SYNTHESIS OF POTENTIAL ORGANIC CONDUCTORS

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ABSTRACT

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Recent interest in highly conducting charge-transfer salts derived from the electron acceptor 7,7,8,8,-tetracyanoquinodimethane (TCNQ) and the electron donor tetrathiafulvalene (TTF) has prompted the design of new organic compounds whose structures would enhance their electrical properties, and consequently advance our understanding about the mechanism of conductivity. We describe here our attempts to prepare the extended conjugated and heteroatom substituted analogs of these systems.

The first area studied was that of the thiazolo[5,4-d]-thiazole ring system, a heteroatom substituted analog of TNAP, which contains two nitrogens and two sulfurs but possess 10-π electrons. The thiazolothiazole ring was constructed by condensation of dithiooxamide with aromatic aldehydes. The synthesis of 2,5-dihydroxymethyl and 2,5-chloromethyl thiazolo[5,4-d]thiazole was described.

The oxidation of substituted 4-hydroxyphenyl derivatives to the corresponding quinoids was also successful.

Methylation of nitrogens on the thiazolo[5,4-d]thiazole heterocycles to give dicationic salts as radical cation precursor was highly successful.

Synthesis of benzo[1,2-d:4,5-d"]diimidazole systems by making use of 1,2,4,5-tetraaminobenzene was also attempted.

Two extended conjugated TTF analogs, the diphenyl and the tetramethyl tetrathionaphtho-2,6-quinodimethane (TTNQ), were prepared. The diphenyl-TTNQ formed a non-stoichiometric charge-transfer complex with iodine.

Synthetic efforts toward 7,8-dicyano-7,8-dinitro-quinodimethane and 11,12-dicyano-11,12-dinitronaphtho-2,6-quinodimethane were described including the preparation of p-bis(cyanonitromethyl)benzene and 2,6-bis(cyano-nitromethyl)naphthalene.

Finally, the attempt to introduce a second cyano group into a carbon center through enamines of active methylene compounds resulted in an unexpected ring closure to afford the 5-aminoisoxazole derivatives.

To my wife Jifang and my parents, without whose support this would not have been possible.

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INTRODUCTION

The capacity for metallic behavior is most common among inorganic compounds: three-quarters of the total number of simple substance formed by elements, some of their compounds, and a large number of alloys are so constructed that the metallic state is the main stable state.[1] By contrast, the majority of organic compounds are poor electrical conductors with room temperature conductivities in the range of 10^{-9} to 10^{-14} $ohm^{-1}cm^{-1}$. Graphite is perhaps the only instance of metallic or semimetallic conductivity.

In the 19th century, during the rapid development of organic synthesis, the idea of possible similarities between alkali metals and organic radicals was quite popular. Research in this direction revealed one of the main difficulties in the preparation of organic metals, namely, the pairing tendency of valence electrons. The synthesis of stable free radicals produced only paramagnetic insulators rather than metals. This is due to the localization of unpaired electrons on separate molecules.

However, strong π-molecular donor (D) and acceptor (A) molecules often react to form organic charge-transfer salts.[2] In contrast to the conventional molecular crystals,

charge-transfer salts have unpaired electrons on the acceptor or both as a result of the simple electron transfer, $D + A \longrightarrow D^{+} A^{-}$.[3] This strikingly simple result opens up a new area of electronic phenomena, for if the unpaired electrons delocalize over all molecular sites, the metallic state results. These materials form the basis of the field of "organic semiconductors", which has been actively studied since the mid-1950's.[4,5]

In the early 1960's, Melby and a duPont group discovered a new powerful π-molecular acceptor, tetracyano-p-quinodimethane (TCNQ). As with other acceptors, the TCNQ radical anion forms organic semiconductors with a large number of cations.[6-9] Only a few cases have been reported where the electrical conductivity is moderately large, with a negative temperature coefficient characteristic of metallic behavior. The primary example is the charge-transfer salt of TCNQ with the cation N-methylphenazinium (NMP)[3], which was among the most electrically conducting organic solids known at that time.

In 1972, it was discovered[10] that the chloride salt of a new organic donor, TTF (tetrathiafulvalene), has a high pellet conductivity (σ (300°K, $\sim$0.2 $ohm^{-1}cm^{-1}$). The following year TCNQ and TTF were brought together to produce a new compound (TTF-TCNQ) and found to have

conductivity which increases dramatically below room temperature, rising as high as 10^4 $ohm^{-1}cm^{-1}$ near 60°K (Figure 2b), high enough to be considered an "organic metal".

A flurry of current research has been directed toward gaining an understanding of the electronic properties of this complex. Solid-state physicists were attracted by the high metal-like conductivity in such an exotic and unusual material and by speculations of possible high-temperature superconductivity.[11] Substantial chemical studies have focused on the synthesis of a remarkable number of new derivatives of TTF and TCNQ.[12,13] Since the emergence of TTF-TCNQ several comprehensive reviews of this field from the perspective of solid state physics, physical chemistry, and synthetic chemistry have been published.[2,12,14-18] Part of the driving force behind this intense interest is the hope that organic chemistry can be utilized to produce new organic solid for electronic applications.

Spectroscopy studies revealed that the TCNQ molecule serves as the electron acceptor while the TTF molecule is the donor. The crystal structure indicates (Figure 3,4) a rather closely spaced plane parallel arrangements of the TCNQ and the TTF molecules as segregated stacks. The interplanar stacking distance (3.17-3.30 Å) and the

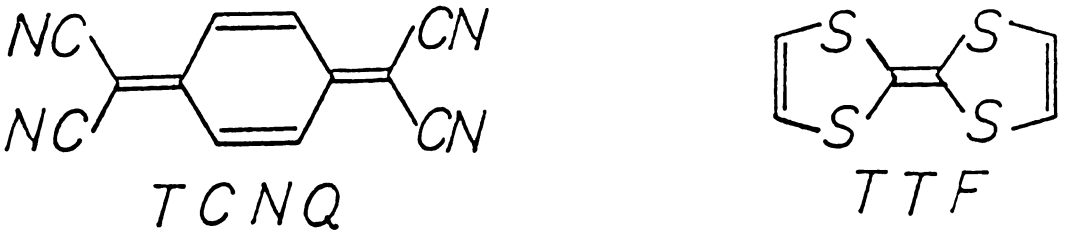


Fig. 1: Structure of TCNQ and TTF.

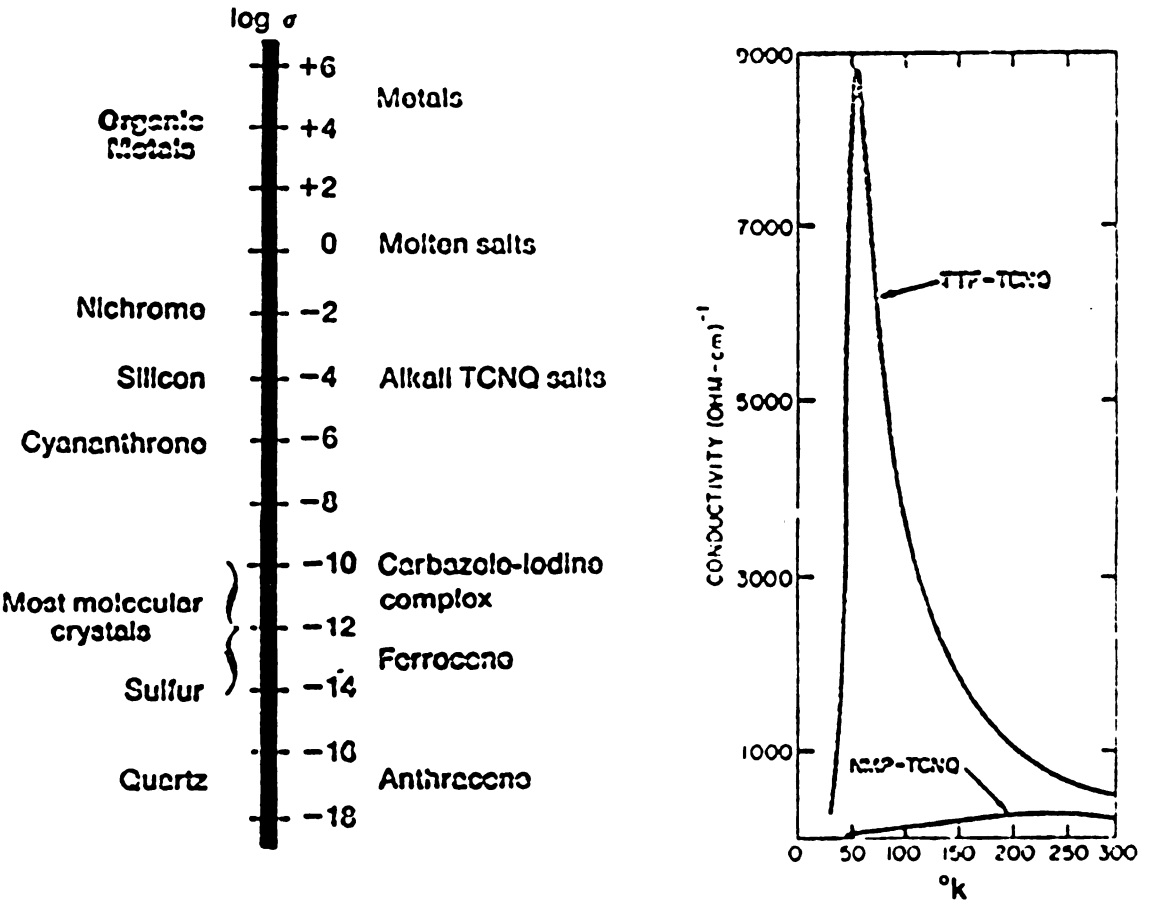
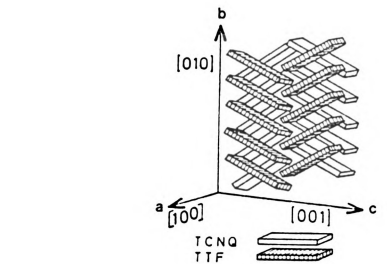
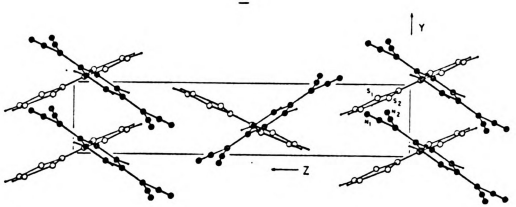


Fig. 2: a) Scale of Approximate Conductivity

b) Comparison of Conductivity of TTF-TCNQ with NMP-TCNQ. (taken from Ref. 12).



a



b

Fig. 3: a) Schematic Representation of TTF-TCNQ.
b) Crystal Structure of TTF-TCNQ Projected along the a-axis. (taken from Ref. 14).

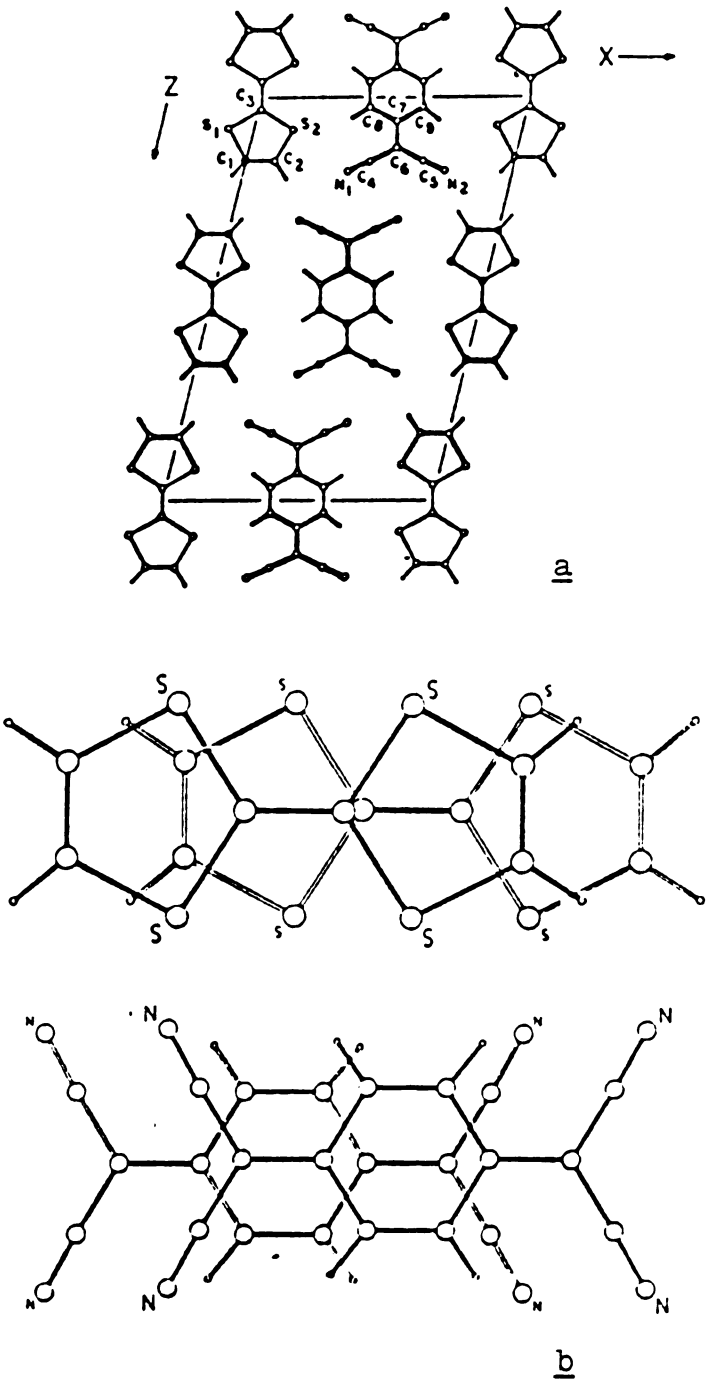


Fig. 4: a) TTF-TCNQ Projected Along Conducting Axis.
b) Molecular Overlap in the Columnar Stacks in TTF-TCNQ. (taken from Ref. 14).

