). The mixture was allowed to stir for 12 h, after which water (1.7 mL), 15% NaOH (1.7 mL) and water (5.1 mL) were added. After an additional 2 h, the mixture was filtered, and the solvent removed under reduced pressure to give 5.37 g (100%) of 45; mp 96-97 °C; ^1H NMR ($CDCl_3$) δ 4.12 (s, 4H), 4.32 (s, 4H), 4.7 (br.s, 2H); ^{13}C NMR ($CDCl_3$) δ 60.15, 66.93, 67.90, 89.25; m/e 244.

Preparation of 1,1'-ferroceno-18-crown-5 (46). To potassium t-butoxide (2.36, 21 mmol) in a mixture of THF (200 mL) and dimethylformamide (50 mL) was added with stirring a mixture of 1,1'-bis(hydroxymethyl)ferrocene (2.44 g, 10 mmol) and tetraethylene glycol ditosylate (5.02 g, 10 mmol) in THF (50 mL). Potassium tosylate (suspended shiny plates) was visible after 0.5 h, but the reaction was allowed to go 10 h. The mixture was then filtered through a diatomatious earth pad, and the filtrate concentrated under reduced pressure. The resulting yellow oil was chormatographed on alumina (400 g, Fisher neutral alumina), and eluted with dichloromethane to remove the first running fractions yellow and yellow-orange). A narrow fraction (orange) which started to move with 0.5% methanol in dichloromethane was collected, and although it gave a good ^1H NMR, the mass spectrum showed higher molecular weight material was present. This fraction was then run through a gel permeation column with THF as solvent. Of the two major bands, the second was found to contain 104 mg 46 (26%) as a brown, air and light sensitive oil; ^1H NMR ($CDCl_3$) δ 3.67

(s, 8H), 3,70 (s, 8H), 4.0-4.2 (br.m, 8H), 4.30 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 67.97, 68.85, 69.01, 69.33, 69.54, 70.70, 71.10, 84.87; UV (95% ethanol) nm max 207 (ε38,720); m/e 404.

Anal. Calcd. for $C_{20}H_{28}O_5Fe$: C, 59.42; H, 6.98; Fe, 13.81. Found: C, 59.28; H, 6.90; Fe, 13.55.

Preparation of 1,1'-ferroceno-15-crown-4 (47). Same as the preparation of 46, except that triethylene glycol ditosylate (4.59 g, 10 mmol) was used, 158 mg (4.4%); ^1H NMR ($CDCl_3$) δ 3.63 (s, 4H), 3.68 (s, 8H), 3.9-4.2 (br.m, 8H), 4.37 (s, 4H); m/e 360.

Anal. Calcd. for $C_{18}H_{24}O_4Fe$: C, 60.01; H, 6.72; Fe, 15.50. Found: C, 59.93; H, 6.79; Fe, 15.29.

Preparation of 1,1'-ferroceno-21-crown-6 (48). Same as the preparation of 46, except that pentaethylene glycol ditosylate (5.47 g, 10 mmol) was used. The compound decomposed prior to final purification on gel permeation column; ^1H NMR ($CDCl_3$) δ 3.6 (br.s, 20H), 4.1 (br.s, 8H), 4.3 (br.s, 4H); m/e 444.

Chapter 5

A Working Minicomputer - Fluorescence Spectrophotometer Interface

Introduction

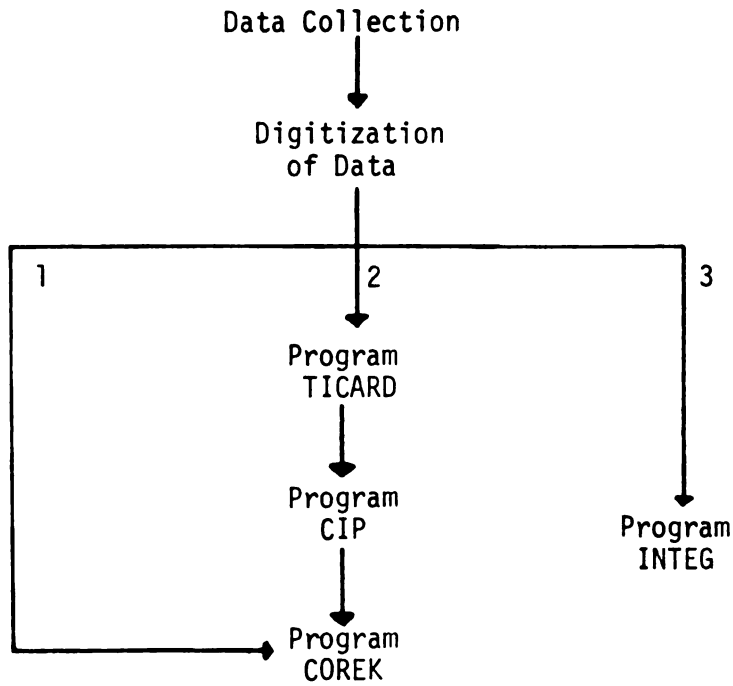
During a recent study on excited state processes of naphthalene crown ether derivatives,[12a,13,14] it became necessary to devise a better way to handle the calculation of fluorescence and phosphorescence quantum yields. Although this only involves comparison of integrated areas, the areas must be expressed in units of cm^{-1} instead of nm, and there is no simple relationship between the areas defined by the two inverse quantities nm and cm^{-1}. To directly obtain spectra which were a function of cm^{-1} would require unreasonably extensive hardware modifications to the fluorescence spectrophotometer. The first method used to solve this problem involved tedious digitization of fluorescence and phosphorescence spectra (sometimes taking up to three months for a set of fifty spectra), running these data points through programs designed to integrate over the spectral regions involved, and comparing the resulting regions to a standard. These progrms are described in more detail in the next section, and are listed in Appendix B.

The decision to interface the Hitachi / Perkin-Elmer fluorescence spectrophotometer to a digital computer was made when it became clear that not only was a backlog of potentially useful data accumulating, but also that an interactive system would facilitate periodic running of standards to check for machine drift. The project entailed design of an analog-to-digital converter (A/D) interface to a PDP8/E,[75] followed by development of software to drive the interface and interact with the

Hitachi / Perkin Elmer. Due to a necessitated operating system change on the PDP8/E, a new software system was written which also gave expanded capabilities. Both of these programs, the first written in BASIC and the second in a mixture of FORTRAN 2 and SABR, are listed in Appendix A.

Results and Discussion

The original system of data collection which depended on digitalization of spectra followed one of three paths, depending on the spectrofluorometer which was used for data collection (see Figuire 25). The main data processing program was COREK (data COREction and reduCtion program). Data could be submitted directly (by cards) into COREK, but the input to COREK was moderately tedious and complicated, and the personel using the programs were moderately unskilled in the use of digital computers. Computer turnaround at this particular time was slow, and an error in the input deck for COREK would usually mean a one day delay in productivity. Also, the typing of repetitive title cards for each spectrum was tedius. Therefore, an interactive system of programs was devised to submit a "gramatically" correct input deck for COREK. TICARD (TItle CARD program) would use as input digitized data punched on cards, and stored on a disk file in the CDC 6500 system. After placing appropriate title cards in the data deck, TICARD would create a file which would serve as input for CIP (Corek Interactive Program). TICARD also checked data for errors in format. CIP would interactively create a deck for submission to COREK. Program COREK read in standard spectra to correct background in the experimental spectra, and after subtracting this background, would convert nm to cm^{-1} and



1. Aminco - Bowman with computing experience.
2. Aminco-- Bowman.
3. Perkin - Elmer.

Figure 25. System for data reduction prior to the computer interface.

integrate. The spectra would then be plotted on the line printer, and if desired, a "good" CALCOMP plot of these spectra could be obtained. The quantum yield was also calculated.

After using this system for several months, a new fluorescence spectrophotometer, the Hitachi / Perkin-Elmer was obtained. The decision was made that all of the plots were not really very useful, and since the Hitachi corrected each spectrum, a program just to convert nm to cm^{-1}, integrate, and calculate quantum yields was all that was needed. Program INTEG (INTEGration program) did just this, and was moderately short.

The laborious part of this whole system was still the digitalization of spectra. In addition to the immediate acquisition of areas and quantum yields, a method to check the Hitachi / Perkin-Elmer for reliability was needed, since the instrument would occasionally drift. A fact which was discovered after the interface was up and working was that visual inspection of spectra could not determine subtle differences which could account for as much as a 10% error in area.

An A/D interface was designed by Mr. Martin Rabb and Dr. Thomas Atkinson. The card which contained the interface for the A/D converter and the PDP8/E also contained a programmable read only memory (PROM) which was wired for field 7 (the highest field of memory) of the PDP8/E. A program to boot several system devices (including SLSi floppy disk drives) as well as load either the RIM loader[76] or the Absoulte Binary Loader[7] was written[78] and placed in the PROM.[79] The A/D interface was software compatible with the Digital Equipment Corporation (DEC) A/D package. Originally, we had not intended to use the 2 V corrected signal which comes from the computer in the corrected spectra accessory

(it serves no other function! - it may have been intended for just such an application). Instead, we had planned on using the 10 mV input to the strip chart recorder. Insurmountable problems were encountered in attempting to amplify this signal adequately. A pulse from the CPU of the PDP8/E was inherent in the circuitry, and interfered with true A/D sampling, showing up as "random" noise. Thus, the 2 V signal was used to record data. This really made more sense, since it seems redundant to cut a 2 V signal to 10 mV for a strip recorder, only to try to amplify it back to a reasonable level.

The method of synchronization between the mechanical movement of the Hitachi and the real time programmable clock[80] in the PDP8/E was the next decision to be made. Ideally, the computer would use a digital-to-analog converter to actuate a response from the Hitachi. The expense and other factors[81] led us to use another method. When the switch which acutates the wavelength advance is closed on the Hitachi, a relay is flipped which starts the chart recorder motor. This recorder output was monitored by a second A/D channel, and when a voltage change was encountered, the computer was freed from a static loop into the actual data collection part of the program. Since the chart recorder and Hitachi wavelength drive had to be well synchronized, the Hitachi and the clock in the PDP8/E were also well synchronized.

One additional feature of hardware (and indirectly software) should be discussed prior to the interface programs. The floppy disks on the computer were extremely unreliable over long periods of time. Although the data collection programs had a restart option included in them, this problem was often more than a minor annoyance. If the floppys had a failure during the running of a program written in BASIC, the system had

to be re-booted, a process which required manually keying in eighteen instructions. The reason for this was that the OS/8 monitor had been swapped out by BASIC, unlike the FORTRAN system which leaves OS/8 in the last page of the first 8 K of core, with location 7600_8 (or 7605_8) available for re-entry into OS/8. Although switching to the FORTRAN system aided in error recovery, the major aid to solving this problem was completion of the PROM bootstrap which resided in locations 77000_8 to 77777_8. The OS/8 handler for the SLSi floppies was also modified to decrease system failures. During diagnostics, it was noted that often when an error occured, it could recover through a re-try, averaging about 5 re-tries when this error occured. Since the old handler only allowed 3 re-tries, that number was changed to 200_8. This fixed a large percentage of the problems. One additional source of problems was the highly "patched" nature of our version of OS/8 version 3C. The BASIC compiler in this version had some severe problems which were "fixed" by patches. However, these patches often led to seemingly random (though often reproducible) errors. When OS/8 version 3D was released, BASIC was much improved, but the library of routines which contained A/D software no longer worked, due to some of BASIC's internal subroutine numbers not being updated in the patch. Since DEC was giving minimul support, the data collection program was rewritten in FORTRAN 2. This software / hardware package seemed to operate with minimal downtime.

As previously mentioned, the first data collection program was written in BASIC. After a certain amount of initialization, the program would request whether or not the current set of runs was a restart. This allowed either a fresh start, or for old areas from previous runs to be read in and stored, with the run counter starting at the next

available run number. One could also change the run number to re-run certain spectra (such as standards). The starting and ending wavelength were then input, as well as the speed at which the data were to be collected. Only three speeds of the Hitachi were truely useful for quantum yield determinations, those being 240, 120, and 60 nm per minute. The number of data points which could be sampled in a second, given BASIC's huge overhead, was about 250. Thus, 240 data points per second was determined to be a "safe" number to collect. Original attempts to use only one A/D conversion to give a data point displayed the considerable noise still inherent on the data line between the Hitachi and the A/D circuitry. By taking many A/D conversions for each data point and averaging, a very reproduceable digital representation of the spectra being taken was obtained. Sampling was done at 240 points per second, and data were stored at 1/2 nanometer increments, so when runing at 120 nm/min, we collected and averaged 60 data points every 1/4 second, then stored this point. For 60 and 240 nm/min, we averaged 120 and 30 data points respectively. Data were collected as soon as the computer was released from a loop by a change in voltage at the recorder relay which was being monitered by the second A/D channel. Within the actual collection routine, the correct number of data points would be sampled, averaged, stored, and then the computer would wait for an overflow from the clock. If an overflow occured before the sampling and averaging was done, a message to note a timing error was printed.

After collection of points, the spectrum had to be integrated. After determining the lowest point in the spectrum, and refering to this point in nm, the program would allow placement of a baseline (which could be sloped). The program also allowed the user to decide where to

start and stop the integration in nm. After integration, this procedure could be repeated if the results were unsatisfactory. Otherwise, the program allowed one to calculate the quantum yields by dividing the integrated areas from individual runs by areas determined for standard compounds and multiplying by the known quantum yield for the standard. A correction for different sensitivity settings and different efficiencies of absorption relative to the standard could be applied. The program then cycled to input the next spectrum.

There were some disadvantages to the data collection program in BASIC. The first was the extensive use of disk that BASIC must make. In fact, it was necessary to put an unnecessary call to the A/D converter in the program so that BASIC would swap out string-handling routines and swap in the routines for A/D conversions. This could not happen in the data collection loop, as it would obviously interfere with the rather delicate timing required for sampling. Another disadvantage was that once sampling started, there was no way to restart the run other than killing the program. This restart was often a necessity if something was not properly set on the Hitachi. A previously mentioned disadvantage was the inability to boot OS/8 directly when BASIC failed.

The second data collection program was written in a combination of FORTRAN 2 and SABR. SABR code is essentially assembly language, and has the advantage of being able to be mixed directly with FORTRAN 2 code. This second program is essentially a direct translation of the first, except that it is much more modular. It also solves the problem of interrupting the data collection routine.

Subroutine AHEM checks to see if a character has been entered from the keyboard. If it has, data collection is irrecoverably terminated,

and the run is restarted. Subroutine CLW waits for the clock to overflow. It does not generate an error if the timing is off, but this feature is not really needed. A conservative estimate of the maximum collection rate in this program is 1000 points per second, much faster than with the slower BASIC. This tended to give us "truer" data points after averaging, but the effect on the areas was not perceptible. Subroutine CLK which starts the real time clock should be changed if rates of higher than 240 nm / min are to be used. The use of disk was minimized in this program, and was used only as a back-up.

The computer to fluorescence spectrophotometer interface allowed virtually instantaneous integration of spectra, with integration taking place in less than five seconds. A typical days run could handle fifty to one hundred spectra, which would have taken several weeks intensive work in the past.

Two other computer programs which are listed in Appendix B are UCHECK and ATOMOV. These programs are intended for usage with a computer program written by Professor J.F. Harrison to perform INDO calculations[82] and have been extensively used.[16] UCHECK is used to check input parameters, and calculate distances within a given cutoff from cartesian coordinates. ATOMOV will generate a vector between two atoms, move one of the two atoms along this vector to a new bond length, and output the cartesian coordinates.

EXPERIMENTAL

General. A Digital Equiptment Corporation PDP8/E minicomputer with 16 K words of memory, a programmable real time clock, and dual Standard Logic Systems floppy disks was interfaced to a Hitachi / Perkin-Elmer Spectrophotofluorometer Model MPF-44A with a computerized corrected spectra accessory. A 2 V corrected signal from the corrected spectrum accessory was converted to a digital value by the A/D converter in the PDP8/E, and the digital value acquired by software. All other computer programs were performed by the MSU-CDC 6500 computer running under the HUSTLER operating system.

Chapter 6

Some Studies Directed Toward the Synthesis of (+)-Disparlure

Introduction

The gypsy moth is a serious defoliator of forest, shade, and orchard trees in the northeastern United States, and is rapidly spreading to the South and more slowly to the West.[83] When DDT (α,α-bis(p-chlorophenyl)-β,β,β-trichloroethane) became available in the late 1940's, it served as an effective weapon against the gypsy moth. However, DDT's use was curtailed in 1958, and has been illegal through most of the 1970's.[84] In 1970, the gypsy moth defoliated 800,000 acres of forest, and in 1971 this figure rose to 1.9 million acres.

The two methods currently in use to attempt to stop the proliferation of the gypsy moth are the following:

1) The importing of parasites and predators which can control the gypsy moth through natural biological processes.

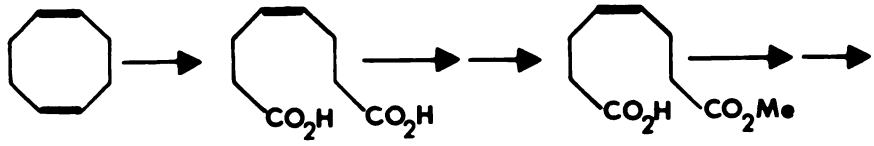
2) Carbaryl (Sevin), an insectiside which is effective against the gypsy moth, but is applied at the rate of one pound per acre.

Other methods including the use of a fatal larval virus have been attempted, but all have had little success in achieving anything but partial control. The gypsy moth population has certainly not been decreased.[83]

In 1970, the structure of disparlure, the sex attractant produced by the female gypsy moth (Lymantria dispar or Porthetria dispar (L.)), was shown to be cis-7,8-epoxy-2-methyloctadecane.[85] With this discovery, coupled with the ability to synthesize disparlure, one could fight a

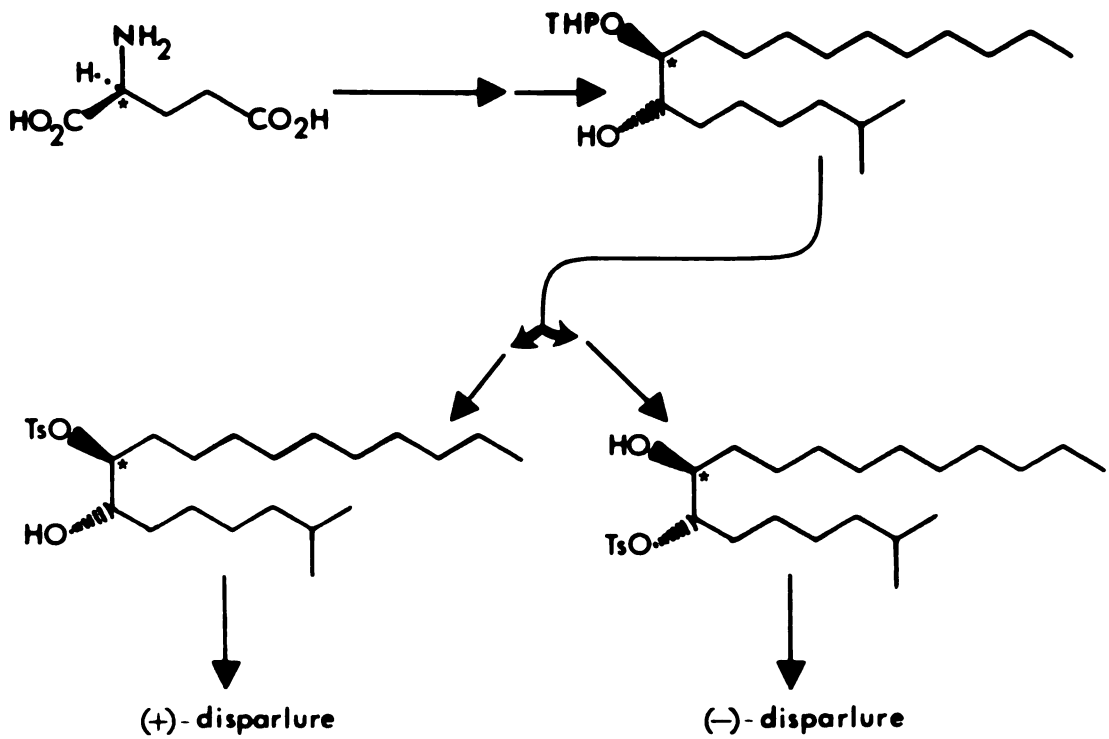
more modern battle with the gypsy moth, using its sex pheremone to disrupt and confuse its mating habits.

The first synthesis of racemic disparlure by Beroza and coworkers[85] involved the epoxidation of the olefin (Z)-2-methyl-7-octadecene, which was in turn prepared by a Wittig synthesis from 6-methylheptyl bromide and undecanal. A very similar synthesis of Bestmann and Vostrowsky[86] used the alcohol formed from isoamyl magnesium bromide and oxetane, followed by hydrogen bromide treatment to give 6-methylheptyl bromide. The synthesis was identical to that of Beroza and coworkers after that point. Several other racemic syntheses have appeared in the literature, but one of the most novel is the work of Kluenenberg and Schaefer,[87] which involves a double Kolbe electrolysis.



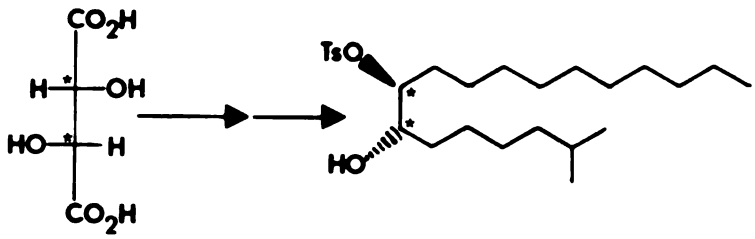
The starting material (Z,Z)-1,5-cyclooctadiene is the source of the (Z)-alkene which is epoxidized to disparlure. The Kolbe electrolysis is used to place the two alkyl groups on each side of the (Z)-alkene. Although these syntheses afford racemic disparlure in good yield, the racemic mixture is not nearly as attractive to the male moths as the (+) enantiomer,[88] making the need for a stereospecific synthesis acute.

The first stereospecific synthesis of (+)-disparlure[89] by Marumo and coworkers[90] established the configuration of the active enantiomer of disparlure through synthesis of both enantiomers and concurrent activity testing of each of these two enantiomers.[91]



The chiral center in (S)-(+)-glutamic acid gives rise to the C-7 center in the final product; the transformation is achieved directly for the (-) enantiomer, and with inversion through S_N2 displacement in the (+) enantiomer. The configuration of the C-8 center is asymmetrically induced. If a tosylate group is attached to C-8, then the center is formed by inversion (-). If a hydroxyl group is attached to C-8, then the configuration is retained during epoxide formation (+). Although the synthesis is elegant, it is fairly long, and would not be adaptable to a larger scale. One fairly intersting entomological result which surfaced from this investigation is that the receptor system in the olfactory organ of the male insects is chiral, responding to the (+)-disparlure preferentially to the (-) enantiomer and the racemate. A severe limitation of the synthesis is that the products are contaminated with at least 5.8% of their enantiomers.

Mori reports a synthesis of (+)-disparlure which is better than 98% enantiomerically pure, and provides sufficient quantities of material (more than 1 gram) for wind tunnel bioassays, electro antennagrams, and field testing.[92] The source of optical activity for Mori's synthesis was (2S:3S)-threo tartaric acid (L-(+)-).



These asymmetric carbons give rise to C-7 and C-8 in disparlure directly. Although the authors point out that the crystalline nature of the immediate precursor to disparlure allows for repeated recrystallization, and therefore high enantiomeric purity, it should be noted that the precursor possesses only two assymetric carbon atoms. The precursor has availiable only two diastereomers, and both would give rise to a trans analog of disparlure. Unless the already highly enriched pro-(+)-cis enantiomer would preferentially recrystallize, the authors only have a method to assure high purity, not high enantiomeric purity. ^{1}H NMR tests of one of the aforementioned precursors gave estimates of greater than 98% purity. Although this synthesis gives high enantiomeric purity, it still suffers from its length. An additional shortcoming of this synthesis is the possibility for racemization in the last step.

Recently, Pirkle and Rinaldi[93a] report a synthesis which generates a non-resolved mixture of enantiomers which are virtually identical to the hydroxysulfide intermediates generated by Farnum et al.,[94] the

difference being that in the Farnum synthesis, the hydroxysulfide has been prepared optically active. Pirkle resolves his intermediate by separation of diastereomers generated from the reaction of hydroxysulfide and (R)-1-(1-naphthyl) isocyanate. This step although acomplishing its goal, requires a very expensive chiral reagent, rendering this synthesis useless for large quantities of disparlure. It may however provide a method[93b] for procuring very pure (+) and (-) disparlure samples, by applying the method two or three times to the hydroxysulfide intermediate of Farnum et al.

Currently, the method of Farnum et al. is the only source for large quantities of disparlure. The modified and scaled-up version has been used to provide a 35 g quantity to the U.S.D.A. for field testing (1978), and with some furthur improvements, should be able to yield kilogram quantities on an industrial scale, perhaps as cheaply as $200 per gram.

The synthesis of Farnum et al. is outlined in Figure 26. Notice that the enantiomerically pure source does not contain an asymmetric carbon which ends up in the final product as do the syntheses of Marumo and Mori. Instead, the (ℓ)-menthol is used to fix the stereochemistry of sulfur in the sulfinic ester, which in turn asymmetrically induces the configuration of the α-carbon atom formed by the subsequent aldol. After condensation with undecanal, one is again left with two diastereomers which must be separated. The sulfur (now in the form of a sulfoxide) is reduced, and therefore loses its asymmetry, although C-7 and C-8 in the pro-cis sulfide have already had their stereochemistry fixed in the preceding aldol-like condensation.

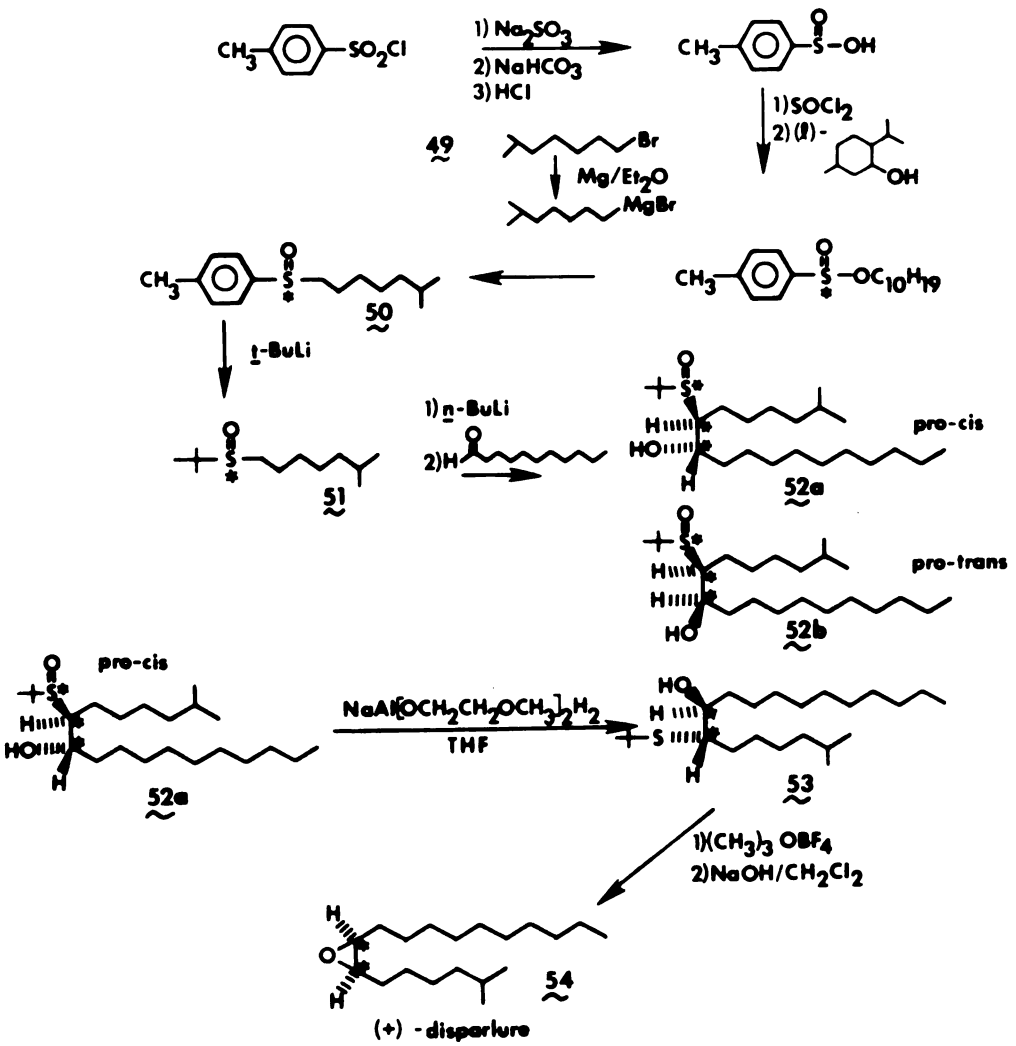


Figure 26. Modified synthesis of Farnum et al.