resulting π-orbital overlap integral between TCNQ ions indicates that the band widths in these solids are rather narrow, probably in the range of 0.1-0.6 of an electron volt.[14]

The overlapping electron cloud can be considered as the conducting media. Because of the geometry of the π-orbitals, the band-widths, and hence the electronic properties are inherently anisotropic. The direction of highest conductivity is in the stacking direction. This is similar to what is know also from graphite and other polymeric compounds.[4] The reaction of TTF and TCNQ formally involves an electron transfer to give TTF radical cations and TCNQ radical anions. For full electron transfer in the solid, the electrostatic repulsion, due to having like charges so close together in the molecular stacks, is expected to be considerable. However, the solid can gain significant stabilization by incomplete or partial charge transfer.[20] In fact, several recent investigations[20-23] have concluded that the extent of charge transfer in TTF-TCNQ is only 0.5-0.6 of one electron. That is to say, that there is a complete and spontaneous electron transfer from a certain fraction of the donors to the acceptors, so that the solid consists of an assembly of now positively charged donor molecules, and negatively charged acceptors, plus a certain fraction of neutral donors and acceptors. Negative charges are mobile because electrons transfer from a negative

acceptor to a neutral acceptor , much the same as in n or p type semiconductors. This situation can be promoted by regulation of the oxidation and reduction potentials of the interacting species. Wheland[24] proposed that the difference between the ionic potential of the donor and the electron affinity of the acceptor would determine the relative conductivity of that complex, thereby suggesting why some donors only form conducting salts with particular acceptors.

Most of the duPont TCNQ salts which have segregated stack structures also have periodically distorted linear chain structure and are insulator.[5] Only the highest conductivity TCNQ salts have both a segregated stack and a non-distorted linear chain structure. The early notable member of this exclusive class were NMP-TCNQ and quinolinium (Q) $(TCNQ)_2$[14].

Another structural feature that makes TTF-TCNQ an attractive candidate for study is the polarizability of the cation portion of the complex. The higher the lattice polarizability, the higher is the local dielectric constant; so that the conduction electron-cation chain exciton coupling can facilitate conduction by reducing the effective Coulomb repulsion (U_{eff}) between two electrons on the same site.[25,26]

Moreover, Perlstein[18] has developed a formalism for the synthesis of new highly conducting organic solids based

on the "local aromaticity" concept. He contended that the most efficient conductors contain molecules a) whose radical ions form a new aromatic sextet upon one-electron oxidation or reduction and b) whose aromaticity can migrate by mix-valence interaction (Figure 5).

More information about the properties of organic metals has been obtained by modifying either the acceptor or the donor in a systematic way. However, compilation of the conductivity data have shown that these factors do not completely explain the phenomena. The problem is presumably due to the fact that more than one structural feature has always been altered.

Cowan[14] summarized some of the organic metal design constraints as following:

1. Stable open-shell (free-radical) salts.
2. Planar molecules with delocalized π-molecular orbitals.
3. Inhomogeneous charge and spin distribution.
4. Segregated stacks of radical ions.
5. Uniform stacks - No periodic distortions.
6. Both cation and anion have open shell.
7. Both cation and anion are nominally divalent.
8. Fractional charge transfer.
9. Polarizable cation.
10. No disorder (symmetric anions and cations).
11. Cation and anion of similar size.

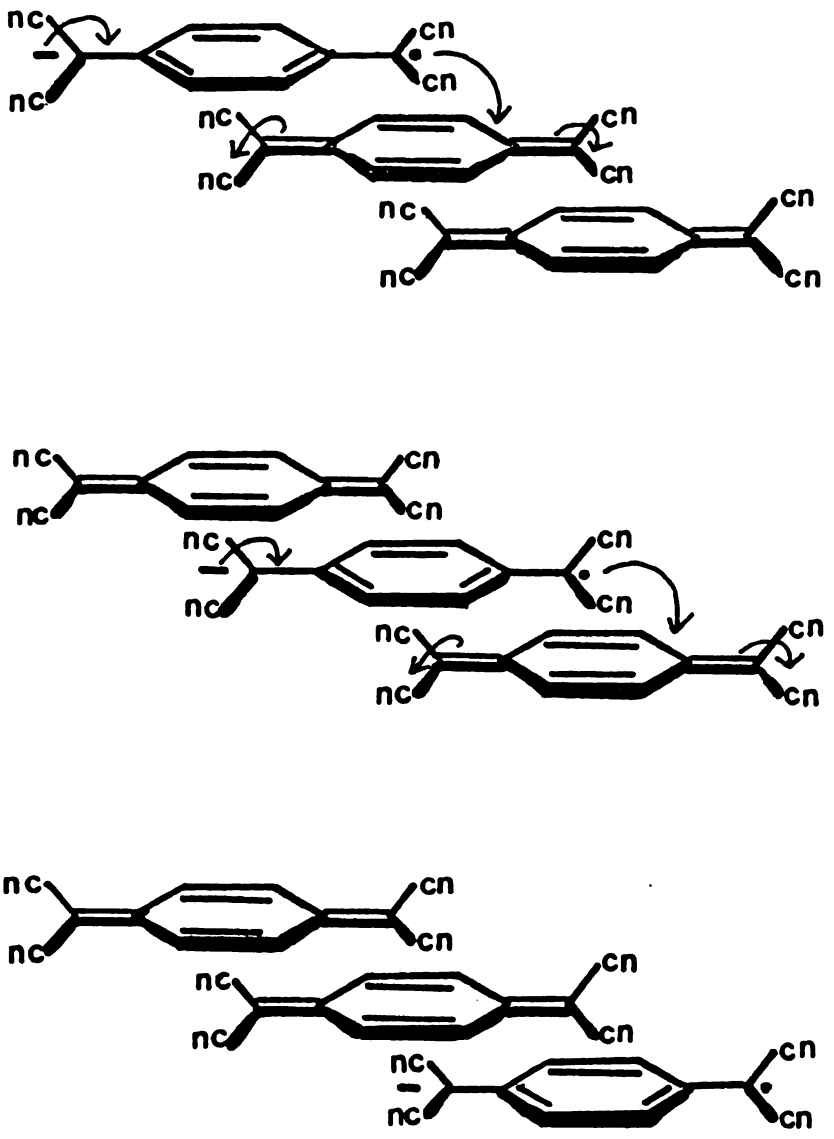


Fig. 5: Migration of Aromaticity along TCNQ stack. (taken from Ref. 18).

To a degree unmatched among other intrinsic conductors, the electronic properties of organic charge-transfer salts are subject to chemical control. However, the design of new donor and acceptor molecules based on these constraints does not guarantee one a good new organic metal. Among the derivatives and analogs of TTF-TCNQ[14], for example, even minor differences in molecular structure often manifest themselves as sharp contrasts in electrical behavior. Such compounds span the full range from insulators to the best organic conductor known.

From a synthetic chemist's point of view, this sensitivity to molecular detail presents an unusual challenge. Certainly it complicates the interpretation of materials in this class, but it also multiplies the amount of information available and the possibilities for design. Since the discovery of TTF-TCNQ complex in 1972, the research in this field has been guided by three major approaches, namely, side-chain modification, heavy atom substitution and conjugated extension. These approaches as well as the synthesis of analogous compounds of the well-known classes TCNQ and TTF are documented in the literature[28-35]. Together with this, there have also appeared communications on highly conductive compounds of new types. In 1977 Sandman[36] synthesized a number of charge transfer complexes of TCNQ with $\Delta^{4,4'}$-bithiopyran (iso-π-electronic to TTF) with same

conductivity as poly-crystalline samples of TTF-TCNQ. Perlstein[18] reported the high conductivity for the charge-transfer complex of the phenyl derivatives of $\Delta^{4,4'}$-bithiopyran with TCNQ. Electrochemical oxidation of tetramethyl tetraselenofulvalene has also been utilized to produce $(TMTSF)_2X$, where X is a symmetrical octahedral anion[37,38]; PF_6^-, AsF_6^-, SbF_6^- or a tetrahedral anion[39], ClO_4^-. These compounds exhibited superconductivity at moderate hydrostatic pressure.

Listed below in Table 1 are several modified donors and the room temperature conductivities of their TCNQ salts.[18] In 1-2, substitution of the TTF molecule with four methyl side chains causes a two-fold increase in the conductivity whereas the octamethyl derivative 1-4 has a much lower value. Besides sidechain modification, extension of the unsaturation was also carried out. The benzo analogs of TTF and TTN (1-13), 1-5 and 1-14 respectively, have recently been prepared as has the phenylene analog of TTF, 1-12. These variations, in general, have not increased the conductivity to any great extent. The third major type of modification, heteroatomic exchange (heavy atom substitution), has resulted in significant improvement in conductivity. At room temperature, for example, the conductivity of 1-10 is about two times higher than that of TTF.

Table 1. TTF analogs and the conductivity of their TCNQ salts.

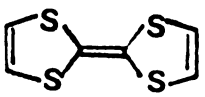
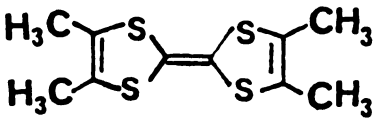
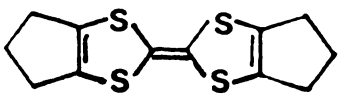
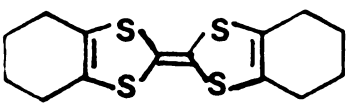
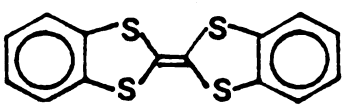
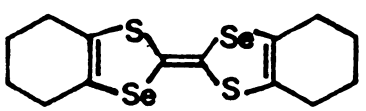
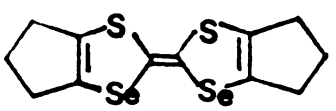
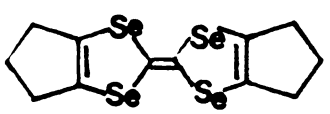
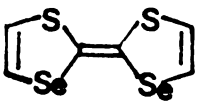
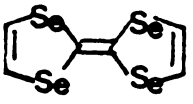
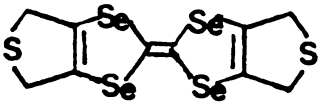
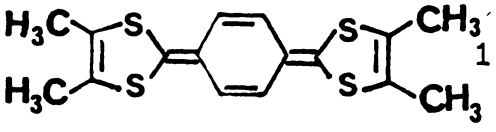
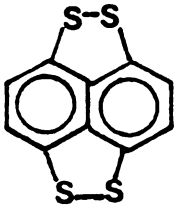
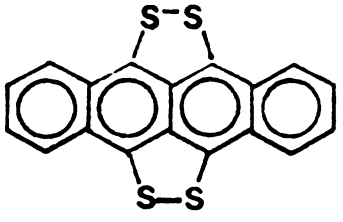
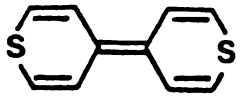
Entry		Ratio: TCNQ	Room Temperature Conductivity (Pellet) $ohm^{-1}\ cm^{-1}$
1		1:1	500
2		1:2	10^3
3		1:1	500
4		1:1	$5x10^{-5}$
5		1:1	10^{-7}
6		1:1	$2x10^{-6}$
7		1:1	100
8		1:1	$2x10^3$

Table 1. (cont'd.).

Entry		Ratio: TCNQ	Room Temperature Conductivity (Pellet) $ohm^{-1}\ cm^{-1}$
9		1:1	550
10		1:1	800
11		1:1	600
12		1:2	10^{-3}
13		1:1	40
14		1:1 1:2	1 100
15		1:1	30

And the most striking example is 1-8, whose TCNQ salt has the highest room temperature conductivity measured thus far.

Regarding modification of the acceptor TCNQ, much less work has been done. The majority of the changes have involved sidechain variations in TCNQ itself. Many derivatives of TCNQ have been synthesized, incorporating F, Cl, Br, I, SR, OR and alkyl substituents onto the ring.[28] Some of these examples with higher conductivities are shown in Table 2, (2-1 - 2-4). The extended conjugated systems 2-5 and 2-6 have been known for some time, with only 2-5 leading to a stable charge transfer complex. Heavy atom substitution in these acceptor molecules is less common, with only mono-sulfur and di-sulfur analogs of TCNQ, 2-10 and 2-11, have been prepared. However, 2-10 has failed to undergo any charge transfer with its donor, whereas 2-11 forms only non-conducting complex with TTF. In the case of 2-8, the dianion could not be oxidized to a stable radical. Instead, the corresponding trianion radical was isolated. Compound 2-9 is rather interesting. Since nitrogen and carbon have very similar covalent radii, it was expected to produce only a minor perturbation on the size and shape of TCNQ. However, the radical "anion" of 2-9 would be a formally neutral molecule and therefore reduce

Table 2. TCNQ analogs and the conductivity of their TTF salts.