Results and Discussion

As previously mentioned, the method of Farnum has been scaled up to provide 35 g of (+)-disparlure. Several problems which this author worked on were the following:

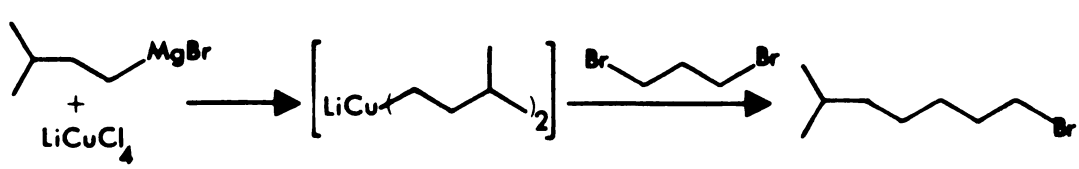
1) A cheap source for 6-methylheptyl bromide (49), previousy purchased from Chemical Samples Company.

2) Scale up of the two hydroxysulfoxide forming reactions (from the tolyl sulfoxide), and some work on the relative yields of pro-cis (52a) and pro-trans (52b) hydroxysulfoxide.

3) Scale up of the reduction of the pro-cis hydroxysulfoxide (52a) to the pro-cis hydroxy sulfide (53).

4) Scale up of the epoxide (disparlure, 54) formation from the pro-cis hydroxysulfide (53).

6-Methylheptyl bromide, although a seemingly simple molecule, turned out to be moderately difficult to obtain cheaply in large quantities. One procedure which failed was the cleavage of 6-methyl-1-heptanol-O,O,O-triester of phosphorthioicacid[95] with aqueous hydrogen bromide to give the alkyl bromide directly. Reductive cleavage of this triester with lithium aluminum hydride also failed to give 6-methylheptanol. Direct Grignard displacement on an alkyl bromide also did not work. However, the Grignard coupling reaction can be made to work by the addition of Cu^{+2},[96] presumably involving the intermediacy of a lithium dialkyl cuprate.[97a]



Apparently the displacement of bromide is a more facile process than

opening the tetrahydrofuran (solvent) ring, a known process for the lithium dialkyl cuprates.

This method, which involves the adition of isoamyl magnesium bromide to 1,3-dibromopropane with a catalytic amount of lithium tetrachlorocuprate, is capable of generating large amounts of 6-methylheptyl bromide; a very careful distillation is required, however, to separate the desired product from 1,3-dibromopropane and unreacted isoamyl bromide.

The scale up of the two step reaction sequence which converts the tolyl sulfoxide (50) to hydroxysulfoxide (52) was plagued by a variety of problems. The first step, which involves displacement of a tolyl group by a tert-butyl anion, was moderately easy to scale up. The only significant change was to transfer the tert-butyl lithium by canula rather than syringe. However, the second step caused two major problems. The first problem was formation of excessive amounts of "pre-cis".[98] This material was identified as 5-pentadecanol on the basis of spectral data. The amount of "pre-cis" could be restricted by allowing longer periods for anion formation (up to one hour instead of several minutes as previously done) and the dropwise addition of undecanal to minimize the side reaction of addition of n-butyl lithium to undecanal. The second major problem was never successfully overcome. The pro-cis to pro-trans hydroxysulfoxide ratio was reported to be 45 to 30 by Farnum et al. This ratio promptly reversed itself during the 35 gram production sequence. The only success towards increasing the amount of pro-cis was to change the aqueous ammonium chloride quench for the reaction from 0°C to -78°C. The reasoning behind this was the following: Although the original aldol-like condensation may have been

completed with a ratio of 45/35 pro-cis to pro-trans, during the warming before the quench, a retrograde aldol may have occurred. If this retro-aldol were followed by an aldol which did not give the same kinetic and / or thermodynamic control as at -78°C, the respective yields would be changed. In this regard, we were partially successful by changing the pro-cis to pro-trans ratio to 35/45. Although we seem to have increased the overall yield of aldol product, we have not decreased the amount of pro-trans formed. Future research into this reaction should include the effect of metal ions on this condensation, in particular the effect of an additional equivalent of either lithium or tetramethylammonium salts as both are known to affect the stereochemistry of the aldol condensation.[98] The results must be carefully checked since salt addition may change the stereoselectivity of the lithium sulfoxenolate formation, and therefore contaminate the product with (-)-disparlure.

Reduction of the hydroxy sulfoxide (52) to the hydroxysulfide (53) b stannous chloride proved to be very difficult to scale up. In addition, the two-step sequence to accomplish the reduction of a sulfoxide to a sulfide seemed tedious. A new method using sodium bis(methoxyethoxy) aluminum hydride (Vite)[99] was employed. Initial experiments using the procedure of Ho and Wong[100] gave not only the desired hydroxy sulfide, but also a vinyl sulfide. Apparently, addition at room temperature induces some elimination. A change of solvent from benzene to tetrahydrofuran, lowering of the temperature during addition to -78°C, and subsequent warming to 65°C gave the desired sulfide in 81% yield, only a 5% decrease from the previous two step method. A small test run in tetrahydrofuran with addition of Vite at room temperature gave eliminated product. Another test run in which Vite was added at

-78°C in tetrahydrofuran, warmed to 25°C, and allowed to stir overnight gave no reduced product. It seems necessary that addition of Vite be done at low temperature, and that in tetrahydrofuran the reagent be warmed to effect reduction. One reagent which should be explored in the future for this reaction is sodium cyanoborohydride with a catalytic amount of crown ether added. Durst et al.[101] use this reagent to reduce alkoxysulfonium salts formed from the reaction of a sulfoxide with methyl flurosulfonate or trimethyloxonium tetrafluoroborate. Their yields were as high as 91% for the two step overall process of reduction from sulfoxide to sulfide.

The last problem undertaken in this synthesis was the scale up of the final epoxidation sequence. The method of choice still remains methylation using trimethyloxonium tetrafluoroborate in nitromethane / methylene chloride, and subsequent epoxide formation using aqueous sodium hydroxide in a two phase system. There are two major problems with this system. One problem is that it is inconvenient to remove the nitromethane / methylene chloride solvent mixture very rapidly, making scale up a tedious procedure. It is necessary, though, since nitromethane would become an excellent nucleophile in the presence of base. The other major problem is that the reaction will occasionally fail and/or give poor yields. This author has not been able to determine the reason for this.

Attempts to change the reaction conditions met with failure. The simplest change seemed to be to use methylene chloride alone in the methylation step. There are several examples in the literature for this.[93,102,103] This methylation seemed to be sluggish, but appeared to work satisfactorily on a 5 gram scale. A scale up to 25 gram failed,

with the yield of disparlure about 20%. The basic problem seems to be insolubility of trimethyloxonium tetrafluoroborate in methylene chloride. A change in methylating agent to methyl fluorosulfate (a much cheaper reagent than trimethyloxonium tetrafluoroborate) might solve this problem as well as reducing the time for methylation to under 5 minutes.[104] Several other methylating agents have been tried on this system by previous workers including methyl iodide and dimethylsulfate. None of these reagents gave acceptable results. Another possibility is to use a co-solvent with methylene chloride which is not nucleophillic in the presence of sodium hydroxide. An excellent choice might be isopropanol. A 25 milligram reaction run with a 1:1 mix of isopropanol and methylene chloride with 1.1 equivalents of trimethyloxonium tetrafluoroborate for 30 minutes, followed by 0.5 N sodium hydroxide treatment gave disparlure (t.l.c.), but no quantification of this reaction was done.

The overall synthesis as it now stands is still the only commercially viable synthesis. With improvements, this synthesis could provide kilograms of (+)-disparlure per year for testing and control of the gypsy moth.

EXPERIMENTAL

General. Gas chromatograms were determined on a F & M Model 700 Laboratory Chromatograph using a 10 foot 30% SE-30 on Chromosorb W column at 170°C. Purities of products were determined by thin layer chromatography (t.l.c.); identification of known compounds was accomplished by t.l.c. or g.c. Final purity of (+)-disparlure was evaluated by gas chromatography on a 50 foot 3% OV-1 on Gaschrom Q microcapillary column in a Packard gas chromatograph in Dr. Ring Carde's lab at M.S.U. All other instrumentation and procedures were as described in earlier portions of this thesis. The following experimental is a bit more detailed than usual to aid those running these reactions with little previous experience. Full spectral data will be published at a later date.[105]

Preparation of 6-methylheptyl bromide (49). To a flame dried 3L three necked round bottom flask, equipped with a mechanical stirrer, condenser with nitrogen outlet, and a condenser with a 1 L addition funnel and nitrogen inlet, were added pentane washed magnesium turnings(146 g, 6.0 mol) and 1 L dry THF. A crystal of iodine was added to the flask, and the dropwise addition of isoamyl bromide (453 g, 3.0 mol) is 500 mL THF was started. The solution was vigorously refluxing in about 5 min. The isoamyl bromide was added over a period of 2 h, and the solution in the flask then refluxed (with additional heating) for another two h To a flame dried 5 L three necked round bottom flask immersed in an ice bath,

equipped with a mechanical stirrer, thermometer, and 1 L addition funnel was added 1,3-dibromopropane (606 g, 3.0 mol) and 30 mL of a 0.1 m solution of lithium tetrachlorocuprate in THF.[106] The Grignard prepared above was added to the 1 L addition funnel in two aliquots. The Grignard was added to the reaction mixture at such a rate thate the internal temperature stayed between 5°C and 10°C. An additional liter of THF was used to effect transfer of the Grignard which had crystallized in the addition funnel upon cooling to room temperature. Two h after the last addition of the Grignard, about 1 L water was added, and the mixture separated in a 6 L separatory funnel. The THF layer was washed with water (2 x 500 mL), and the resulting mixture concentrated to give 950 g crude product. Careful distillation at atmospheric pressure through a 50 cm by 30 mm glass helices packed column gave a 142 g (24.5%) 6-methylheptyl bromide fraction distilling over at 174-176°C[107] which was greater than 99% pure (g.c., NMR). Additional fractions cut from either side of material which contained approximately 55% 6-methylheptylbromide (250 g, 43%) and could be redistilled; ^{1}H NMR ($CDCl_3$) δ 0.85 (d, 6H, J = 6Hz), 1.03 - 2.13 (br.m, 9H), 3.33 (t, 2H, J = 6Hz).

Preparation of tert-butyl-6-methylheptylsulfoxide (51). To a flame dried 3 L three necked round bottom flask, equipped with a mechanical stirrer, rubber septum, and nitrogen outlet tube, was added tolylsulfoxide (50, 20.1 g, 0.08 mol) dissolved in 2 L dry ether. The system was then cooled to -78°C in a dry ice / acetone bath. 177 mL of tert-butyllithium (1.8 M, 0.32 mole) was added (slowly at first) to the solution by means of a canula which first went to a serum capped

graduated cylinder. The mixture was allowed to stir an additional three hours at -78°C, and the cold bath was then removed. Distilled water (300 mL) was added slowly to quench the reaction mixture. Upon warming to 0°C to 10°C, the layers were separated, the ether layer extracted with water (150 mL), and the combined aqueous layers back-extracted with ether (3 x 100 mL). The ether extracts were combined, dried with sodium sulfate, concentrated, and further dried (0.5mm, 6 H) to give 98-105% of tert-butylsulfoxide (51). In the next step, (51) is used without further purification, and should not be stored for extended periods since it appears to be moderately unstable. Storage at 0°C for less than 24 h appeared to be acceptable.

Preparation of 7S,8S-2-Methyl-8-hydroxyoctadecan-7-yl-tert-butyl-sulfoxide (52a, cis precursor) and its diastereomer (52b, trans precursor, 7S,8R). To a flame dried 500 mL three necked flask equipped with a mechanical stirrer, rubber septum, and 125 mL addition funnel with a nitrogen outlet tube, was added crude tert-butyl-6-methylheptylsulfoxide (51, 9.47g, 0.0434 mol) in 130 mL of dry ether. The system was then cooled to -78°C in a dry ice / acetone bath. 23.9 mL n-butyllithium (2.0 M in hexane, 10% excess) was added to the solution. The generated anion (color change from light yellow to dark yellow or yellow brown) was allowed to stir for 45 to 60 minutes, after which freshly distilled (54°C, 0.13 mm) undecanal (8.86 g, 0.521 mol, 20% excess) was added. The reaction mixture was allowed to stir for an additional 45-60 minutes. 100 mL of cold saturated ammonium chloride solution was added dropwise from the addition funnel. After addition was complete, the ice bath was removed. Upon warming to 0-10°C, the

phases were separated, the aqueous phase back-extracted with ether (2 x 100 mL) and the combined ether extracts dried with sodium sulfate. Concentration of the ether extracts gave 32.3 g crude product. Separation by column chromatography (silica gel ; ether) yielded 10.8 g (35% from 50) of 52a (cis precursor) and 13.9 g (45% from 50) of 52b (trans precursor) .