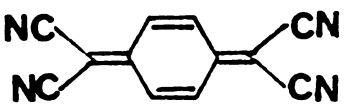
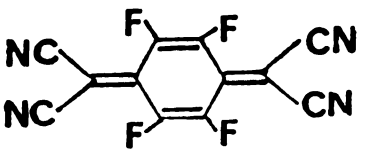
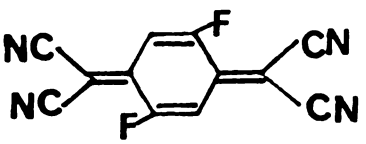
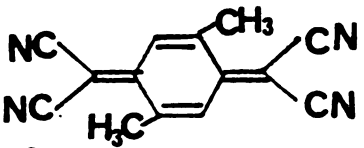
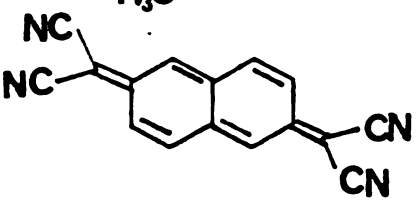
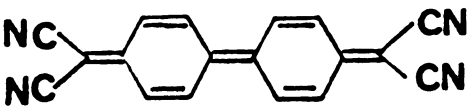
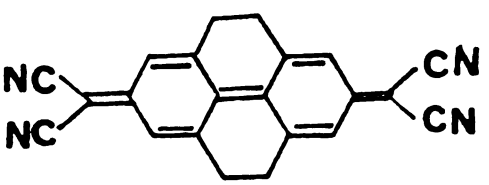
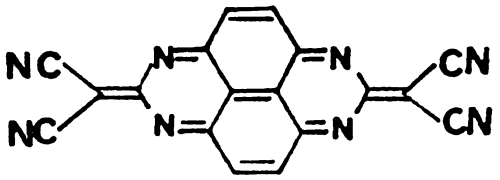
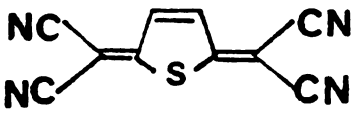
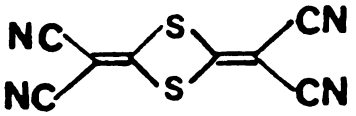
Entry		Room Temperature Pellet Conductivity $ohm^{-1}\ cm^{-1}$	Reference
1		500	28
2		---	28
3		$2x10^{-5}$	29
4		3	30
5		40	31
6		---	32
7		$2x10^{-1}$ (with TMTTF)	33

Table 2. (cont'd.)

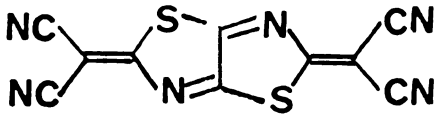
Entry		Room Temperature Pellet Conductivity $ohm^{-1}\ cm^{-1}$	Reference
8		---	35
9		10^{-2}	14
10		---	34
11		10^{-6}	34

the intermolecular repulsion in stacking.

It is generally believed that no one single factor could solely control the conductivity of charge-transfer complex, and that one of the important long-range goals is the development of predictive criteria for the stability of organic conductors. In order to achieve this goal and to better understand the conduction mechanism, more derivatives need to be synthesized and studied. In light of the work done thus far, we decided that the most promising direction to follow was the modification of the most conductive charge transfer complex TCNQ and TTF molecules.

Our first target molecule 1 demonstrated perfectly our idea of heavy atom substitution. By substituting nitrogen and sulfur for carbons, one increases the electron affinity of the molecule.[35] Upon one-electron reduction, 1 generates a 10 π-electron heterocycles thiazolo[5,4-d]thiazole, and therefore is the heterocyclic analog of TNAP (Table 2, Entry 5). We also would attempt to combine this 10 π-electron heterocycles with the well-known chloranil type electron acceptor. Molecules 2 and 3 are the result of this combination.

The synthesis of 4 was also attempted, bearing in mind that it would provide three new aromatic sextets upon receiving one electron.



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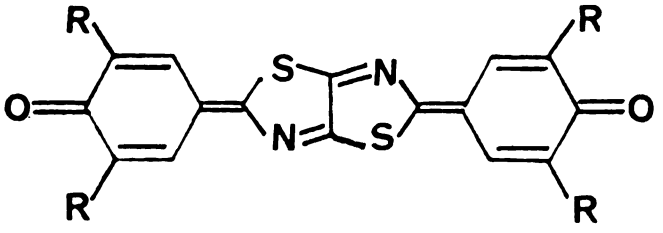

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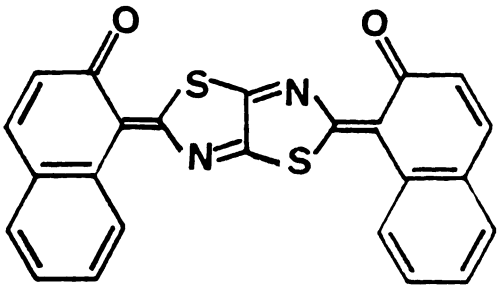

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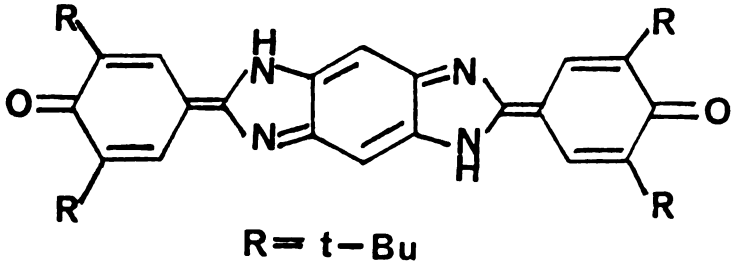

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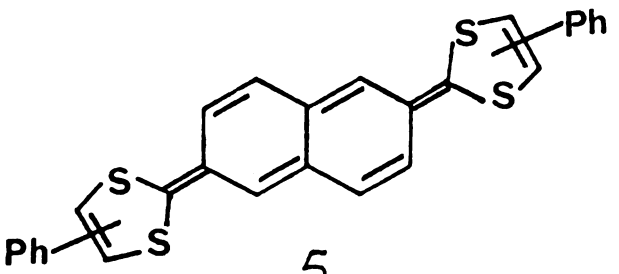
The methylation of the nitrogens on thiazolo[5,4-d]-thiazole derivatives was successful to produce the di-cationic salts.

The third part of this work was devoted to the synthesis of extended TTF systems, 5 and 6. The relation between molecule 5, 6 and TTF should be similar to that between TMAP and TCNE.

The fourth part will describe the synthetic work of dicyanodinitroquinodimethane 7 and dicyanodinitronaphtho-2,6-quinodimethane 8. We expected that the nitro groups would stabilize the radical anion as well as cyano groups and not to disturb significantly the molecular packing.

In the last part of this work we described an unexpected ring closure of the enamine of phenylacetonitrile and the first example of using sodium azide as a reducing agent.



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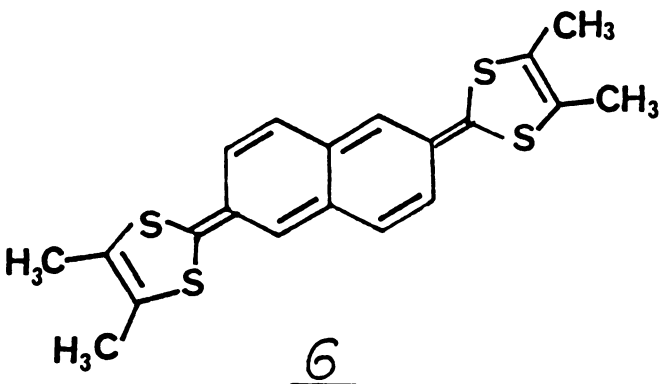

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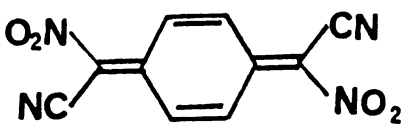

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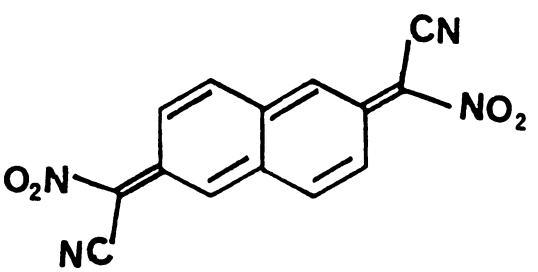


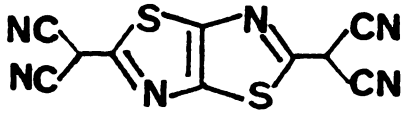
8

RESULTS AND DISCUSSION

I. CHEMISTRY OF THIAZOLO[5,4-d]THIAZOLE

A. 2,5-Disubstituted thiazolo[5,4-d]thiazole nucleus

The first modification we made on the TTF-TCNQ system was the heteroatomic exchange. We tried to introduce nitrogen and sulfur into the system so that the molecules would have larger polarizability and better electron affinity as compared with simple carbon skeleton. In theory, the higher the polarizability, the smaller the coulomb repulsion energies of the odd electrons on the neighboring stacks. Simply speaking, molecules with heteroatoms would tolerate more drastic electronic change in the environment without disturbing their packing. The key molecule in this project 2,5-bis(propanedinitrile)thiazolo[5,4-d]thiazole 9 is of special interest to us.



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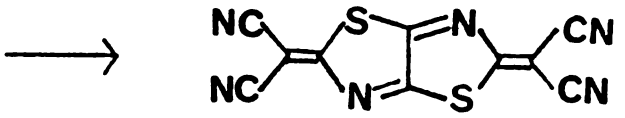
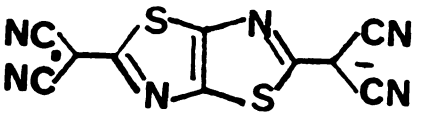


1



The thiazolo[5,4-d]thiazole heterocycles at the center of compound 9 possesses 10 π-electrons just like a naphthalene nucleus. Upon oxidation, 9 would give the quinoid moiety 1, a close analog of TNAP (Table 2, Entry 5). Besides the extra polarizability and affinity, the electronic properties of 1 should be similar to that of TNAP.

The formation of thiazolothiazole through a simple condensation of dithiooxamide (rubeanic acid) with aromatic aldehydes has been investigated extensively by Johnson and co-workers.[40,41] The initial step in this condensation was proposed to involve the nucleophilic attack of nitrogen on the carbonyl group of the aldehyde followed by cyclization to form an intermediate dihydro-thiazolothiazole. Loss of two hydrogens complete the formation of thiazolothiazole (Figure 6).

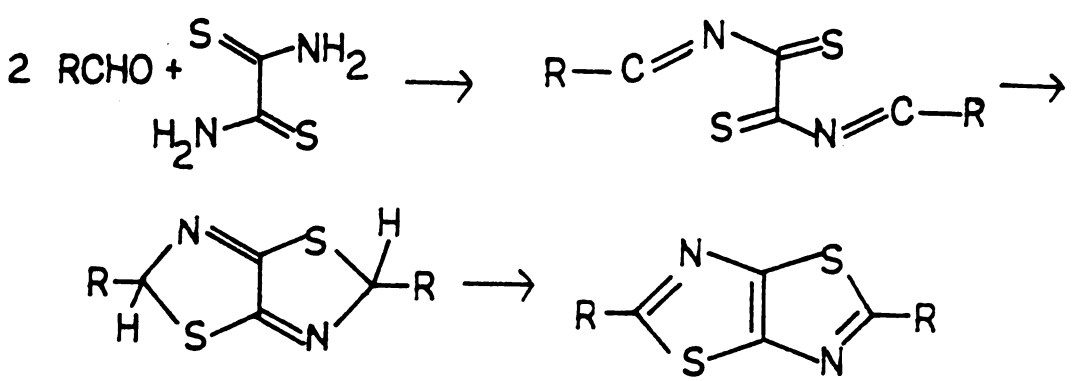


Figure 6. Condensation of dithiooxamide with aldehyde

The nucleophilicity of dithiooxamide illustrated in this mechanism suggested a possible one step synthesis of compound 1, provided the nucleophilicity of nitrogen and sulfur of dithiooxamide was strong enough to displace a leaving group at a sp^2-carbon (Figure 7).