Preparation of 7S,8S-2-methyl-8-hydroxyoctadecan-7-yl-tert-butylsulfide (53, cis precursor). To a one necked 500 mL round bottom flask, equipped with a West condenser topped with an addition funnel, was added 52a (20.0 g, 51.4 mmol) in 150 mL of dry tetrahydrofuran. The system was cooled to -78°C, and sodium bis(methoxyethoxy)aluminum hydride (40.0 mL, 80% solution in benzene) in 100 mL dry THF was added in a dropwise fashion over a period of two h. The system was allowed to warm to room temperature over a half h period, and then warmed to 68°C for at least eight h. The aqueous layer and resulting salts were extracted with additional benzene (3 x 300 mL), the combined extracts dried with magnesium sulfate, concentrated, and purified by column chromatography (silica gel ; benzene) to give 15.5 g (81%) of 53, which should be at least 95% pure (one t.l.c. spot).

Preparation of (+)-disparlure (54). To a one necked 500 mL round bottom flask was added 53 (10.0 g, 28.6 mmol) and 100 mL of solvent (methylene chloride : nitromethane ; 1:1) under nitrogen. After cooling to 0°C, trimethyloxonium tetrafluoroborate[108] (7.94 g, 53.7 mmol) was added, and the system allowed to vigorously stir for 1 h and 10 min. The solvent was then removed by distillation, with the temperature not rising above 25°C. The total reaction time should not exceed 2 h. Dichloromethane

(200 mL) and 0.5 N sodium hydroxide (200 mL) were then added to the reaction flask, and allowed to stir moderately vigorously for 10-12 h. The reaction mixture was allowed to separate, and the aqueous layer was extracted with dichloromethane (3 x 200 mL), and the combined extracts filtered through a 60 x 20 mm plug of silica BEFORE concentration.[109] After concentration, the material was chromatographed (silica gel ; benzene) to give 4.43 g (58.4%) of 54. This material was distilled to remove a very minor yellow impurity (molecular distillation, 110°C, 0.5 mm), and the resulting disparlure determined to be at least 99% pure by t.l.c. and v.p.c.

REFERENCES

REFERENCES

(1) C.J. Pederson, *J. Am. Chem. Soc.*, 89, 7017 (1967).

(2) C.J. Pederson, *Aldrichimica Acta*, 4, 1 (1971).

(3) For some reviews of crown ether chemistry see (a) C.J. Pederson and H.K. Frensdorf, *Angew. Chem., Int. Ed. Engl.*, 11, 16 (1972); (b) J.J. Christensen, D.J. Eatough, and R.M. Izatt, *Chem. Rev.*, 74, 351 (1974); (c) D.J. Cram and J.M. Cram, *Science*, 183, 803 (1974); (d) J.-M. Lehn, *Structure and Bonding (Berlin)*, 16, 1 (1973); (e) G.W. Gokel and H.D. Durst, *Synthesis*, 168 (1976); (f) G.W. Gokel and H.D. Durst, *Aldrichimica Acta*, 9, 3 (1976).

(4) D.J. Sam and H.E. Simmons, *J. Am. Chem. Soc.*, 94, 4024 (1972).

(5) C.L. Liotta and H.P. Harris, *J. Am. Chem. Soc.*, 96, 2250 (1974).

(6) (a) J.S. Valentine and A.B. Curtis, *J. Am. Chem. Soc.*, 97, 224 (1975); (b) E.J. Corey, K.C. Nicolaou, M. Shibassaki, Y. Machida, and C. Shoner, *Tetrahedron Lett.*, 83 (1975).

(7) R.A. Bartsch, *Acc. Chem. Res.*, 8, 239 (1975).

(8) R. Boden, *Synthesis*, 783 (1975).

(9) (a) R.A. Bartsch, H. Chen, N.F. Haddock, P.N. Juri, *J. Am. Chem. Soc.*, 98, 6753 (1976); (b) Samples of crowns 3, 6, and 9, given to Dr. Bartsch have been found to inhibit the reactions of aryl diazonium salts to some degree. R. A. Bartsch, presented in part at the First and Second Symposium on Macrocyclic Compounds, Provo, Utah, August 1977 and 1978.

(10) D.J. Cram and J.M. Cram, *Acc. Chem. Res.*, 11, 8 (1978).

(11) D.J. Cram, R.C. Helgeson, L.R. Sousa, J.M. Timco, M. Newcomb, P. Moreau, F. DeJong, G.W. Gokel, D.H. Hoffman, L.A. Domier, S.C. Peacock, K. Madan and L. Kaplan, *Pure and Applied Chem.*, 43, 327 (1975).

(12) (a) L.R. Sousa and J.M. Larson, *J. Am. Chem. Soc.*, 99, 307 (1977); (b) L.R. Sousa, J.M. Larson and H.S. Brown, submitted for publication.

(13) (a) J.M. Larson and L.R. Sousa, *J. Am. Chem. Soc.*, 100, 1943 (1978); (b) J.M. Larson and L.R. Sousa, results with crown 9 were presented in part at the 174th National Meeting of the ACS, Chicago, Illinois, August 1977; (c) J.M. Larson and L.R. Sousa, results with crowns 3, 6, and 9 were presented in part at the First Symposium on Macrocyclic Compounds, Provo, Utah, August 1978.

(14) James M. Larson, "Investigation of the Perturbation of the Excited State Processes of Naphthalene Crown Ether Derivatives by Complexation of the Cations of Alkali Metal Chlorides, Barium Bromide, and Silver Triflate; Investigation of the External Heavy Atom Perturbation of the Excited State Processes of Naphthalene Crown Ether Derivatives by Ethyl Bromide and by Means of Complexed Haloalkylammonium Cations", Ph. D. Dissertation, Michigan State University, 1979.

(15) L.R. Sousa and M.R. Johnson, *J. Am. Chem. Soc.*, 100, 344 (1978); (b) L.R. Sousa, M.R. Johnson and H. S. Brown, Second Symposium on Macrocyclic Compounds, Provo, Utah, August 1978.

(16) Mark R. Johnson, "Part 1: Heterocyclic Photochemistry: The Photochemical Synthesis of β-Lactams; Part 2: The ^{13}C NMR Spectra of Naphthalene Crown Ether Complexes: Field Induced π-polarization and Crown Ether Conformational Changes", Ph.D. Dissertation, Michagan State University, 1978.

(17) D.L. Ward, H.S. Brown and L.R. Sousa, submitted for publication.

(18) D.L. Ward, H.S. Brown and L.R. Sousa, *Acta Cryst.*, B33, 3537 (1977).

(19) (a) J.M. Timko, R.C. Helgeson, M. Newcomb, G.W. Gokel and D.J. Cram, *J. Am. Chem. Soc.*, 96, 7097 (1974); (b) D.N. Reinhoudt and R.T. Gray, *Tetrahedron Lett.*, 2015 (1975); (c) D.N. Reinhoudt, R.T. Gray, C.J. Smit and I. Veenstra, *Tetrahedron*, 1161 (1976); (d) M. Newcomb, G.W. Gokel and D.J. Cram, *J. Am. Chem. Soc.*, 96, 6810 (1974); (e) F. Voetgle and M. Zuber, *Tetrahedron Lett.*, 561 (1972).

(20) R.N. Green, *Tetrahedron Lett.*, 1793 (1972).

(21) H.J. Dauben, Jr. and L.L. McCoy, *J. Am. Chem. Soc.*, 81, 4863 (1959).

(22) E.D. Bergmann and J. Szmuszkovicz, *J. Am. Chem. Soc.*, 75, 2760 (1953).

(23) T.A. Geissman and L. Morris, *J. Am. Chem. Soc.*, 66, 716 (1944).

(24) V.M. Micovic and M.LJ. Mihailovic, *J. Org. Chem.*, 18, 1190 (1953).

(25) K.J. Laidler, "Chemical Kinetics", Mc Graw-Hill, Inc., New York, 1965, p89.

(26) Benzophenone Tetracarboxylic Dianhydride. A one pound sample of this material was generously donated by Gulf Chemicals, Houston, Texas.

(27) W.L. Mosby, *J. Am. Chem. Soc.*, 75, 3600 (1953).

(28) This sample of 1,4,5,8-tetramethyl naphthalene was provided by Mr. David Makowski in Dr. H. Hart's group. It's origin is unknown to this author, although it's preparation is in the literature. J. Mosby, *J. Am. Chem. Soc.*, 74, 2564 (1952).

(29) Lumilux is the brand name for a fluorescent indicator used in UV-254 sorbants, and is currently marketed by Brinkmann Instruments.

(30) For recent reviews, see (a) N.K. Dalley, "Synthetic Multidentate Macrocyclic Compounds", *Progress in Macrocyclic Chemistry*, 1, Academic Press, Inc., New York, 1978, Chapter 4; (b) M.R. Truter, *Structure and Bonding (Berlin)*, 16, 71 (1973).

(31) M.A. Busch and M.R. Truter, *J.C.S. Chem. Comm.*, 1439 (1970).

(32) M.R. Truter, Personal Communication, August 1977, Provo, Utah.

(33) D. Live and S.I. Chen, *J. Am. Chem. Soc.*, 98, 3769 (1976).

(34) The numbering scheme was chosen for simplicity and convenience, and is not consistent with I.U.P.A.C. nomenclature rules.

(35) Ref. 30(a), p208.

(36) D. Bright, I.E. Maxwell, and J. deBoer, *J.C.S. Perkin II*, 2101 (1973).

(37) J.-B. Robert, J.S. Sherfinski, R.E. Marsh, and J.D. Roberts, *J. Org. Chem.*, 39, 1152 (1974).

(38) J. Handal, J.G. White, R.W. Franck, Y.H. Yuh, and N.L. Allinger, *J. Am. Chem. Soc.*, 99, 3345 (1977).

(39) "Tables of Interatomic Distances and Configuration in Molecules and Ions", Spec. Publ. No. 18, The Chemical Society, London (1960).

(40) M. Davis and O. Hassel, *Acta Chem. Scand.*, 17, 1181 (1963).

(41) J.D. Dunitz, M. Dobler, P. Seiler, and R.P. Phizackerley, *Acta Cryst.*, B30, 2733 (1974).

(42) (a) M. Mercer and M.R. Truter, *J. Chem. Soc., Dalton Trans.*, 2215, (1973); (b) M. Mercer and M.R. Truter, *J. Chem. Soc., Dalton Trans.*, 2469, (1973).

(43) (a) I. Goldberg, *Acta Cryst.*, B31, 754 (1975); (b) I. Goldberg, *Acta Cryst.*, B31, 2592 (1975); (c) I. Goldberg, *Acta Cryst.*, B32, 41 (1976).

(44) K.-T. Wei and D.L. Ward, *Acta Cryst.*, B32, 2768 (1976).

(45) G. Germain, P. Main and M.M. Woolfson, *Acta Cryst.*, A27, 368 (1971).

(46) C.K. Johnson, *ORTEP*, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1965).

(47) These programs were acquired from Dr. Allan Zalkin by Dr. Donald Ward, and modified for use on the MSU CDC-6500.

(48) P.A. Doyle and P.S. Turner, *Acta Cryst.*, A24, 390 (1968).

(49) R.F. Stewart, E.R. Davidson and W.T. Simpson, *J. Chem. Phys.*,42 3175 (1965).

(50) D.T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

(51) T. Foerster, *Discussions Faraday Soc.*, 27, 7 (1959).

(52) For a good general discussion on energy transfer, see A.A. Lamola and N.J. Turro, "Energy Transfer and Organic Photochemistry", *Technique of Organic Chemistry, Volume XIV*, Interscience division of John Wiley and Sons, New York, 1969.

(53) O. Schaepp and M. Levy, *J. Am. Chem. Soc.*, 84, 172 (1962).

(54) A.A. Lamola, P.A. Leermakers, G.W. Byers, and G.S. Hammond, *J. Am. Chem. Soc.*, 87, 2322 (1965).

(55) H. Hart, J.L. Reilly, and J.B.-C. Jiang, *J. Org. Chem.*, 42, 2684 (1977).

(56) These spectra are in the possession of Dr. L.R. Sousa.

(57) R.A. Keller and L.J. Dolby, *J. Am. Chem. Soc.*, 89, 2768 (1967).

(58) V.M. Berenfeld and V.A. Kroagauz, *Izu. Akad. Nauk., SSSR, Ser. Fiz*, 32, 1575 (1968).

(59) Sandra E. Klassen, "Synthesis of 3,4-(20-Crown-6)Benzophenone: A Potential Selective Triplet Sensitizer", M.S. Thesis, Michigan

State University, 1976, p37.

(60) E.J. Corey and J.W. Suggs, *Tetrahedron Lett.*, 2647 (1975).

(61) Beil., V7, p454.

(62) T.J. Kealy and P.L.Pauson, *Nature*, 168, 1039 (1951).

(63) S.A. Miller, J.A. Tibboth, and J.F. Tremaine, *J. Chem. Soc.*, 632 (1952).

(64) D.E. Bublitz and K.L. Rhinehart, Jr., *Organic Reactions*, 17, 1 (1969), and 40 references to reviews contained therin.

(65) F.A. Cotton and G. Wilkenson, "Advanced Inorganic Chemistry, Third Edition", John Wiley and Sons, New York, 1972, p737.

(66) G. Wilkenson, M. Rosenblum, M.C. Whiting and R.B. Woodward, *J. Am. Chem. Soc.*, 74, 2125 (1952).