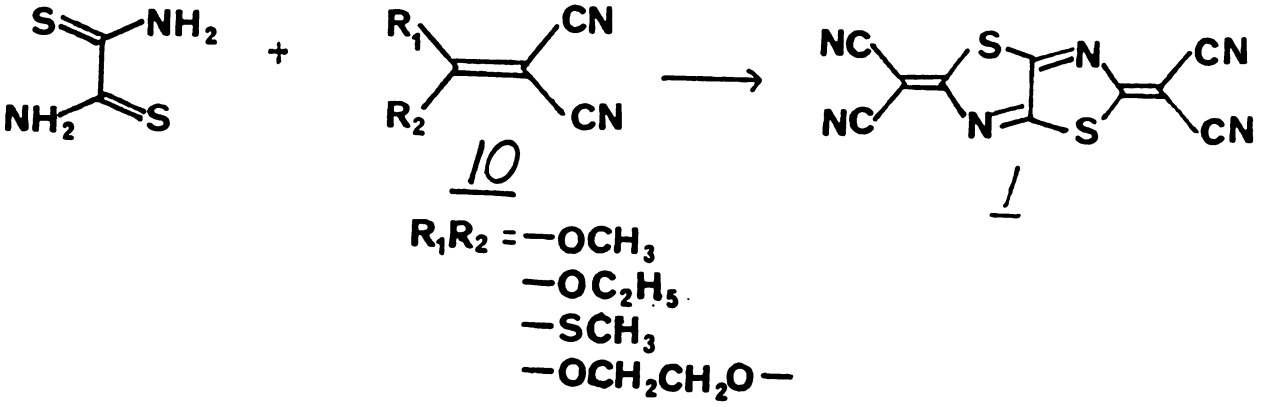


Figure 7. Reaction of dithiooxamide with active dicyano methylene compounds.

We proposed this synthetic possibility because displacement of leaving groups at sp^2-carbon of active methylene compounds by nitrogen, oxygen and sulfur nucleophiles have been well-documented. For example, reaction of [Bis(methylthio)methylene]malononitrile (10, $R_1 = R_2 = -SCH_3$) with ethylenediamine[42], ethanolamine[43], O-phenylenediamine[42], O-aminophenol[44], and 2-aminothiophenol[42] produced the desired products in fairly good yields. Wudl[45] has utilized this approach in his synthesis of tetracyanoquinoquinazolinoquinazoline (TCQQ) (Figure 8).

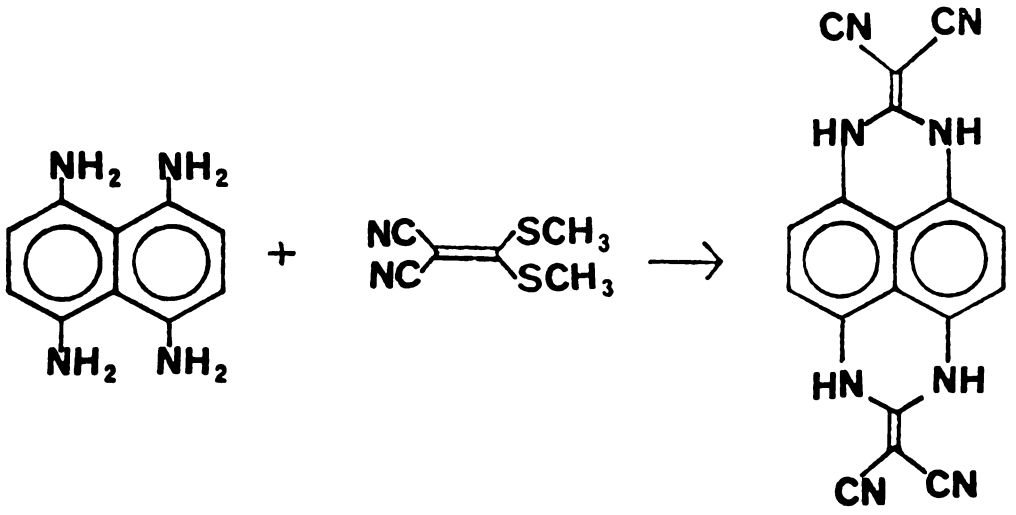


Figure 8. Synthesis of TCQQ.

However, when dithiooxamide was refluxed with 10 (R_1R_2= $-OCH_3$, $-OC_2H_5$, $-SCH_3$ and $-OCH_2CH_2O-$) in a series of different solvents such as ether, tetrahydrofuran, ethanol, butanol and pyridine, 60%-80% of the starting materials were recovered in most cases accompanied by 20%-40% of decomposed and unidentified residues. More drastic reaction condition and longer reaction time only increased the amount of decomposition. Under any circumstances, no trace of desired product was detected.

Failure to condense dithiooxamide with active dicyano methylene compounds prompted us to reconsider a classical but indirect route that had been utilized in the synthesis of TNAP (Figure 9).

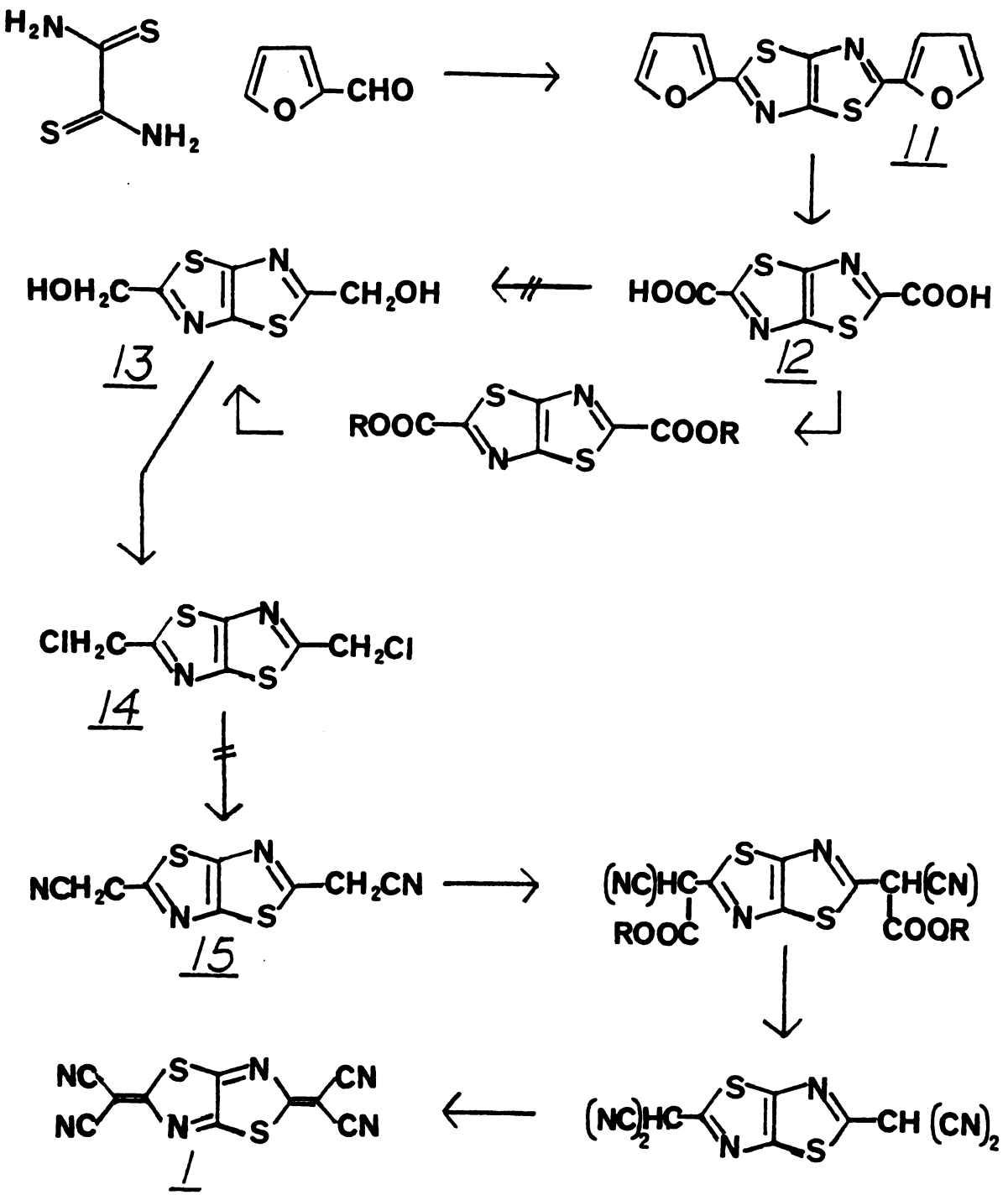


Figure 9. Classical route to tetracyanoquinones.

2,5-Bis(2-furyl)thiazolothiazole 11 was prepared by the condensation of dithiooxamide with furfural[41]. Oxidation with potassium permanganate yield 2,5-thiazolo[5,4-d]-thiazoledicarboxylic acid 12 as white crystals. Reduction of the diacid 12 should yield the diol 13, which through halogenation and substitution by cyanide ion would yield the bis-acetonitrile 15. Carboalkoxylation of 15 followed by hydrolysis, decarboxylation and oxidation would possibly provide the tetracyano compound 1.

Some problem arose when 12 was subjected to reduction with lithium aluminum hydride (LAH). When treated with LAH in THF, the solution of 12 changed color rapidly, indicating a reaction had occured. However, the isolation of the product was unsuccessful. The rationale for this was that nitrogen and sulfur of thiazolothiazole have coordinated with aluminum so strongly that separation of the two was impossible. Lithium triethylborohydride (Super-Hydride) was introduced as an ideal reducing agent in this case since the boron atom was protected by ethyl groups and the possibility of coordination would be greatly reduced. Indeed, the dialkyl ester of 12, when treated with Super-Hydride in THF[46], was reduced cleanly to the diol 13. This diol was converted to the corresponding bis-chloro-methyl thiazolothiazole 14 by simply warming with thionyl chloride. The substitution of chloride by cyanide ion was

carried out by the procedures of Storm[47](KCN, CH_3OH) and Sandman[48](NaCN, alc. dioxane). Neither of them afforded the desired bis-acetonitrile 15. Only starting materials were recovered. Upon surveying the literature, this bis-benzylic type displacement was found to be of only poor yield. In the case of TNAP, the published result in dimethyl sulfoxide is 8%[49]. Changing the solvent to methanol in that case gave 25% of the product. It is possible that the cyanide ion may be acting as a base to deprotonate the product or may just be less reactive under such polar condition. The use of a more soluble reagent tetraethylammonium cyanide as previously reported[50], a rapid darking of the reaction mixture was observed. After usual work-up, a brown, insoluble and high melting solid was obtained, which showed no signal corresponded to the desired bis-acetonitrile 15 in mass spectra. This was presumed to be the result of polymerization. Similar difficulties were also encountered in the attempted introduction of cyano group into thieno[3,2-d]thiophene nucleus[50]. Therefore, this indirect synthesis of 1 was also abandoned.

At this point, we were led to believe that dithiooxamide would react only with aromatic aldehydes.[51] Nevertheless, this easily accessible route toward heterocycles as complex as thiazolothiazole encouraged our

continuing efforts toward the synthesis of molecules possess thiazolothiazole center , with benzoquino substituents at 2,5 positions. For benzoquino type compounds such as chloranil are well-known electron acceptors. Furthermore, a recent article[52] dealing with the synthesis and properties of 2,5-dihydroxyl thieno[3,2-d]thiophenes showed that oxidation of the corresponding dianion led to solutions of stable oxygen radical anions (Figure 10).

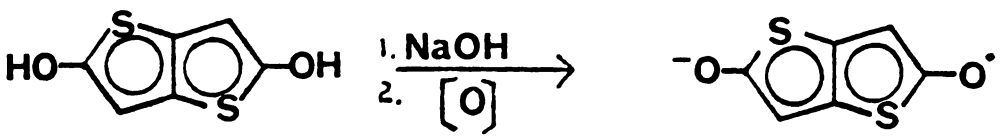


Figure 10. Known stable oxygen radical anion.

With these in mind, we attempted the synthesis of quino 2a (Figure 11). Upon one electron reduction, 2a would convert itself to an oxygen radical 18 with concurrent generation of three aromatic systems, a necessary condition for a good electron acceptor according to Perlstein.[18]

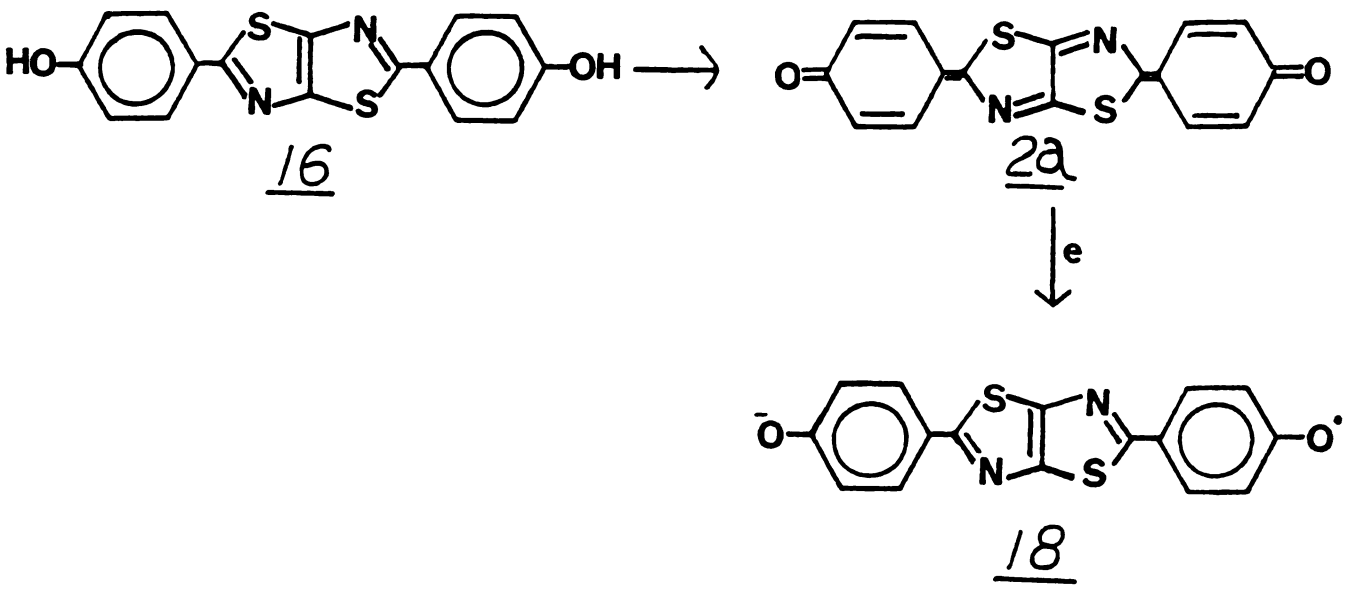


Figure 11. Synthesis of 2,5-Bis(2,5-cyclohexadiene-1-diylidene-4-oxo)thiazolo[5,4-d]thiazole 2a

16 was easily prepared by the method of Johnson[40] as a highly insoluble yellow solid. However, its solubility in basic solvent allowed us to perform the oxidation with $K_3Fe(CN)_6$ in alkaline aqueous solution to afford a deep green microcrystalline solid. Mass spectrum showed a parent peak at 324, an indication of the quinoid 2a. Compound 2a was found to be in equilibrium with 16. In the absence of excess oxidizing agent, the peak at m/e 326 (16) in mass spectrum increased its intensity with time until the equilibrium was reached. Heat favors the phenol form 16. The reaction mixture discolored rapidly when external heat was applied. We explained this discoloration as the result of re-aromatization and the consequent rotation

of the benzene rings with respect to the plane of thiazolothiazole. If 16 could be oxidized in the presence of a suitable electron donor, the direct complexation of 2a with the donor might be realized. If the rotation of the benzene ring was somewhat hindered, the quinoid form should have higher stability. To justify this hypothesis, 2,5-Bis(3,5-di-tert-butyl-4-hydroxylphenyl)thiazolo[5,4-d]-thiazole[53], 19, and 2,5-Bis(2-hydorxynaphthyl)thiazolo-[5,4-d]thiazole, 20, were prepared.[54]

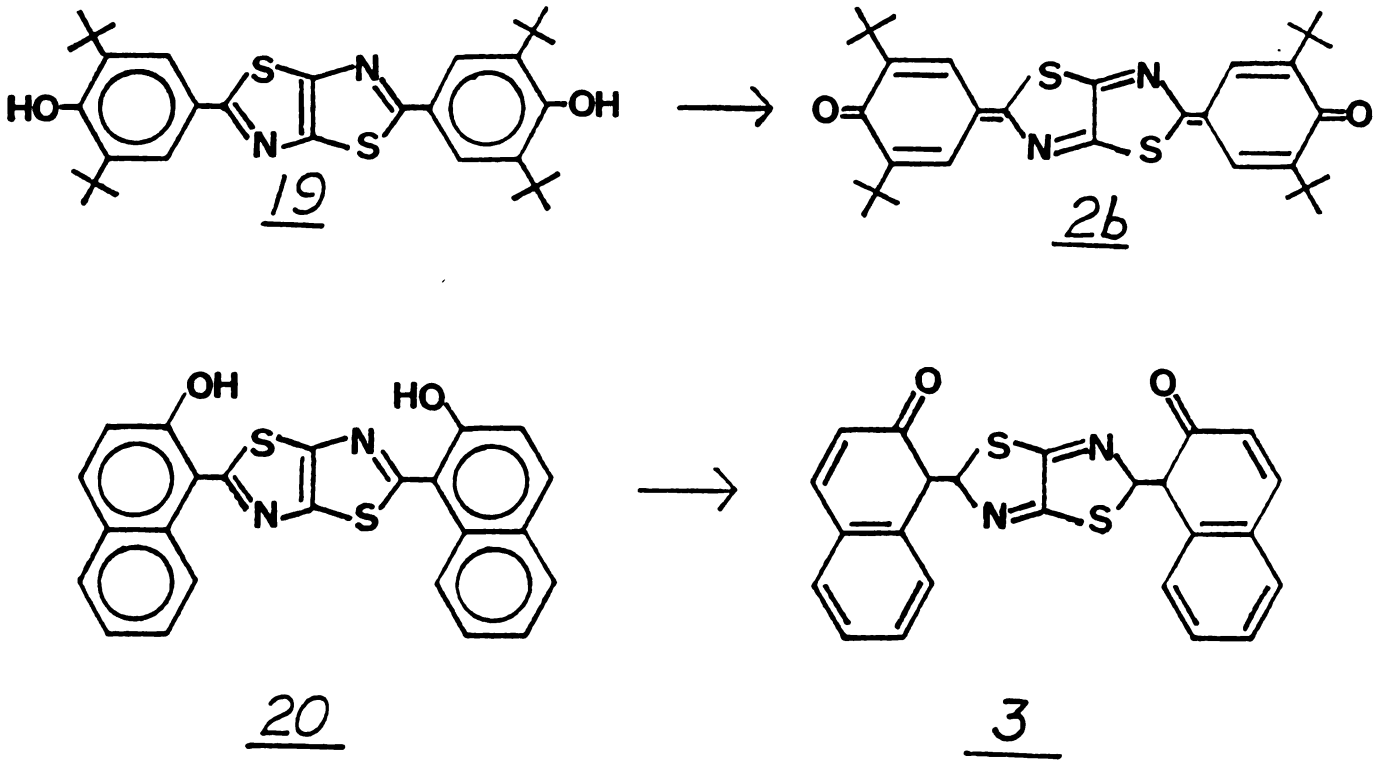


Figure 12. Preparation of compound 2b and 3.

Oxidation of 19 was carried out with lead peroxide in methylene chloride to give 2b in 60% yield. Quinoid 2b exhibits a strong absorption in visible spectra ($\lambda_{max.}$: 600 nm, ϵ: 300,000), an indication of the long conjugation (Figure 12).

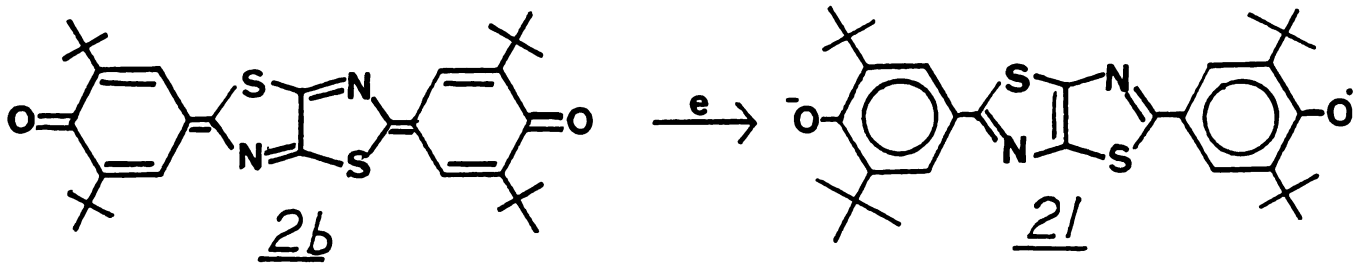
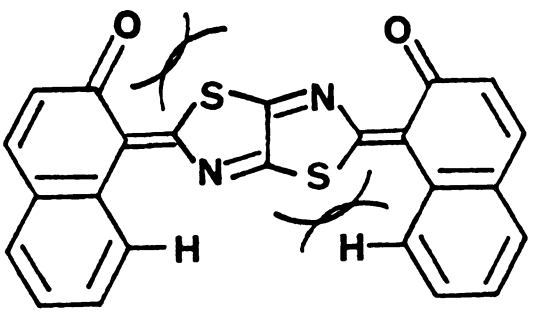


Figure 13. Radical anion of 2b

The oxidation of 20 was similarly done with lead peroxide in benzene to yield a green compound 3 with $\lambda_{max.}$ at 680 nm in visible spectrum. Solution of 3, in the absence of PbO_2, lost its color presumably due to reductive aromatization. The interaction between the d-orbitals of sulfur and the carbonyl group or C-8 proton of naphthalene might contribute to the distortion of the supposed planar molecule 3.



Some efforts have been given to construct a TTF analog with thiazolothiazole core (Figure 14). If the diol 13 were to be oxidized to di-aldehyde, 22, condensation with 1,2-ethanedithio would give the corresponding bis-dithioacetal. Oxidation with DDQ would produce the TTF analog 23.
The oxidation of 13 was carried out in methylene chloride with MnO_2. Mass spectroscopic analysis indicated the major component in the reaction mixture to be mono-oxidation product. No di-aldehyde 22 was detected even with large excess of MnO_2.

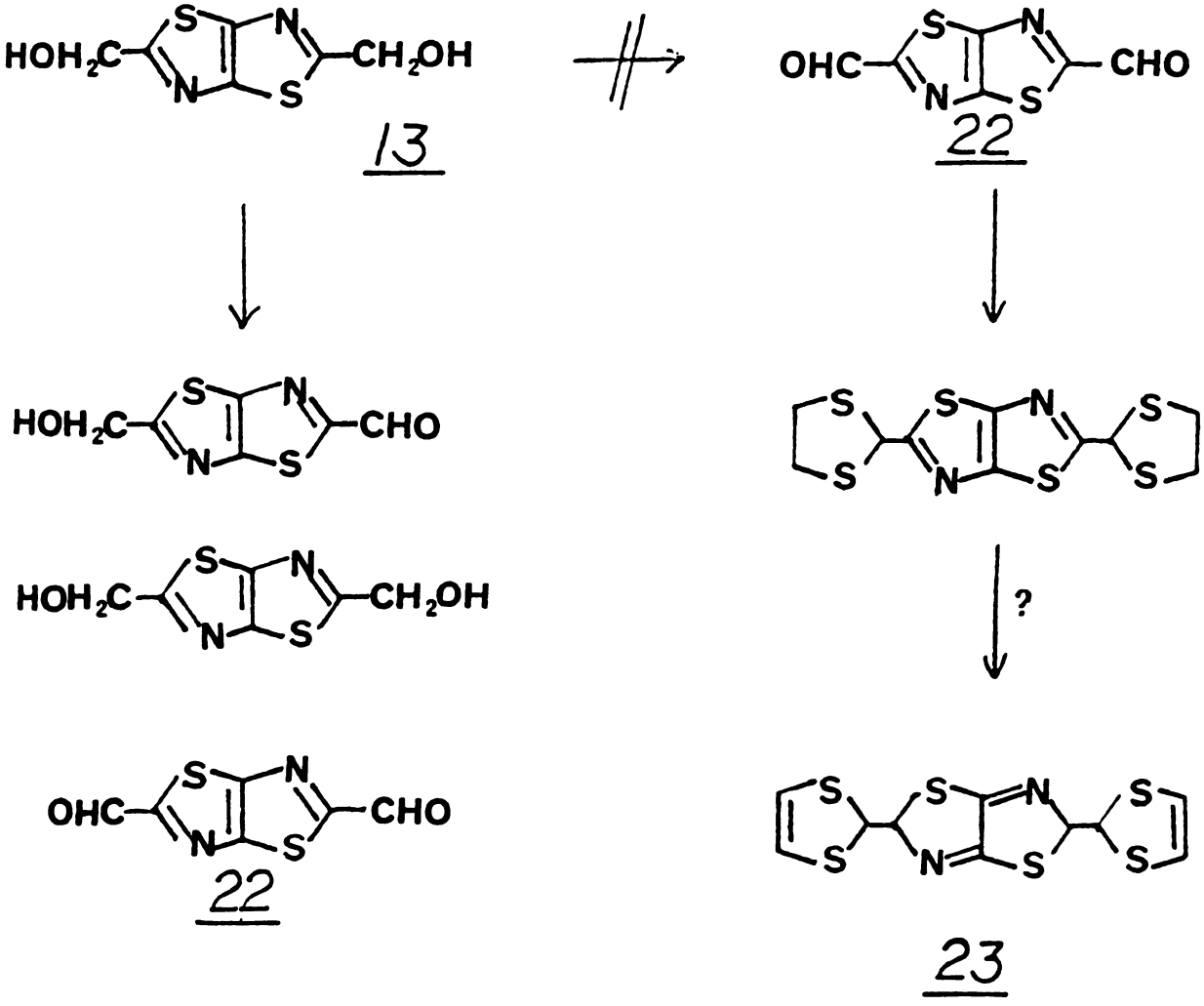


Figure 14. Thiazolothiazole-TTF.

B. Synthesis of Thiazolo[5,4-d]thiazole dicationic salts.

1. METHYLATION OF NITROGENS

There are two main methods in the synthesis of radical cations. The majority of ion-radical salts was obtained by direct interaction of the neutral donor and acceptor in solution. Another general method for preparing highly conductive ion-radical salts involves the reduction of dicationic salts of the donors. The synthesis of thiazolothiazole derivatives with double positive charges, therefore, would be interesting as a potential cation radical precursor. In the literature, the only thiazolothiazole derivative with two positive charges was the 2,5-Bis(N,N'-dimethyl-4-pyridyl)thiazolothiazole reported by Schimamura and co-workers[55]. (Figure 15).