(67) (a) R.B. Woodward, M. Rosenblum and M.C. Whiting, *J. Am. Chem. Soc.*, 74, 3458 (1952); (b) A.N. Nesmeyanov, E.G. Perevalouva and Z.A. Beinoravichute, *Proc. Acad. Sci., USSR*, 112, 439 (1957).

(68) M.D. Rausch and D.J. Ciappenelli, *J. Organometal. Chem.*, 10, 127 (1967).

(69) N.M. Yoon, C.S. Pak, H.C. Brown, S. Krishnamurthy and T.P. Stocky, *J. Org. Chem.*, 38, 2786 (1973).

(70) S.I. Goldberg, *J. Org. Chem.*, 25, 482 (1960).

(71) F.H. Stodola, *J. Org. Chem.*, 29, 2490 (1964).

(72) Some preliminary equilibrium constant measurements on 1,1'-ferrocene-18-crown-5 (46) in ethanol show the equilibrium constant with potassium to be about 400, despite the fact that CPK models show a good fit for potassium in this crown.

(73) M. Rosenblum and R.B. Woodward, *J. Am. Chem. Soc.*, 80, 5443 (1958).

(74) A.N. Nesmeyanov, E.G. Perevalova, R.V. Golovnya and O.A. Nesmeyanova, *Dokl. Akad. Nauk. SSSR*, 97, 459 (1954).

(75) This A/D interface was designed and built by Mr. Martin Rabb and Dr. Thomas Atkinson, Department of Chemistry, Michigan State University.

(76) "OS/8 Handbook", Digital Equipment Corporation, Maynard, Massachusetts, p8-2.

(77) Ref. 76, p1-108.

(78) Software was written in PAL8 by Dr. Thomas Atkinson with help

(and encouragement) from this author.

(79) The PROM was programmed on a PDP11/40 by Dr. Thomas Atkinson and Mr. Timothy Kelly.

(80) B.K. Hahn and C.G. Enke, *Anal. Chem.*, 45, 651A (1973).

(81) P.J. Wagner, private communication.

(82) This program uses the method of J.A. Pople, D.L. Beveridge, and P.A. Dobash, *J. Chem. Phys.*, 47, 2026 (1967).

(83) M. Beroza and E.F. Knipling, *Science*, 177, 19 (1972).

(84) F. Acree, Jr., M. Beroza, R.F. Holbrook, H.L. Haller, *J. Econ. Entomol.*, 63, 943 (1970).

(85) B.A. Bierl, M. Beroza, and C.W. Collier, *Science*, 170, 87 (1970).

(86) (a) H.J. Bestmann and O. Vostrowsky, *Tetrathedron Lett.*, 207 (1974); (b) H.J. Bestmann, O. Vostrowsky and W. Stramsky, *Chem. Ber.*, 109, 3375 (1976).

(87) K. Kluenenberg and H.J. Schafer, *Angew. Chem. Int. Ed. Engl.*, 17, 47 (1978).

(88) R.T. Carde, C.C. Doane, T.C. Baker, S. Iwaki and S. Marumo, *Environ. Entomol.*, 6, 768 (1977).

(89) For a very good review on the "Synthesis of Chiral Components of Insect Pheromones" including disparlure, see R. Rossi, *Synthesis*, 413 (1978).

(90) S. Iwaki, S. Marumo, T. Saito, M. Yamada and K. Katagiri, *J. Am. Chem. Soc.*, 96, 7842 (1978).

(91) Structure proof through optical rotations alone were almost impossible due to the small magnitude of the rotation compiled with the low yield of pheremone from the insects.

(92) K. Mori, T. Takigawa and M Matsui, *Tetrahedron Lett.*, 3953 (1976).

(93) (a) W.H. Pirkle and P.L. Rinaldi, *J. Org. Chem.*, 44, 1025 (1979); (b) W.H. Pirkle and P.L. Rinaldi, *J. Org. Chem.*, 43, 3803 (1978).

(94) D.G. Farnum, T. Vesoglu, A.M. Carde, B. Duhl-Emswiler, T.A. Pancoast, T.J. Reitz, and R.T. Carde, *Tetrahedron Lett.*, 4009 (1977).

(95) Comercially available from Pfaltz and Bauer, Inc.

(96) L. Friedman and A. Shani, *J. Am. Chem. Soc.*, 96, 7101 (1974).

(97) (a) M. Tamura and J.K. Kochi, *Synthesis*, 303 (1971); (b) J. Millon and G. Linstrumelle, *Tetrahedron Lett.*, 1095 (1976).

(98) H.O. House, "Modern Synthetic Reactions, Second Edition", W.A. Benjamin, Inc., Menlo Park, California, 1972, p631, 672, and references cited therin.

(99) Sodium bis(methoxyethoxy)aluminum hydride is sold by Columbia Organic Chemicals as "Vite", by Aldrich Chemicals as "Red-Al", and by Eastman Organic Chemicals as "Vitride".

(100) T. Ho and C.M. Wong, *Org. Prep. and Proc.*, 7, 163 (1975).

(101) H.D. Durst, J.W. Zubrick and G.R. Kieczykowski, *Tetrahedron Lett.*, 1777 (1974).

(102) J.R. Shanklin, C.R. Johnson, J. Ollinger and R.M. Coates, *J. Am. Chem. Soc.*, 95, 3429 (1973).

(103) J.E. Baldwin, R.E. Hackler and D.P. Kelly, *J. Am. Chem. Soc.*, 90, 4758 (1968).

(104) (a) R.W. Alder, *Chem. Ind.*, 983 (1973); (b) Anja Carde, private communication.

(105) D.G. Farnum et al., manuscript in preparation.

(106) M. Tamura and J. Kocki, *Synthesis*, 303 (1972).

(107) At this point, fractions were being cut every 25 mL, and each was checked by g.c..

(108) T.J. Caurphey, *Org. Syn.*, 51, 142 (1971).

(109) Extensive destruction of disparlure will occur at room temperature over an eight hour period if this is not done immediately.

APPENDIX A

LISTING OF INTEREFACE PROGRAM WRITTEN IN BASIC PAGE 1

```
100 PRINT PNT(26)
110 PRINT "PDP-8 HITACHI INTERFACE PROGRAM,";
120 PRINT " VERSION 2.5-NA"
130 PRINT "FOR BASIC VERSION 4.0, OS-8 3C"
140 PRINT "WRITTEN BY: HOUSTON S. BROWN"
150 PRINT "          : DEPARTMENT OF CHEMISTRY"
160 PRINT "          : MICHIGAN STATE UNIVERSITY"
170 PRINT "          : COPYRIGHT @ 1977"
180 PRINT "          : BY THE L.R. SOUSA GROUP"
190 PRINT "          : AND THE BOARD OF REGENTS"
200 UDEF INI(N),PLY(Y),DLY(N),DIS(S,E,N,X)
210 UDEF SAM(C,N,P,T),CLK(R,O,S),CLW(N),ADC(N)
220 UDEF GET(M,L),PUT(M,L),DRI(N),DRO(M,N)
230 S0=1
240 J=1
250 I9=1
260 DIM A(400)
270 DIM B(10)
280 DIM C(100)
290 USE A
300 USE B
310 USE C
320 H4=120
330 PRINT "RESTART (Y OR N)";
340 INPUT Q$
350 IFQ$="N" GO TO 440
360 IF Q$<>"Y" GO TO 330
370 FILE#1:"FLP0:AREAS."
380 INPUT #1:J,A1,A2
390 FOR I=1 TO J
400 INPUT #1:C(I),A1,A2
410 NEXT I
420 CLOSE #1
430 J=J+1
440 PRINT PNT(7)
450 I9=1
460 X=INI(0)
470 Z1=-300
480 Z2=-300
490 Z3=-300
500 A$="FLP1:"
510 B$="DATA"
520 E$=".DA"
530 D$=STR$(J)
540 PRINT "RUN # "&D$;
550 INPUT A1
560 IF A1<0 GO TO 440
570 IF A1=0 GO TO 600
580 D$=STR$(A1)
590 J=A1
600 I$="STARTING"
610 G$=" LAMDA "
```

```
620 H$="ENDING"
630 PRINT I$&G$&STR$(H1);
640 INPUT A1
650 IF A1<0 GO TO 440
660 IF A1=0 GO TO 680
670 H1=A1
680 PRINT H$&G$&STR$(H2);
690 INPUT A1
700 IF A1<0 GO TO 440
710 IF A1=0 GO TO 730
720 H2=A1
730 H3=((H2-H1)*2)+1
740 J$="N.M./"
750 K$="MIN = "
760 PRINT J$&K$&STR$(H4);
770 INPUT A1
780 IF A1<0 GO TO 440
790 IF A1=0 GO TO 810
800 H4=A1
810 IF H4=240 THEN 840
820 IF H4=120 THEN 860
830 IF H4=60 THEN 880
840 X9=30
850 GO TO 900
860 X9=60
870 GO TO 900
880 X9=120
890 GO TO 900
900 H5=(1000/H4)*300
910 PRINT STR$(X9)&" POINTS AVERAGED PER DATA POINT"
920 X=CLK(4,1,0)
930 Y=CLW(0)
940 X=ADC(0)
950 PRINT "HIT RETURN TO START CYCLE TO COLLECT DATA";
960 INPUT A1
970 IF A1<0 GO TO 440
980 L9=0
990 Y=ADC(L9)
1000 Z3=Z2
1010 Z2=Z1
1020 Z1=Y
1030 Z4=(Z1+Z2+Z3)/3
1040 IF Z4<-10 GO TO 990
1050 Q=ADC(1)
1060 X=CLK(4,H5,0)
1070 FOR I5=1 TO H3
1080 FOR I1=1 TO X9
1090 Q=ADC(1)
1100 Q1=Q1+Q
1110 NEXT I1
1120 Q1=Q1/X9
1130 A(I5)=Q1
```

```
1140 Q1=0
1150 X7=CLW(0)
1160 NEXT I5
1170 PRINT PNT(7)
1180 IF X7=0 THEN 1200
1190 PRINT "***** CAUTION *****  TIMING ERROR DETECTED"
1200 M$="LEFT "
1210 N$="RIGHT"
1220 L$=" BASE"
1230 REM START INTEGRATION BUT FIRST NORMALIZE VALUES TO ZERO
1240 I0=50000
1250 FOR I=1 TO H3
1260 IF A(I)>=I0 GO TO 1290
1270 I9=I
1280 I0=A(I)
1290 NEXT I
1300 FOR I=1 TO H3
1310 A(I)=A(I)-I0
1320 NEXT I
1330 I9=(I9/2)+H1-0.5
1340 PRINT "LOW POINT AT "&STR$(I9)&" NM"
1350 J2=I9
1360 J3=I9
1370 J4=I9
1380 PRINT "START INT AT THIS LBA"&STR$(J1);
1390 INPUT A1
1400 IF A1=-100 GO TO 1380
1410 IF A1<0 GO TO 440
1420 IF A1=0 GO TO 1440
1430 J1=A1
1440 PRINT "END INT AT THIS LBA"&STR$(J2);
1450 INPUT A1
1460 IF A1=-100 GO TO 1380
1470 IF A1<0 GO TO 440
1480 IF A1=0 GO TO 1500
1490 J2=A1
1500 PRINT "LBA OF BASE LEFT"&STR$(J3);
1510 INPUT A1
1520 IF A1=-100 GO TO 1380
1530 IF A1<0 GO TO 440
1540 IF A1=0 GO TO 1560
1550 J3=A1
1560 PRINT "LBA OF BASE RIGHT"&STR$(J4);
1570 INPUT A1
1580 IF A1=-100 GO TO 1380
1590 IF A1<0 GO TO 440
1600 IF A1=0 GO TO 1620
1610 J4=A1
1620 R1=0
1630 R2=0.0
1640 D1=J1+0.5
1650 D2=(1/J1)*1.0E04
```

```
1660 REM J5 IS ARRAY ADDRESS OF LEFT BASELINE
1670 REM J6 "    "      "    "  RIGHT   "
1680 REM J7 "    "      "    "  LEFT INTEGRATION START
1690 REM J8 "    "      "    "  RIGHT     "        "
1700 J5=((J3-H1)*2)+1
1710 J6=((J4-H1)*2)+1
1720 J7=((J1-H1)*2)+1
1730 J8=((J2-H1)*2)+1
1740 REM J9 IS THE DIFFERENCE (CM-1) BETWEEN LEFT AND RIGHT
1750 J9=((1/J1)-(1/J2))*1.0E04
1760 REM A4 IS THE DIFFERENCE IN INTENSITY BETWEEN LEFT AND RIGHT BASE
1770 A4=(A(J6)-A(J5))
1780 N=J7
1790 REM D5 IS THE STARTING INCREMENT OF WAVELENGTH FOR
1800 REM  SLOPING BASELINE
1810 D5=(1/J1)-(1/(((J1+0.5)+(J1))/2))
1820 D5=D5*1.0E04
1830 D6=(1/J1)*1.0E04
1840 FOR E1=D1 TO J2 STEP 0.5
1850 D3=(1/E1)*1.0E04
1860 REM A5 IS DELTA X (WAVE LENGTH)
1870 A5=D2-D3
1880 M=N+1
1890 REM A6 IS Y TOP
1900 A6=(A(M)+A(N))/2.0
1910 REM A8 IS THE INCREMENT FOR THE SLOPING BASELINE
1920 A8=A4*(D5/J9)
1930 REM A8 IS NEGATIVE AS CALCULATED, HENCE IS ADDED TO A(J5)
1940 REM A7 IS Y BOTTOM
1950 A7=A(J5)+A8
1960 REM R1 ACCUMULATES AREA
1970 R1=R1+((A6-A7)*A5)
1980 N=N+1
1990 D2=D3
2000 D5=D5+A5
2010 NEXT E1
2020 PRINT "AREA = ";R1
2030 PRINT
2040 C(J)=R1
2050 CLOSE#0
2060 FILEV#1:"FLP0:AREAS."
2070 PRINT#1:J
2080 FOR I=1 TO J
2090 PRINT#1:C(I)
2100 NEXT I
2110 CLOSE#1
2120 FILE#0:"TTY:"
2130 A3=0
2140 PRINT "QUANTUM YIELDS ARE NOW CALCULATED"
2150 PRINT "NUMBER OF STANDARDS (99-(RETURN) STARTS NEW RUN)";
2160 INPUT A1
2170 IF A1=99 GO TO 2400
```

```
2180 IF A1=0 GO TO 2150
2190 IF A1=-100 GO TO 1380
2200 IF A1<0 GO TO 440
2210 FOR I=1 TO A1
2220 PRINT "STANDARD NUMBER";
2230 INPUT A2
2240 A3=C(A2)+A3
2250 NEXT I
2260 A3=A3/A1
2270 PRINT "QUANTUM YIELD STANDARD = "&STR$(Q9);
2280 INPUT A1
2290 IF A1=0 GO TO 2310
2300 Q9=A1
2310 PRINT "SENSITIVITY = "&STR$(S0);
2320 INPUT A1
2330 IF A1=0 GO TO 2350
2340 S0=A1
2350 R2=(R1/A3)*Q9*S0
2360 PRINT "QUANTUM YIELD FOR RUN "&STR$(J)&" IS "&STR$(R2)
2370 PRINT "RETURN 100 TO RECALCULATE";
2380 INPUT A1
2390 IF A1=100 GO TO 2130
2400 J=J+1
2410 GO TO 440
2420 END
```

```
C=====PDP-8 / HITACHI INTERFACE PROGRAM
C**********************************************
      COMMON A,C
      DIMENSION A(400),C(100)
      CALL TYPE(154)
      CALL START(1)
      SO=1
      J=1
      I9=1
      IH1=1
      IH2=0
      IH4=120
5     WRITE(1,1000)IDUM,
      READ(1,1001)IANS
      IF(IANS-1)5,10,15
10    CALL IOPEN('FLP0','AREAS')
      READ(4,1001)J
      DO 13 I=1,J
13    READ(4,1002)C(I)
      J=J+1
15    IF(IANS-2)16,16,5
16    I9=1
      WRITE(1,1003)J,
      READ(1,1001)IANS
      IF(IANS)16,20,17
17    J=IANS
20    WRITE(1,1004)IH1,
      READ(1,1001)IANS
      IF(IANS)16,25,23
23    IH1=IANS
25    WRITE(1,1005)IH2,
      READ(1,1001)IANS
      IF(IANS)16,30,28
28    IH2=IANS
30    IH3=((IH2-IH1)*2)+1
31    WRITE(1,1006)IH4,
      READ(1,1001)IANS
      IF(IANS)16,35,33
33    IH4=IANS
35    IF(IH4-120)50,45,40
40    IF(IH4-240)31,41,31
41    IX9=30
      IY9=125
      GO TO 55
45    IF(IH4-120)31,46,31
46    IX9=60
      IY9=250
      GO TO 55
50    IF(IH4-60)31,51,31
51    IX9=120
      IY9=500
55    WRITE(1,1007)IX9
```

```
      CALL ADC(0,L1)
      WRITE(1,1008)IDUM,
      READ(1,1001)IANS
      IF(IANS)16,56,57
56    CALL ADC(0,L1)
      CALL TYPE(135)
      IF(L1)56,57,57
57    CALL ADC(0,L1)
      IF(L1)56,58,58
58    CALL ADC(0,L1)
      IF(L1)56,60,60
60    CALL CLK(IY9)
      DO 80 I5=1,IH3
      Q=0
      DO 70 I=1,IX9
      CALL ADC(1,L)
70    Q=Q+FLOAT(L)
      A(I5)=Q/FLOAT(IX9)
      Q=0.
      CALL AHEM(NUTS)
      IF(NUTS)80,80,16
80    CALL CLW
      CALL TYPE(135)
90    ALOW=50000.
      I9=1
      DO 100 I=1,IH3
      IF(ALOW-A(I))100,100,95
95    ALOW=A(I)
      I9=I
100   CONTINUE
      DO 110 I=1,IH3
110   A(I)=A(I)-ALOW
      AI9=(FLOAT(I9)/2.)+FLOAT(IH1)-0.5
115   WRITE(1,1014)IDUM
      WRITE(1,1009)AI9
      WRITE(1,1010)AJ1,
      READ(1,1001)IANS
      IF(IANS+100)118,115,118
118   IF(IANS)16,120,119
119   AJ1=FLOAT(IANS)
120   WRITE(1,1011)AJ2,
      READ(1,1001)IANS
      IF(IANS+100)122,115,122
122   IF(IANS)16,125,124
124   AJ2=FLOAT(IANS)
125   WRITE(1,1012)AJ3,
      READ(1,1001)IANS
      IF(IANS+100)127,115,127
127   IF(IANS)16,130,129
129   AJ3=FLOAT(IANS)
130   WRITE(1,1013)AJ4,
      READ(1,1001)IANS
```

```
      IF(IANS+100)132,115,132
132   IF(IANS)16,135,134
134   AJ4=FLOAT(IANS)
135   R1=0.
      R2=0.
      D1=AJ1+0.5
      D2=(1./AJ1)*1.0E04
      J1=IFIX(AJ1+0.001)
      J2=IFIX(AJ2+0.001)
      J3=IFIX(AJ3+0.001)
      J4=IFIX(AJ4+0.001)
      J5=((J3-IH1)*2)+1
      J6=((J4-IH1)*2)+1
      J7=((J1-IH1)*2)+1
      J8=((J2-IH1)*2)+1
      AJ9=((1./AJ1)-(1./AJ2))*1.0E04
      A4=(A(J6)-A(J5))
      N=J7
      D5=(1./AJ1)-(1./(((AJ1+0.5)+(AJ1))/2.0))
      D5=D5*1.0E04
      D6=(1./AJ1)*1.0E04
      IEN=IFIX(((AJ2-AJ1)*2.0)+0.01)
      DO 150 I=1,IEN
      E1=(FLOAT(I)*0.5)+AJ1
      D3=(1./E1)*1.0E04
      A5=D2-D3
      M=N+1
      A6=(A(M)+A(N))/2.
      A8=A4*(D5/AJ9)
      A7=A(J5)+A8
      R1=R1+((A6-A7)*A5)
      N=N+1
      D2=D3
150   D5=D5+A5
      WRITE(1,1015)R1
      C(J)=R1
      WRITE(1,1016)IDUM,
      READ(1,1001)IANS
      IF(IANS-1)115,155,115
155   CALL OOPEN('FLP0','AREAS')
      WRITE(4,1001)J
      DO 160 I=1,J
160   WRITE(4,1002)C(I)
      CALL OCLOSE
169   A3=0
      WRITE(1,1017)IDUM
      WRITE(1,1018)IDUM,
      READ(1,1001)IANS
      IF(IANS-99)170,225,170
170   IF(IANS)171,169,171
171   DO 175 I=1,IANS
      WRITE(1,1019)IDUM,
```

```
      READ(1,1001)IA2
175   A3=C(IA2)+A3
      A3=A3/FLOAT(IANS)
      WRITE(1,1020)Q9,
      READ(1,1002)ANS
      AANS=ANS*1000.01
      IANS=IFIX(AANS)
      IF(IANS)176,180,176
176   Q9=ANS
180   WRITE(1,1021)S0,
      READ(1,1002)ANS
      AANS=ANS*10.01
      IANS=IFIX(AANS)
      IF(IANS)183,185,183
183   S0=ANS
185   R2=(R1/A3)*Q9*S0
      WRITE(1,1022)J,R2
      WRITE(1,1023)IDUM,
      READ(1,1001)IANS
      IF(IANS-100)225,169,225
225   J=J+1
      GO TO 16
1000  FORMAT('RESTART (Y=1, N=2)',I0)
1001  FORMAT(I5)
1002  FORMAT(E16.8)
1003  FORMAT('RUN # ',I3,' ?')
1004  FORMAT('STARTING LAMDA = ',I3)
1005  FORMAT('ENDING LAMDA = ',I3)
1006  FORMAT('N.M./MIN. = ',I3,'(ONLY 240, 120 OR 60 ALLOWED)')
1007  FORMAT(I3,' POINTS AVERAGED PER DATA POINT')
1008  FORMAT('HIT RETURN TO PUT COMPUTER IN CONTROL OF HITACHI'/
     +'ANY KEY ESCAPES FROM DATA COLLECTION',I0)
1009  FORMAT('LOW POINT AT ',F5.1,' N.M.')
1010  FORMAT('START INTEGRATION AT THIS LAMDA ',F5.1)
1011  FORMAT('END INTEGRATION AT THIS LAMDA ',F5.1)
1012  FORMAT('LAMDA OF BASELINE LEFT ',F5.1)
1013  FORMAT('LAMDA OF BASELINE RIGHT ',F5.1)
1014  FORMAT('-100 WILL RESTART INTEGRATION',I0)
1015  FORMAT('AREA = ',F13.6)
1016  FORMAT('O.K.?(1 TO CONTINUE, OTHER WILL REINTEGRATE)',I0)
1017  FORMAT('QUANTUM YIELDS ARE NOW CALCULATED',I0)
1018  FORMAT('NUMBER OF STANDARDS (99(RETURN) STARTS A NEW RUN)',I0)
1019  FORMAT('STANDARD NUMBER -',I0)
1020  FORMAT('QUANTUM YIELD STANDARD = ',F10.5)
1021  FORMAT('SENSITIVITY = ',F10.5)
1022  FORMAT('QUANTUM YIELD FOR RUN',I3,' IS ',F10.6)
1023  FORMAT('100(RETURN) TO RECALCULATE, ELSE (RETURN)',I0)
      END
```

LISTING OF START SUBROUTINE PAGE 1

```
C=====START-UP SUBROUTINE
      SUBROUTINE START(N)
      WRITE(1,100)
      WRITE(1,101)
      WRITE(1,102)
      WRITE(1,103)
      WRITE(1,104)
      WRITE(1,105)
      WRITE(1,106)
      WRITE(1,107)
      WRITE(1,108)
      WRITE(1,109)
      RETURN
100   FORMAT('** PDP-8/HITACHI INTERFACE PROGRAM **')
101   FORMAT('************ VERSION 3.0 ************')
102   FORMAT('* FORTRAN2/SABR VERSION 4A, OS8 V3D *')
103   FORMAT('WRITTEN BY: HOUSTON S. BROWN')
104   FORMAT(10X,': DEPARTMENT OF CHEMISTRY')
105   FORMAT(10X,': MICHIGAN STATE UNIVERSITY')
106   FORMAT(10X,': COPYRIGHT  1978')
107   FORMAT(10X,': BY HOUSTON S. BROWN')
108   FORMAT(10X,': FOR THE LYNN R. SOUSA GROUP')
109   FORMAT(10X,': AND THE BOARD OF REGENTS')
      END
```

#LISTING OF CLOCK OVERFLOW SUBROUTINE PAGE 1

```
C=====SUBROUTINE TO WAIT UNTIL CLOCK OVERFLOWS
      SUBROUTINE CLW
SWAIT,6131
S     JMP WAIT
S     6135
S     CLA
      RETURN
      END
```

LISTING OF ATTENTION SUBROUTINE PAGE 1

```
C======SUBROUTINE TO GET ATTENTION FROM PDP8 WHILE INTEGRATING
      SUBROUTINE AHEM(NUTS)
S     CLA
S     6031   /SKIP IF KEYBOARD FLAG SET
S     JMP NOPE
S     JMP YUP
S NOPE, 7000
      NUTS=0
      RETURN
S YUP, 7000
      NUTS=1
      RETURN
      END
```

```
LISTING OF CLOCK SET ROUTINE                                    PAGE  1

C=====SUBROUTINE TO START THE CLOCK
C=====N1 IS THE NUMBER OF TICKS TO OVERFLOW
C=====1000 TICKS/SEC AT CLOCK RATE 3
      SUBROUTINE CLK(N1)
      N=-N1
S     CLA
S     TAD     |N
S     6133
S     CLA
S     TAD  ENABLE
S     6132
S     6135
S     CLA
      RETURN
SENABLE, 5300
      END
```

```
#LISTING OF ADC SUBROUTINE                                      PAGE  1

C=====SUBROUTINE TO DO A/D CONVERSION
C=====NADC IS THE A/D CHANNEL
C=====LADC IS THE VALUE RETURNED
      SUBROUTINE ADC(N,L)
      NADC=N
      LADC=0
S     6530
S     CLA
S     TAD     |NADC
S     6531
S     6532
S ST, 6534
S     JMP ST
S     6533
S     DCA     |LADC
      L=LADC
      RETURN
      END
```

```
LISTING OF KEYBOARD ECHO ROUTINE                                PAGE  1

C=====SUBROUTINE TO ECHO CHARACTERS TO KEYBOARD
C=====N IS THE DECIMAL EQUIVALENT OF ASCII BEING PASSED
      SUBROUTINE TYPE (N)
      M=N
S     CLA
S     TAD |M
S     TLS
S B1, TSF
S     JMP B1
S     CLA
      RETURN
      END
```