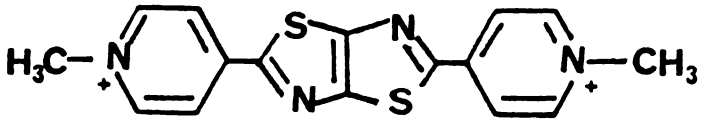


Figure 15. 2,5-Bis(N,N'-dimethyl-4-pyridyl)thiazolo-[5,4-d]thiazol .

We attempted to methylate the nitrogen on the parent rings of thiazolothiazole (Figure 16).

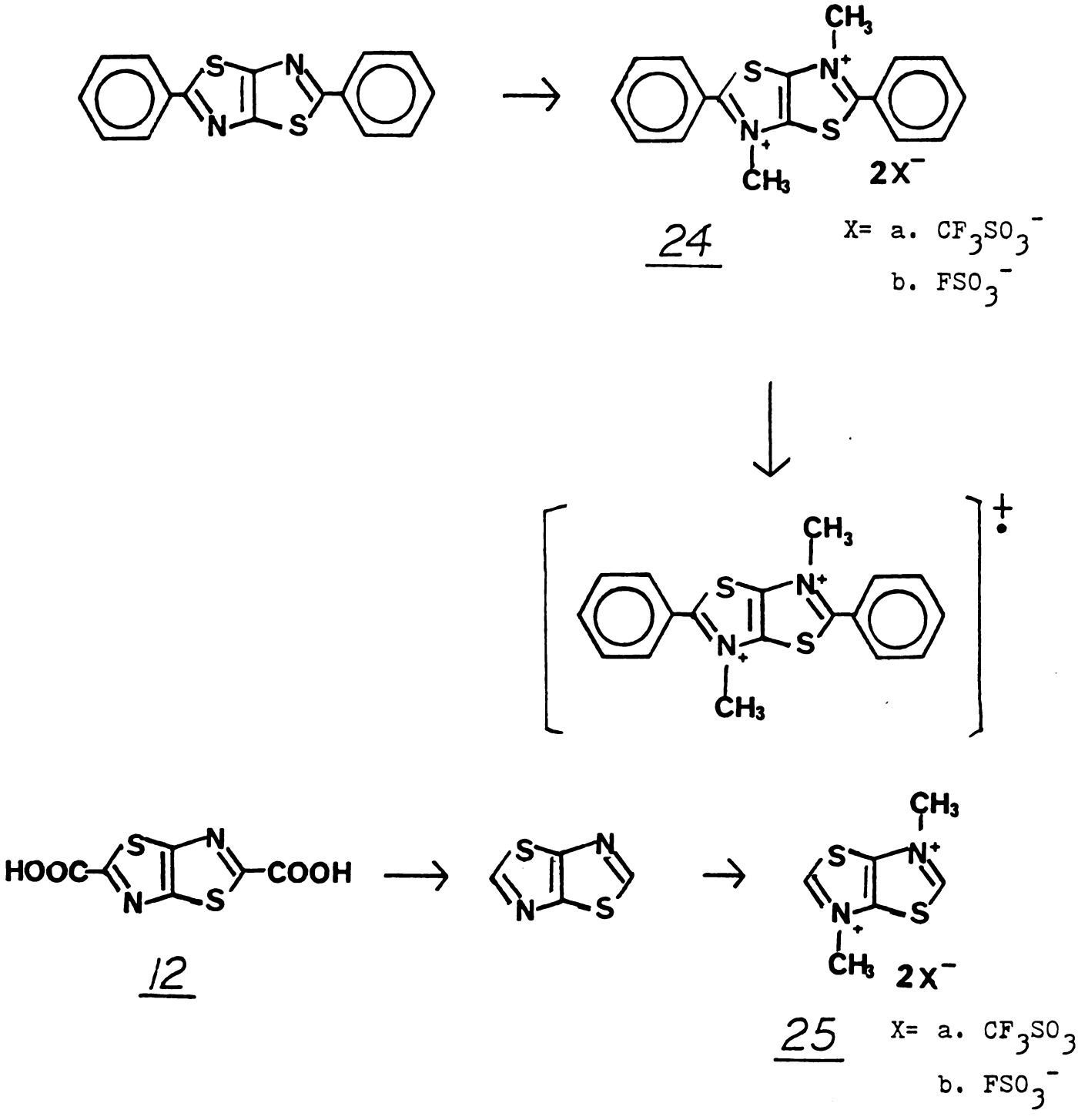
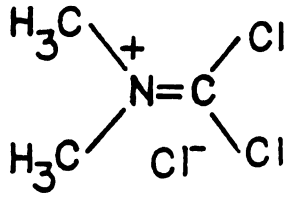


Figure 16. Methylation of thiazolothiazole heterocycles

A mixture of 2,5-diphenylthiazolothiazole and methyl-fluorosulfonate or methyl trifluoromethanesulfonate in a sealed tube was warmed by a steam bath to give 24a or 24b respectively. Compounds 25a and 25b were similarly prepared. 24a and 24b are stable for an indifinite period of time while 25a and 25b decomposed in contact with air. Treatment of an acetonitrile solution of 24a with a solution of $Li^{+}TCNQ^{-}$ indicated no apparent formation of complex. Simple metal reduction of 24 with Mg or Zn resulted only in the recovery of the starting materials. No evidence was found to suggest the formation of radical mono-cation.

2. REACTION OF DITHIOOXAMIDE WITH PHOSGENE IMMONIUM CHLORIDE

The chemistry of phosgene immonium chloride has been investigated extensively by Viehe[56]. Owing to its greater double bond polarization the immonium salt dichloromethylene-dimethylammonium chloride (phosgene immonium chloride) 26 should be more reactive than phosgen 27 and methylchloro-formimidoyl chloride 28 in nucleophilic chloride substitution.



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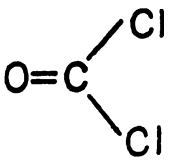

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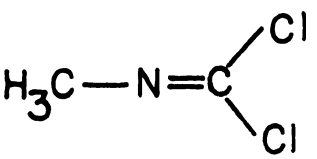

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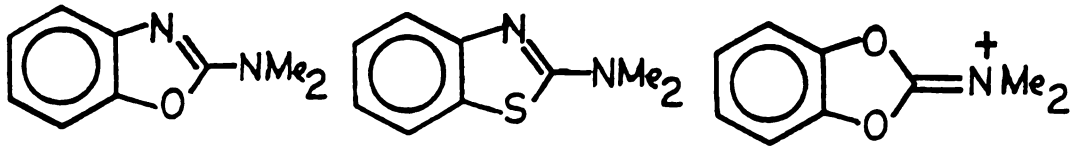
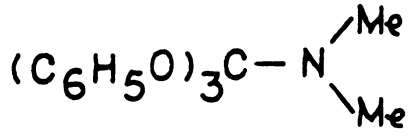
By reaction of phosgene immonium chloride 26 with O-aminophenol, O-aminothiophenol and O-dihydroxylbenzene, compounds 29, 30 and 31 were obtained respectively.



29 30 31

It was reported that when there were more than one acidic proton on either nucleophilic site, loss of the third molecule of HCl was observed. In fact, in the cases of O-aminophenol and O-aminothiophenol, 29 and 30 were the only products isolated. Although the reactions were monitored carefully by NMR spectroscopy until formation of the heterocycles were complete, no intermediate chloride salts has ever been detected. While phosgene immonium chloride was treated with phenol, the product we isolated was 32 according to the NMR analysis.



32

For our purpose of making doubly charged molecules, we needed to have the immonium chloride intact. However, when we went ahead and reacted phosgene immonium chloride with dithiooxamide we found only the recovered starting materials.

II. BENZO[1,2-d:4,5-d']DIIMIDAZOLE

As part of their continuing efforts in synthesizing TCNQ analogs, Wudl has reported[35] the preparation of 2,7-bisdicyanoquinomethano-2,7,H,H-quinazolino[6,5,4-def]-quinazoline (TCQQ) and its electrochemical behavior. We decided to carry out the same type of reaction by using 1,2,4,5-tetraaminobenzene (Figure 17), for the projected synthesis of compound 34 appeared to be straightforward.

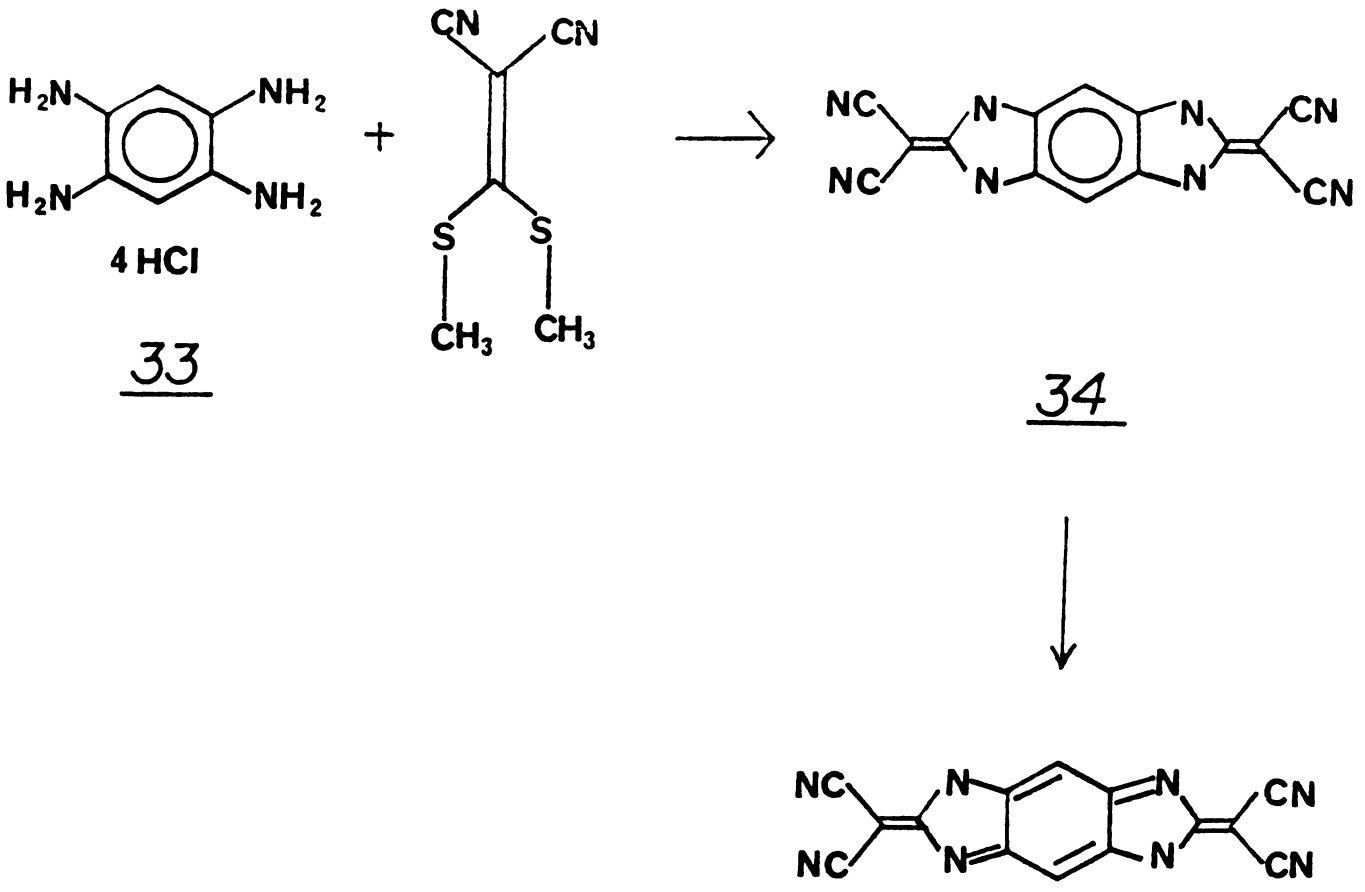
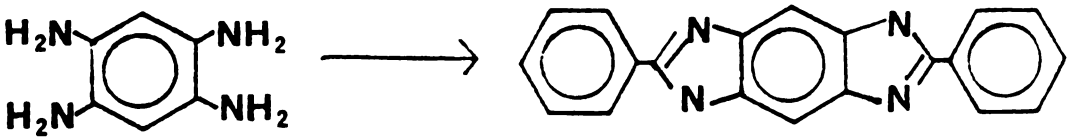


Figure 17. Projected synthesis of compound 34

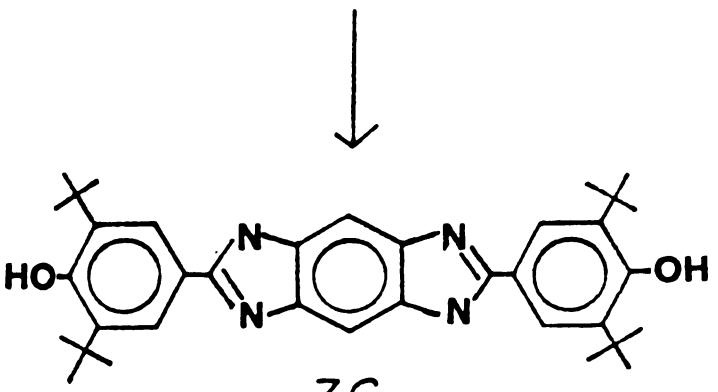
Treatment of 1,2,4,5-tetraaminobenzene tetrahydrochloride 33 with bisdithiomethyl dicyanoethylene in refluxing ethanol recovered only the starting materials. We contended that the protonated amines were not strong enough nucleophile to bring about the direct displacement. On the other hand, however, reaction of 33 with benzaldehyde or 3,5-di-t-butyl-4-hydroxylbenzaldehyde went smoothly to produce the desired products 35 and 36 in fair yields.



4 HCl

33

35



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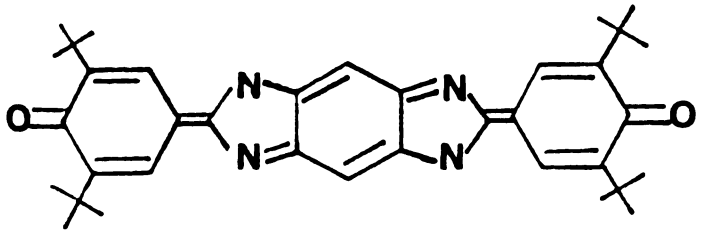
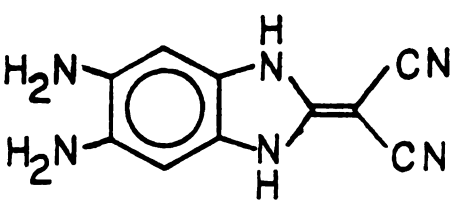


4

These two reactions are in direct support of our earlier observations that the formation of aromatic-stabilized imines (Figure 6) is the decisive factor for the reaction to proceed. That even the less reactive hydrochloride salt reacted quite nicely. Oxidation of 36 with lead peroxide in dimethyl sulfoxide gave a green solution ($\lambda_{max.}$ 750 nm), which seemed to contain quinoid 4. However, green color faded away rapidly without the presence of excess oxidizing agent. Further characterization were fruitless.

A search in the literature revealed that the liberation of 1,2,4,5-tetraaminobenzene from tetrahydrochloride could be achieved by treatment with an ice-cold sodium hydroxide solution. When this procedure was followed and the resulting free amine protected under nitrogen, bis-dithiomethyl dicyanoethylene was added and refluxed in ethanol. An air sensitive product was isolated, which darkening slowly on the shelf but decomposed rapidly in solution. Spectroscopic analysis characterized this compound as 38.

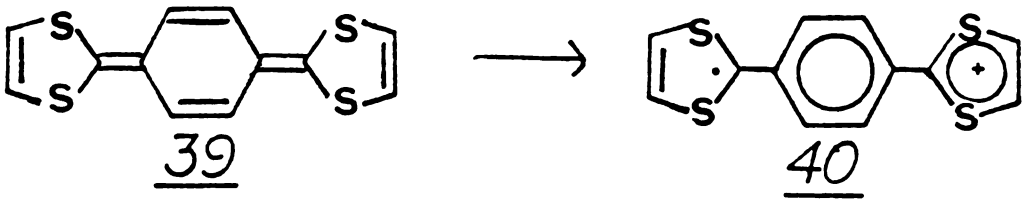


38

Variation in reaction conditions has been attempted, but the tetra-functional benzene reacted only on one side of the molecule. Possibly due to the electron-withdrawing power of the cyano groups that deactivated the nucleophilicity of the amino groups on the opposite side.

III. SYNTHESIS OF 2,2'-(2,6-NAPHTHALENE-DIYLIDENE)BIS(1,3-DITHIOLE)

The overlap of π-orbitals in a segregated stack of radical ions was believed to be the major factor governing the conducting behavior of the charge-transfer salt. Therefore, the unknown heterocycle 39 presents particularly interesting structural feature, since it combined in one molecule the p-quinodimethane of TCNQ with two 1,3-dithiolidine moieties of TTF, and has more conjugated structure than TTF. By releasing one electron, TTQ molecule would restore two aromatic sextets. The incentive for TTQ to donate electron, in terms of gaining aromaticity, should be strong.

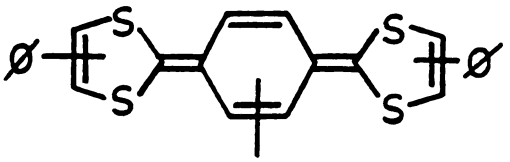


39 → 40

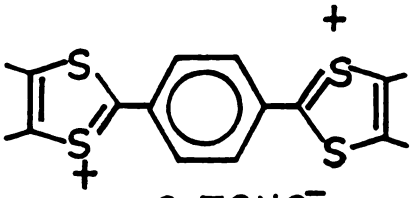
TTQ

(Tetrathioquinodimethane)

Only one patent article in the literature described the structure of TTQ[58]. However, no identification, preparation, as well as physical and chemical properties were given. Ueno[59] and co-workers first reported the synthesis of the diphenyl derivative of TTQ. They found the compound was able to form complex with iodine, 41.

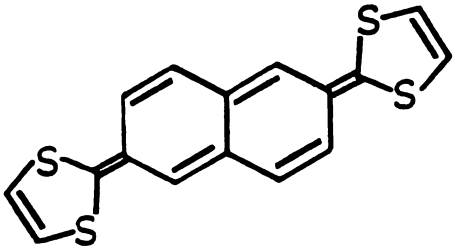


In 41



2 TCNQ⁻

Fabre[60] later revealed the structure of tetramethyl-TTQ:TCNQ complex, 42. We decided to extend the conjugation of TTQ to that of naphthalene, 43. The relationship between



2,2'-(2,6-Naphthalenediylidene)bis(1,3-dithiole), [Tetrathionaphtho-2,6-quinodimethane (TTNQ)], 43.

the conjugated system of TTF and TTNQ should be expected to be similar to that between tetracyanoethylene (TCNE) and TNAP, although the former two compounds are donors and the latter are acceptors.

2,6-Bis(bromomethyl)naphthalene was prepared according to the method of Diekmann[49]. Hitherto, the unknown tetrathio-2,6-naphthalic acid 44 was successfully synthesized by the application of the methods of Ueno[59] and Becke[61], isolated as dipiperidinium salt 44b in 58% yield, mp 154-156°; IR: 1000 cm^{-1} (CSS^-). The free tetrathio-2,6-naphthalic acid, from acidification of 44a, was unstable. It decomposed in the air to give a brown, unidentified solid.

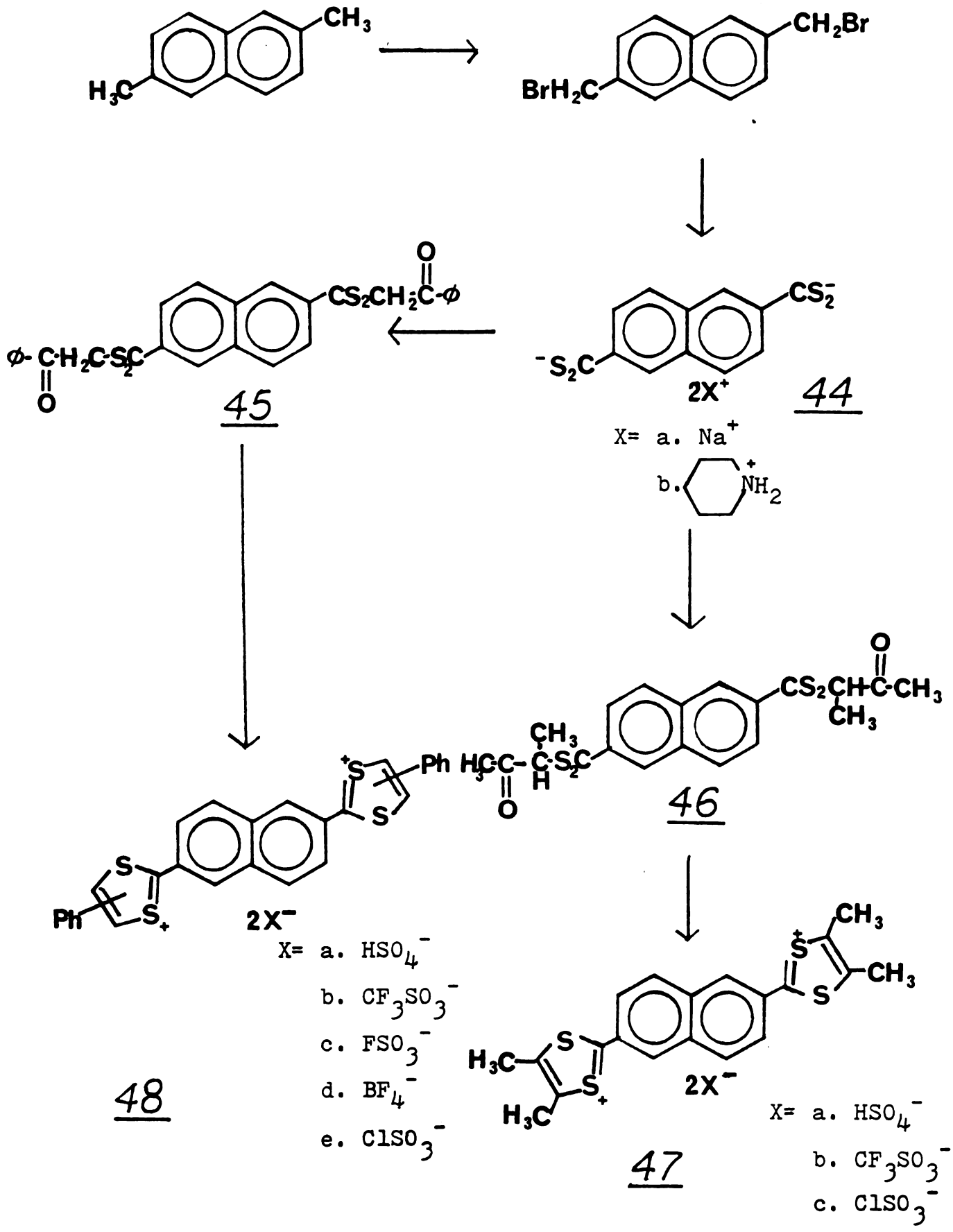


Figure 18. Synthesis of TTNQ derivatives

Diphenacyl ester 45 and dibutanone ester 46 were easily prepared in 87.2% and 30% yields by the reaction of salt 44b with phenacyl bromide and chlorobutanone respectively.

The cyclization reactions were simply carried out by dissolving the ester 45 or 46 in cold concentrated sulfuric acid, fluorosulfonic acid, trifluoromethane sulfonic acid or chlorosulfonic acid. The corresponding salts were isolated as orange or yellowish orange solid by diluting the reaction mixture with ethyl acetate.

The structure of 47 and 48 were substantiated by spectral data. The absence of C=O and C=S bands in the IR spectra indicates the dehydrative cyclization is complete at both β-ketodithioester functions. The NMR spectrum of 48 has, in addition to the central aromatic protons (6H) at δ 8.2-8.4 ppm, a singlet of 1,3-dithiolium ring protons (2H) at δ 8.8 ppm. And the spectrum of 47 has 12 allylic protons at δ 2.8 ppm plus 6 aromatic protons at around 7.6 ppm. Appearance of the above signals at considerable down-field indicates the highly electron deficient cationic structure of 47 and 48. The fluoroborate salts were prepared by refluxing the corresponding dithioester with phosporus pentasulfide, fluoroboric acid in acetic acid[62] . Elemental analysis indicates that 48b existed as a monohydrate whereas 47a complexed with one molecule of sulfuric acid.

Treatment of 48 with sodium methoxide in methanol yielded 49 in 72% yield (Figure 19). The 1,3-dithiol ring protons of 49 appeared at δ 6.4 ppm, a 2.4 ppm up-field shift from 48. Under the same reaction condition,

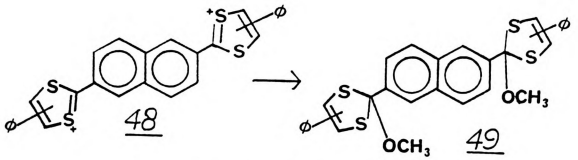


Figure 19. Reaction of 48 with sodium methoxide

47 gave 50 in almost quantitative yield (Figure 20).

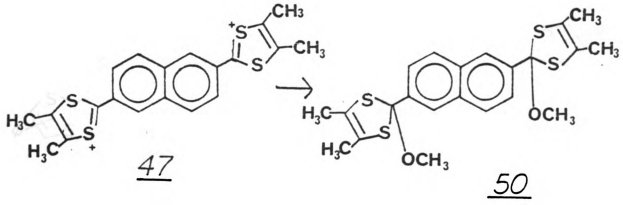


Figure 20. Reaction of 47 with sodium methoxide

The drastic up-field shift observed in going from 48 to 49 has a precedent in the chemical shift change recorded in diphenyl-TTQ system (Figure 21).

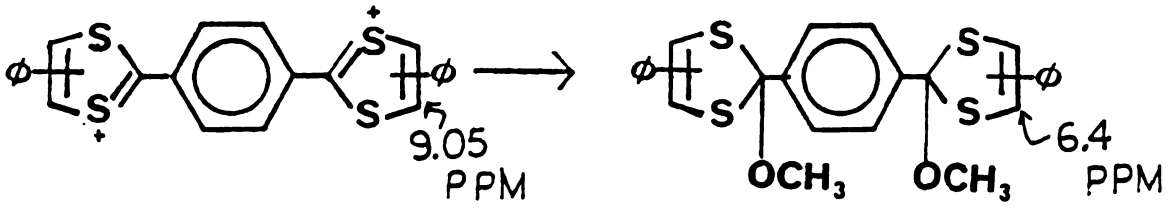


Figure 21. Chemical shift change from dicationic salt to dimethoxy derivative.