APPENDIX B

```
      PROGRAM COREK(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C  -COREK- CORRECTS FLUORESCENCE AND PHOSPHORESCENCE SPECTRA
      REAL NORNAP,NORSAM,NAP
      DIMENSION CORSAM(50,3),TRUNAP(50),OBNAP(50,3),OBSAM(50),
     1NORNAP(50,3),NORSAM(50,3),WAVNO(52),CORFAC(50),T(8),
     2NAP(50),CON(8,4),OBNAPL(3),SUMSAM(3),QSAM(3),C(56),NAME(8),
     3PLOTAV(52)
      INTEGER OPT1
      EXTERNAL FUNC
      DATA CORSAM,TRUNAP,OBNAP,OBSAM,NORNAP,NORSAM,WAVNO,PLOTAV,
     1CORFAC,NAP,CON,OBNAPL,C,NAME,T/1011*0.0/
      DATA BLANK,STAR/1H ,1H*/
      ICOUNT=1
C  N= NO. OF DATA PTS. TO BE EVALUATED
C  NCORSP=THE NUMBER OF NAPHTHALENE SPECTRA RUN AS STANDARDS
C  QNAP= ACCEPTED VALUE FOR NAPHTHALENE QUANTUM YIELD
C  SENS = SENSITIVITY CORRECTION FOR QUANTUM YIELD
C  OPT1 = TO READ VALUES TO CORRECT CORECTION FACTORS, SET = TO 1
C  IPLOT=1, THEN WRITE A CALCOMP PLOT FILE
      READ(5,102)N,NCORSP,QNAP,SENS,OPT1,YLIM,IPLOT,ICOST
      YLIMT=YLIM
      READ(5,103)(NAME(I),I=1,8)
      NM=50*NCORSP
C  READ IN UNNORMALIZED TRUE AND OBSERVED NAPHTHALENE DATA AND WAVE NUMB
      READ(5,104)(NAP(J),J=1,N)
      READ(5,104)(WAVNO(J),J=1,N)
      IF(OPT1.NE.1)GO TO 19
      CALL FIX(CORFAC,C)
   19 DO 20 I=1,NCORSP
      I1=I+1
      READ(5,103)(CON(J,I1),J=1,8)
   20 READ(5,104)(OBNAP(J,I),J=1,N)
C  NORMALIZE NAPHTHALENE DATA
      CALL NORM(N,NAP,TRUNAP,NAPL)
      DO 30 I=1,NCORSP
   30 CALL NORM(N,OBNAP(1,I),NORNAP(1,I),OBNAPL(I))
C  PRINT OUTPUT LABELS
      WRITE(6,101)
      WRITE(6,136)QNAP,(OBNAPL(J),J=1,3)
      DO 31 I=1,NCORSP
      I2=I+1
   31 WRITE(6,135)(CON(J,I2),J=1,8)
      WRITE(6,138)
      WRITE(6,137)
C  CALCULATE AND PRINT CORRECTION FACTORS
      DO 12 I=1,N
      TEMP=((NORNAP(I,1)+NORNAP(I,2)+NORNAP(I,3))/NCORSP)
      IF(TEMP.LT.1.0E-10)TEMP=1.0E30
      CORFAC(I)=TRUNAP(I)/TEMP
   12 WRITE(6,139) WAVNO(I),NAP(I),(OBNAP(I,I3),I3=1,3),CORFAC(I)
      CALL PLOTH(1,6,WAVNO,CORFAC,N,N,0,FUNC,0,0.0,0.0,2.0,0.0001)
```

```
      WRITE(6,142)
      IF(OPT1.NE.1)GO TO 34
      CALL FIX1(CORFAC,C)
C
C NOW START THE PROCESSING OF SPECTRA TO BE CORRECTED
C
   34 READ(5,103)(T(J),J=1,8)
      IF(EOF(5))36,60
   60 WRITE(6,101)
      WRITE(6,141)(T(J),J=1,8)
      READ(5,104)(OBSAM(J),J=1,N)
      WRITE(6,115)
C  NORMALIZE, CORRECT, AND PRINT SAMPLE VALUE
   65 DO 210 I=1,N
      DO 205 I3=1,NCORSP
      IF(OBNAPL(I3).LT.0.0005)GO TO 203
      NORSAM(I,I3)=OBSAM(I)/OBNAPL(I3)
  203 CORSAM(I,I3)=NORSAM(I,I3)*CORFAC(I)*SENS
  205 CONTINUE
      SAS=BLANK
      IF(CORFAC(I).EQ.C(I))SAS=STAR
  210 WRITE(6,118) WAVNO(I),OBSAM(I),(NORSAM(I,I3),I3=1,3),
     1(CORSAM(I,I3),I3=1,3),CORFAC(I),SAS
C  QUANTUM YIELD CALCULATION
C  CALCULATE AREAS OF NAPHTHALENE AND SAMPLE CURVES
      CALL AREA(TRUNAP,WAVNO,N,SUMNAP)
      DO 310 I=1,NCORSP
  310 CALL AREA(CORSAM(1,I),WAVNO,N,SUMSAM(I))
C  CALCUCATE CORRECTION FACTOR
      QCOR=QNAP/SUMNAP
C  CALCULATE AND PRINT QUANTUM YIELD FOR SAMPLE
      WRITE(6,133)SENS
      DO 320 I=1,N
      PLOTAV(I)=0.
      DO 315 J=1,NCORSP
  315 PLOTAV(I)=CORSAM(I,J)+PLOTAV(I)
      PLOTAV(I)=PLOTAV(I)/NCORSP
  320 CONTINUE
      XMAX=WAVNO(N)
      XMIN=WAVNO(1)
      YMAX=0.0
      YMIN=0.0
      CALL PLOTH(ICOUNT,6,WAVNO,PLOTAV,N,N,0,FUNC,1,
     1XMAX,XMIN,YMAX,YMIN)
      XMAX=WAVNO(N)
      XMIN=WAVNO(1)
      YMAX=YLIM
      YMIN=-0.1
      CALL PLOTH(ICOUNT,6,WAVNO,PLOTAV,N,N,0,FUNC,0,
     1XMAX,XMIN,YMAX,YMIN)
      IF(IPLOT.EQ.1)CALL CALPLT(N,T,YLIMT,WAVNO,PLOTAV,ICOST)
C  RETURN TO PROGRAM WITH NEXT SET OF DATA
```

```
      CALL ZERO(OBSAM,50)
      ICOUNT=ICOUNT+1
      GO TO 34
   36 STOP
  101 FORMAT(*1*)
  102 FORMAT(2I5,F5.0,F5.0,I5,F5.0,2I5)
  103 FORMAT(8A10)
  104 FORMAT(8F10.4)
  115 FORMAT(3X,"WAVE NO.",5X,"OBS. VALUE",5X,"NORMALIZED VALUE",25X,"CO
     1RRECTED VALUE",17X,"CORRECTION FACTOR")
  118 FORMAT(F10.0,3X,F10.4,5X,3F10.4,10X,3F10.4,3X,F10.4,A1)
  132 FORMAT(3X,"QUANTUM YIELD",I2," ="2X,F10.4)
  133 FORMAT(* THE QUANTUM YIELDS HAVE BEEN MULTIPLIED BY A FACTOR OF*,
     1F10.4)
  135 FORMAT(* *,8A10)
  136 FORMAT(* CORRECTION FACTORS FROM NAPHTHALENE*,//,* ACCEPTED VALUE
     1FOR QUANTUM YIELD OF NAPHTHALENE IS *,F7.4,//,
     2* 1ST NAPHTH PEAK MAX =*,F7.4,/,
     3* 2ND NAPHTH PEAK MAX =*,F7.4,/,
     4* 3RD NAPHTH PEAK MAX =*,F7.4,/)
  137 FORMAT(3X,*WAVE NO.*,5X,*CORRECT. NAP.*,5X,*OBS. NAP.*,25X,
     1*CORRECTION FACTOR*,/)
  138 FORMAT(/)
  139 FORMAT(F10.0,2X,F10.4,5X,3F10.4,6X,F10.4)
  141 FORMAT(///,* *,8A10,///)
  142 FORMAT(///,* PLOT OF CORRECTION FACTORS*,///)
      END



      SUBROUTINE AREA(G,XY,N,SUMNAP)
C NOTE - AREA ASSUMES BASELINE OF ZERO
      DIMENSION G(50),XY(50)
      SUMNAP=0.0
      M=1
   10 L=M+1
      IF(M.EQ.N)RETURN
      ARE=ABS(((G(L)+G(M))/2.0)*(XY(L)-XY(M)))
      SUMNAP=ARE+SUMNAP
      M=M+1
      GO TO 10
      END
```

```
      SUBROUTINE CALPLT(N,NAME,YLIM,A,B,IPLOT)
C CURRENT CAPACITY IS 50 POINTS
C MAKE SURE TO ADD 2 EXTRA LOCATIONS TO A AND B OVER THE NUMBER OF
C POINTS DESIRED                                    ----
      DIMENSION A(52),B(52),IBUF(257),NAME(8)
      INUM=0
      IF(IPLOT.EQ.1)INUM=2
      CALL PLOTS(IBUF,257,INUM)
      N1=N+1
      N2=N+2
      XL=8.0
      YL=9.0
      CALL PLOT(0.0,0.5,-3)
      CALL SCALE(A,XL,N,1)
      CALL SCALE(B,YL,N,1)
      CALL AXIS(0.0,0.0,17HWAVELENGTH (CM-1),-17,XL,0.0,A(N1),A(N2))
      CALL AXIS(0.0,0.0,20HRELATIVE PEAK HEIGHT,20,YL,90.0,B(N1),
     1B(N2))
      DO 20 I=1,N
      X=(A(I)-A(N1))/A(N2)
      Y=(B(I)-B(N1))/B(N2)
   20 CALL SYMBOL(X,Y,0.024,11,0.,-1)
      CALL SYMBOL(0.5,9.5,0.07,NAME,0.0,80)
      CALL PLOT(12.0,0.0,999)
      RETURN
      END



      SUBROUTINE FIX(CORFAC,C)
      DIMENSION CORFAC(50),C(56)
      DO 15 I=1,50,8
      N=I+7
   15 READ(5,102)(C(J),J=I,N)
      RETURN
      ENTRY FIX1
   51 DO 60 I=1,50
      IF(C(I).EQ.-1.0)CORFAC(I)=0.0
   60 IF(C(I).GT.0.)CORFAC(I)=C(I)
   70 RETURN
  102 FORMAT(8F10.0)
      END
```

```
      SUBROUTINE NORM(N,IN,NOR,INL)
C  -NORM- NORMALIZES INPUTED DATA
C  N= NO. OF DATA PTS., IN= INPUT VALUES, NOR= NORMALIZED OUTPUT
      REAL IN,NOR,INL
      DIMENSION IN(50),NOR(50)
      K=1
      L=1
    8 IF(L.GE.N) GO TO 9
      L=L+1
      IF(IN(K).GE.IN(L)) GO TO 8
      K=L
      GO TO 8
    9 DO 10 I=1,N
   10 NOR(I)=IN(I)/IN(K)
      INL=IN(K)
      RETURN
      END



      SUBROUTINE ZERO(Z,N)
      DIMENSION Z(150)
      DO 35 I=1,N
   35 Z(I)=0.0
      RETURN
      END
```

LISTING OF COREK INTERACTIVE PROGRAM (CIP) PAGE 1

```
      PROGRAM CIP(INPUT=65,OUTPUT=65,TAPE99=65,TAPE64=65,TAPE75=65,
     1TAPE69=65,TAPE5=INPUT,TAPE6=OUTPUT)
C TAPE 64 = STANDARD NAPHTH
C TAPE75 = DATA
C TAPE99 = OUTPUT FOR COREK
      INTEGER LFN(4),FL1,FL2,PH1,PH2
      DIMENSION C(56),A(8),NAME(8)
      DATA IYES,NO/1HY,1HN/
      DATA LFN1/10H          /
      DATA C/56*0.0/
      DATA NAME/8*1H /
      DATA IP,IF1/1HP,1HF/
      DATA FL1/10HFLUORESCEN/,FL2/2HCE/,PH1/10HPHOSPHORES/,
     1PH2/5HCENCE/
      CALL NOBLANK
      IOPT=0
      ICOST=0
      ICHECK=0
      WRITE(6,101)
      WRITE(6,102)
    1 WRITE(6,103)
      WRITE(6,104)
      READ(5,105)NPT
      IF(NPT.GT.0.AND.NPT.LT.51)GO TO 2
      WRITE(6,121)
      GO TO 1
    2 WRITE(6,106)
      WRITE(6,104)
      READ(5,105)NCORSP
      IF(NCORSP.LT.4.AND.NCORSP.GT.0)GO TO 3
      WRITE(6,122)
      GO TO 2
    3 WRITE(6,107)
      WRITE(6,104)
      READ(5,108)QNAP
      WRITE(6,109)
      WRITE(6,104)
      READ(5,108)SENS
      WRITE(6,110)
      WRITE(6,104)
      READ(5,108)YLIM
    4 WRITE(6,123)NPT,NCORSP,QNAP,SENS,YLIM
      WRITE(6,124)
      WRITE(6,104)
      READ(5,115)IANS
      IF(IANS.EQ.IYES)GO TO 1
      IF(IANS.EQ.NO)GO TO 8
      WRITE(6,126)
      GO TO 4
    8 DO 10 I=1,4
```

```
   10 LFN(I)=LFN1
      WRITE(6,111)
      WRITE(6,104)
      READ(5,112)(LFN(I),I=1,4)
      WRITE(6,119)(LFN(I),I=1,4)
      CALL PFSTUFF(6LTAPE64,LFN,ICHECK)
      JCHECK=ICHECK
      KCHECK=JCHECK.AND.777B
      IF(KCHECK.EQ.0)GO TO 18
      ICHECK=0
      WRITE(6,117)
      WRITE(6,118)(LFN(I),I=1,4)
      GO TO 8
   18 DO 20 I=1,4
   20 LFN(I)=LFN1
      WRITE(6,113)
      WRITE(6,104)
      READ(5,112)(LFN(I),I=1,4)
      WRITE(6,119)(LFN(I),I=1,4)
      CALL PFSTUFF(6LTAPE75,LFN,ICHECK)
      JCHECK=ICHECK
      KCHECK=JCHECK.AND.777B
      IF(KCHECK.EQ.0)GO TO 30
      ICHECK=0
      WRITE(6,117)
      WRITE(6,118)(LFN(I),I=1,4)
      GO TO 18
   30 WRITE(6,114)
      WRITE(6,104)
      READ(5,115)NANS
      IF(NANS.EQ.NO)GO TO 50
      IF(NANS.EQ.IYES)GO TO 34
      WRITE(6,126)
      GO TO 30
   34 IOPT=1
      WRITE(6,135)
      WRITE(6,104)
      READ(5,115)NANS
      IF(NANS.EQ.NO)GO TO 35
      IF(NANS.EQ.IYES)GO TO 40
      WRITE(6,126)
      GO TO 34
   40 WRITE(6,136)
      WRITE(6,104)
      DO 42 I=1,4
   42 LFN(I)=LFN1
      READ(5,112)(LFN(I),I=1,4)
      WRITE(6,119)(LFN(I),I=1,4)
      CALL PFSTUFF(6LTAPE69,LFN,ICHECK)
      JCHECK=ICHECK
      KCHECK=JCHECK.AND.777B
      IF(KCHECK.EQ.0)GO TO 45
```

```
      ICHECK=0
      WRITE(6,117)
      WRITE(6,118)(LFN(I),I=1,4)
      GO TO 40
   45 DO 47 I=1,50,8
      K=I+7
   47 READ(69,133)(C(J),J=I,K)
      GO TO 50
   35 WRITE(6,116)
      READ(5,105)K
      IF(K.EQ.-1)GO TO 50
      IF(K.LT.1.OR.K.GT.50)GO TO 35
      WRITE(6,104)
      READ(5,108)C(K)
      GO TO 35
   50 CONTINUE
      IPLOT=0
      WRITE(6,125)
      WRITE(6,104)
      READ(5,115)IANS
      IF(IANS.EQ.IYES)IPLOT=1
      IF(IANS.EQ.IYES)GO TO 54
      IF(IANS.EQ.NO)IPLOT=0
      IF(IANS.EQ.NO)GO TO 55
      WRITE(6,126)
      GO TO 50
   54 ICOST=0
      WRITE(6,128)
      WRITE(6,104)
      READ(5,115)IANS
      IF(IANS.EQ.IYES)ICOST=1
   55 WRITE(99,131)NPT,NCORSP,QNAP,SENS,IOPT,YLIM,IPLOT,ICOST
   56 WRITE(6,127)
      WRITE(6,104)
      READ(5,115)IANS
      IF(IANS.EQ.IF1)NAME(1)=FL1
      IF(IANS.EQ.IF1)NAME(2)=FL2
      IF(IANS.EQ.IF1)GO TO 57
      IF(IANS.EQ.IP)NAME(1)=PH1
      IF(IANS.EQ.IP)NAME(2)=PH2
      IF(IANS.EQ.IP)GO TO 57
      WRITE(6,126)
      GO TO 56
   57 WRITE(99,132)(NAME(I),I=1,8)
      L=NPT/8
      L1=L*8
      IF(L1.NE.NPT)L=L+1
      L2=L*2
      DO 60 J=1,L2
      READ(64,132)(A(I),I=1,8)
   60 WRITE(99,132)(A(I),I=1,8)
      IF(IOPT.NE.1)GO TO 65
```

```
      DO 63 I=1,50,8
      J=I+7
   63 WRITE(99,133)(C(N),N=I,J)
   65 READ(75,132)(A(I),I=1,8)
      IF(EOF(75))67,66
   66 WRITE(99,132)(A(I),I=1,8)
      GO TO 65
   67 WRITE(6,134)
      WRITE(6,104)
      READ(5,105)IRG
      WRITE(6,120)
      ENDFILE 99
      REWIND 99
      CALL WRITER(IRG)
      STOP
  101 FORMAT(* COREK INPUT PROGRAM - V.1  25-JAN-76*)
  102 FORMAT(* INPUT*)
  103 FORMAT(* HOW MANY DATA POINTS*)
  104 FORMAT(2H *)
  105 FORMAT(I3)
  106 FORMAT(* HOW MANY STANDARDS*)
  107 FORMAT(* WHAT IS THE LITERATURE QUANTUM YIELD FOR THE STANDARD*)
  108 FORMAT(F10.0)
  109 FORMAT(* WHAT IS THE SENSITIVITY FACTOR*,)
  110 FORMAT(* WHAT IS THE UPPER LIMIT ON THE PLOT*)
  111 FORMAT(* WHAT IS THE P. FILE WITH THE STANDARD NAPH CALLED*)
  112 FORMAT(4A10)
  113 FORMAT(* WHAT IS THE P. FILE WITH THE DATA CALLED*)
  114 FORMAT(* DO YOU WISH TO INPUT OVERRIDE CORRECTION FACTORS*)
  115 FORMAT(A1)
  116 FORMAT(2H $)
  117 FORMAT(* ILLEGAL PERMANENT FILENAME*)
  118 FORMAT(* FILENAME *,4A10,* IS INVALID*)
  119 FORMAT(* FILENAME *,4A10)
  120 FORMAT(* C.I.P. FINISHED*)
  121 FORMAT(* SORRY - COREK PRESENTLY IS SET UP FOR 50 OR LESS POINTS*)
  122 FORMAT(* SORRY - COREK PRESENTLY ONLY CORRECTS 3 OR LESS SPECTRA*)
  123 FORMAT(* NO. OF PTS =*,I5,/,* NO. OF STANDARDS =*,I5,/,
     1* ACCEPTED Q.Y. =*,F5.3,/,* SENS. FAC. =*,F5.3,/,
     2* LIMIT ON PLOT =*,F5.3)
  124 FORMAT(* DO YOU WISH TO CHANGE ANY OF THESE VALUES*)
  125 FORMAT(* DO YOU WANT A CALCOMP PLOT RUN*)
  126 FORMAT(* RESPONSE INVALID*)
  127 FORMAT(* IS THIS PHOSPHORESCENCE OF FLUORESCENCE*)
  128 FORMAT(* IS THIS A PUBLICATION PLOT(EXPENSIVE PAPER, HIGH QUALITY)
     1*)
  131 FORMAT(2I5,2F5.3,I5,F5.2,2I5)
  132 FORMAT(8A10)
  135 FORMAT(* DO YOU WANT TO INPUT CORRECTION FACTORS WITH A DATA SET*)
  136 FORMAT(* WHAT IS THE P.FILE WITH OVERRIDE CORRECTION FACTORS CALLE
     1D*)
  133 FORMAT(8F10.4)
```

```
  134 FORMAT(* WHAT RATE GROUP WOULD YOU LIKE THIS RUN AT*)
      END
```

```
          IDENT    WRITER
          ENTRY    WRITER
          EXT      CPC
EXC       MACRO    START,ENDC
          SX6      ENDC-START
          LX6      1
          SX1      START
          LX1      12
          BX6      X1+X6
          SA6      =SEXECREQ
          EXECM    EXECREQ,RB
EXC       ENDM
WRITER    BSS      1
          SA1      X1
          SA1      X1+RG123-1
          BX6      X1
          SA6      RGX
          INTRCOM  =SSOURCE,RECALL
          SA1      SOURCE
          SA2      =2
          BX1      X1*X2
          ZR       X1,BATCH
*
*         TELETYPE SELECTION OF CODE
*
TTY       EXC      START1,END1
          ENDRUN
*
*         BATCH SECTION OF CODE
*
BATCH     EXC      START2,END2
          SA1      EXECREQ
          NG       X1,BOMB
          ENDRUN
*
*         ERROR PROCESSING SECTION OF CODE
*
BOMB      MESSAGE  MSG,,RECALL
          ABORT
MSG       DIS      ,/CONTROL CARD BUFFER OVERFLOW./
*
*         TELETYPE CONTROL CARD BUFFER
*
START1    BSS      0
          DIS      ,/DAYMSG,OFF./
          DIS      ,/EDITOR./
          DIS      ,/USE,ZZZZJOB,ZZZSAVE./
          DIS      ,/SYSTEM,BATCH./
          DIS      ,/END./
          DIS      ,/ATTACH,ZZZTEXT,HSBCONTROL./
          DIS      ,/EDITOR./
          DIS      ,/OLD,ZZZTEXT,FROM,100,BY,10./
```

```
          DIS       ,/INSERT,TAPE99,AT,*L,BY,10./
RGX       BSS       1
          DIS       ,/,NV./
          DIS       ,/END./
          DIS       ,/DAYMSG,ON./
          DIS       ,/EDITOR./
          DIS       ,/BATCH./
          DIS       ,/END./
          DIS       ,/DAYMSG,OFF./
          DIS       ,/EDITOR./
          DIS       ,/USE,ZZZSAVE,ZZZZJOB./
          DIS       ,/END./
          DIS       ,/RETURN,ZZZZJOB,ZZZSAVE,ZZZTEXT./
          DIS       ,/HAL,L*EXP,KEEP./
          DIS       ,/DAYMSG,ON./
END1      BSS       0
*
*         BATCH CONTROL CARD BUFFER
*
START2    BSS       0
          DIS       ,/BOMB./
END2      BSS       0
RG123     DIS       1,/$/=/1/,*F
          DIS       1,/$/=/2/,*F
          DIS       1,/$/=/3/,*F
*         END
          END
```

LISTING OF TITLE CARD PROGRAM (TICARD) PAGE 1

```
      PROGRAM TICARD(INPUT=65,OUTPUT=65,TAPE99=65,TAPE64=65,TAPE5=INPUT,
     1TAPE6=OUTPUT)
      INTEGER LFN(4),IDAT(20,10),LOC(10),ICARD(80),IFL(20)
      DIMENSION DAT(8,6)
      DATA LFN1/10H          /,LOC/10*0/
      DATA IDAT/200*0/,IBLANK/1H /,ISTAR/1H*/
      ICHECK=0
      I10=0
      WRITE(6,101)
      CALL NOBLANK
      WRITE(6,115)
      WRITE(6,105)
      READ(5,116)NUM
      N=NUM/6
      NCHECK=N*NUM
      IF(NCHECK.NE.NUM)N=N+1
      WRITE(6,117)N
   10 DO 12 I=1,4
   12 LFN(2)=LFN1
      WRITE(6,102)
      WRITE(6,105)
      READ(5,103)(LFN(I),I=1,4)
      CALL PFSTUFF(6LTAPE64,LFN,ICHECK)
      JCHECK=ICHECK
      KCHECK=JCHECK.AND.777B
      IF(KCHECK.EQ.0)GO TO 18
      ICHECK=0
      WRITE(6,104)(LFN(I),I=1,4)
      GO TO 10
   18 DO 20 I=1,N
      READ(64,108)(DAT(J,I),J=1,8)
      IF(EOF(64))90,20
   20 CONTINUE
      GO TO 22
   21 WRITE(6,110)
   22 WRITE(6,107)
      READ(5,109)NC
      CALL VALID(ICHECK,NC)
      IF(ICHECK.EQ.0)GO TO 21
      IF(ICHECK.GT.0)GO TO 40
      CALL READR(NC,LOC,IDAT)
      GO TO 22
   40 IF(ICHECK.NE.11)GO TO 45
      CALL WRITR(ICARD,LOC,IDAT)
   45 IF(ICHECK.NE.12)GO TO 50
      CALL WRITR(ICARD,LOC,IDAT)
      WRITE(99,111)(ICARD(I),I=1,80)
      DO 47 I=1,N
   47 WRITE(99,108)(DAT(J,I),J=1,8)
      I10=I10+1
      GO TO 18
```

```
   50 IF(ICHECK.NE.13)GO TO 55
      STOP
   55 IF(ICHECK.NE.14)GO TO 60
      WRITE(6,105)
      READ(5,114)N1
      WRITE(6,112)(DAT(I,N1),I=1,8)
   60 IF(ICHECK.NE.15)GO TO 22
      IF(I10.LT.1)GO TO 21
      I10=I10-1
      N2=2*N
      DO 65 I=1,N2
   65 BACKSPACE 5
      DO 70 I=1,N
   70 BACKSPACE 99
      GO TO 18
      GO TO 22
   90 WRITE(6,113)
      IRG=3
      CALL WRITER(IRG)
      STOP
  101 FORMAT(* TICARD V.1*)
  102 FORMAT(* INPUT FILENAME*)
  103 FORMAT(4A10)
  104 FORMAT(* FILENAME *,4A10,* IS INVALID*)
  105 FORMAT(2H *)
  106 FORMAT(2H $)
  107 FORMAT(2H =)
  108 FORMAT(8F10.3)
  109 FORMAT(20A1)
  110 FORMAT(* INVALID PARAMETER*)
  111 FORMAT(80A1)
  112 FORMAT(* *,8F10.3)
  113 FORMAT(* TICARD FINISHED*)
  114 FORMAT(I1)
  115 FORMAT(* HOW MANY DATA POINTS*)
  116 FORMAT(I4)
  117 FORMAT(* *,I4,* CARDS WILL BE READ ON EACH PASS*)
      END
```

LISTING OF PROGRAM ATOMOV PAGE 1

```
      PROGRAM ATOMOV(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      READ(5,10)OX,OY,OZ
      READ(5,10)CX,CY,CZ
      WRITE(6,14)
      WRITE(6,15)OX,OY,OZ
      WRITE(6,16)
      WRITE(6,15)CX,CY,CZ
      ALENS=((OX-CX)**2+(OY-CY)**2+(OZ-CZ)**2)
      ALEN=ALENS**0.5
      WRITE(6,17)ALEN
      WRITE(6,18)
      XFAC=(OX-CX)/ALEN
      YFAC=(OY-CY)/ALEN
      ZFAC=(OZ-CZ)/ALEN
C     INPUT LENTHS
5     READ(5,11)AXYZ
      IF(AXYZ.LT.0.)GO TO 30
      WRITE(6,20)AXYZ
      AX=-(XFAC*AXYZ)+OX
      AY=-(YFAC*AXYZ)+OY
      AZ=-(ZFAC*AXYZ)+OZ
      WRITE(6,25)AX,AY,AZ
      GO TO 5
30    STOP
10    FORMAT(3F20.0)
11    FORMAT(F20.0)
14    FORMAT(1H1,10H ORIGIN AT,/)
15    FORMAT(3H X=,F20.10,3H Y=,F20.10,3H Z=,F20.10,/)
16    FORMAT(13H WITH ATOM AT,/)
17    FORMAT(8H LENTH =,F20.10)
18    FORMAT(1H1)
20    FORMAT(12H NEW LENTH =,F20.10)
25    FORMAT(22H NEW ATOM COORDS-   X=,F20.10,3H Y=,F20.10,3H Z=,F20.10,
     1/////)
      END
```