The reduction of dication 48 with lithium iodide or tetrabutylammonium iodide proceeded cleanly to give the black microcrystals of iodine complex 51 in 80% yield (Figure 22). A bathochromic shift of 210 nm was observed in the visible spectra of 51. This shows clearly the highly conjugated structure of 51 instead of the simple dicationic structure like 52. The formation of 51 might be best

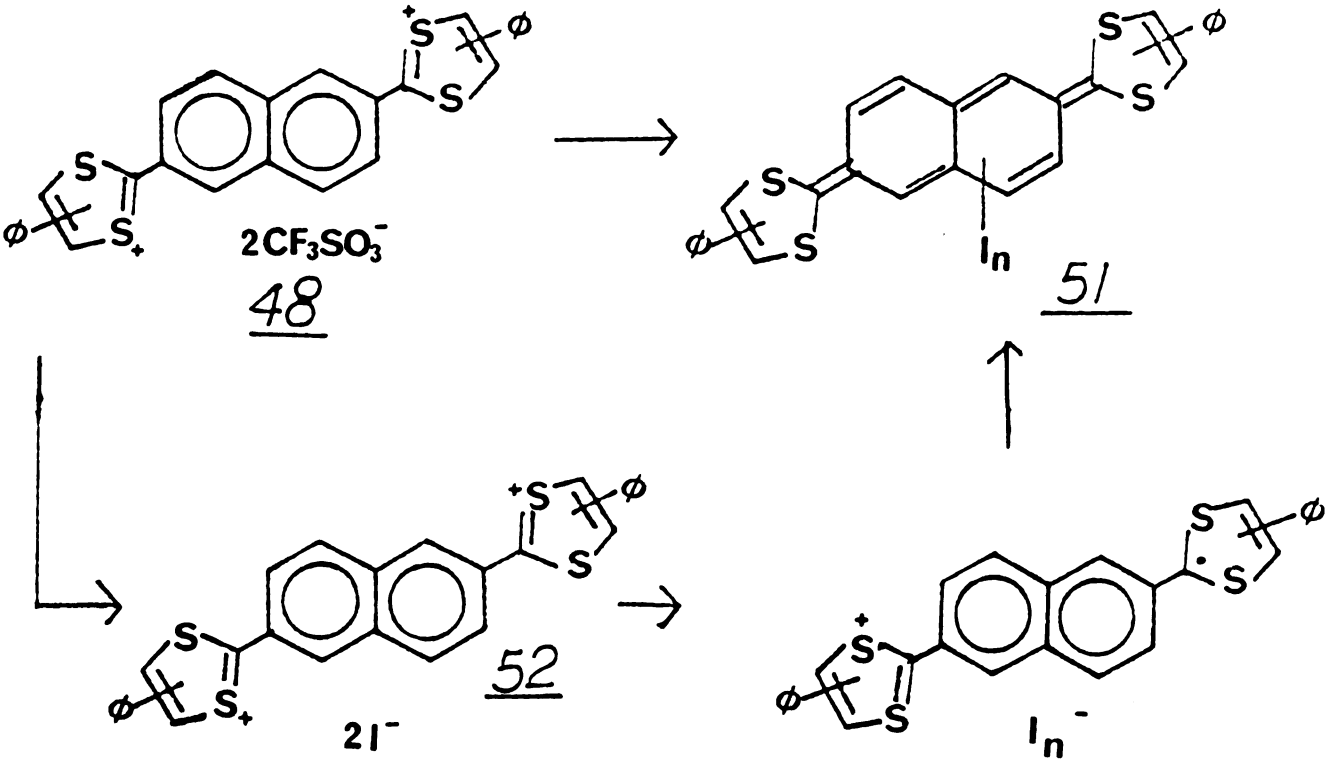
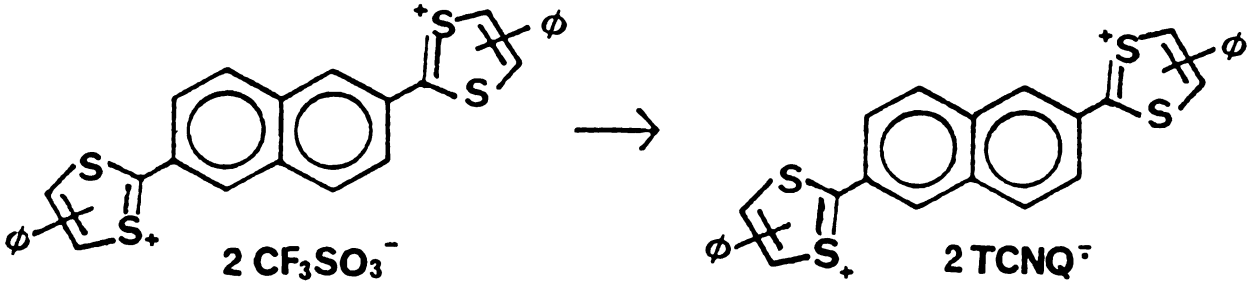


Figure 22. Iodine complex of Diphenyl-TTNQ

explained by the electron transfer[63] from iodide anion to the dication and further aggregation of iodine moiety. The ratio of the diphenyl derivative of TTNQ and iodine moiety in 51 was estimated to be 25:49 (n=1.96) by the elemental analysis.[64] The starting material 48 was recovered from complex 51 by treating with excess concentrated acid.

To form a complex of diphenyl-TTNQ with TCNQ, 48b was treated with Li^+TCNQ^- in acetonitrile[60], to give, after stirring overnight, a dark green solution which displayed strong TCNQ° plus $TCNQ^-$ absorption in UV spectra (Figure 23). It was known that when TTF formed



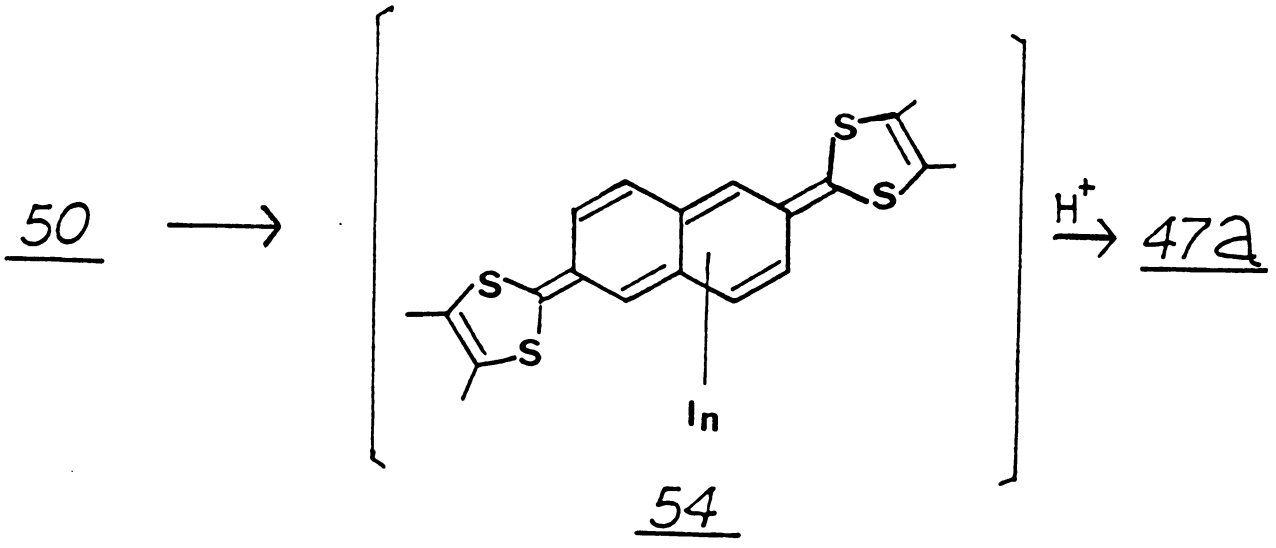
48b 53

Figure 23. Complex of 48b with Li^+TCNQ^-

simple charge-transfer complex with TCNQ, no absorption due to neutral TCNQ was observed.[9] Therefore, the presence of the neutral TCNQ in 53 represents the possibility of the formation of a mix-valence complex $(TCNQ)^+(TCNQ)°(TCNQ)^-$; since example of oxidation-reduction between donor and

acceptor with concomitant formation of the complex salt has been reported.[6] Or possibly it was simply the result of the incomplete redox reaction between 48b and $TCNQ^-$. More information is needed before a conclusion can be reached. An ideal situation would be to crystallize the complex 53. However, a suitable solvent has yet to be found.

Attempts have been made to prepare the iodine complex of 47 by treatment of 47 in acetonitrile with tetrabutylammonium iodide. The reaction mixture turned slightly darker, but no formation of any complex was realized. Therefore, an indirect route of complex formation was approached. A solution of dimethoxy derivative 50 was treated with aqueous HI solution followed by dilution with ethyl acetate to give a black-brown solid, presumably 54 (Figure 24). The salt 47a could be re-generated by treating 54 with concentrated sulfuric acid. Further characterization

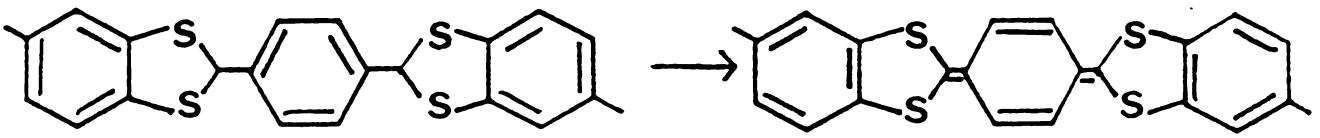


54

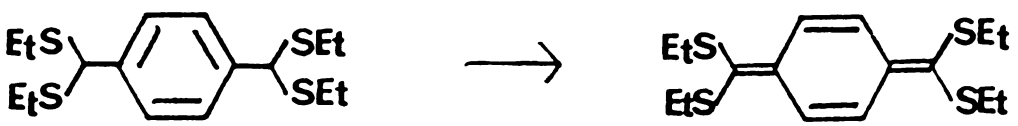
Figure 24. Iodine complex of Tetramethyl-TTNQ

were, however, unsuccessful.

Ueno and coworkers[66] have reported the preparation of cyclohexa-2,5-diene-1,4-diylidene-bis-1,3-benzodithiole (CBDT) 55 and tetraethylthioquinodimethane 56 through the oxidation of corresponding bis-dithioacetals (Figure 25).



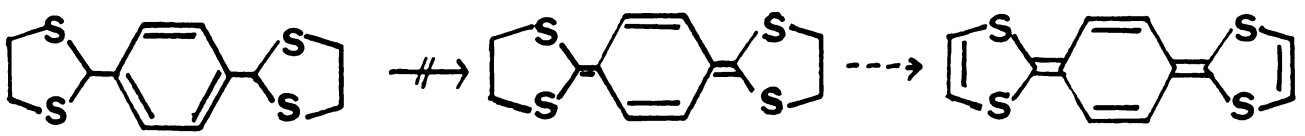
55



56

Figure 25. Syntheses of TTF analogs 55 and 56.

If this reaction were applicable to bis-1,2-dithioethane acetal of terephthaldehyde 57, the successful synthesis of 39 (TTQ) would be one step closer (Figure 26).



57 39

Figure 26. Proposed synthesis of TTQ

Unfortunately, treatment of 57 with DDQ under several different reaction conditions resulted in only extensive darking with no trace of the product was detected. The dark material obtained might be the complex of 39 with DDQ.

counter ion	48		47	
	mp	yield	mp	yield
HSO_4^-	246-249 (d)	85%	>350	72.5%
$CF_3SO_3^-$	227-230 (d)	95%	313-314 (d)	61.5%
FSO_3^-	256-257 (d)	90%	---	---
BF_4^-	249-252 (d)	86.2%	---	---
$ClSO_3^-$	268-270 (d)	73%	>320	37.5%

Table 3. Melting points and yields of TTNQ derivatives

IV. PREPARATION OF 7,8-DICYANO-7,8-DINITROQUINODIMETHAN AND 11,12-DICYANO-11,12-DINITRONAPHTHO-2,6-QUINODIMETHAN

At room temperature, TCNQ and TNAP form the two best conducting complexes with TTF. Both theory and experiment suggest that in TCNQ and TNAP the odd electron resides to a large extent on the terminal portions of the molecule containing the four electron attracting nitrile groups. The replacement of nitrile group by nitro group was of special interest to us since nitro groups are stronger electron-withdrawing groups and therefore might better stabilize the resulting radical anion, provided the nitro groups stay in the plane of the aromatic ring. On the other hand, the planarity requirement is not very stringent. The intermolecular interaction of compounds in the conducting stack of charge-transfer complex is realized through interaction of molecular π-orbitals formed by wave function of unpaired electrons. Despite the directional character of the π-orbitals, they are delocalized and belong, to a certain extent, to the entire (20-30 Å) organic molecule. This is one of the reason why deviations from planarity are permissible. Thus, fulvalene rings in the TTF molecule are slightly distorted, deviating from planarity by 2° [67,68]; the cyano groups in TCNQ are also arranged slightly out of the ring plane.[69] Small substituents in TTF and TCNQ do not destroy the metallic state in the corresponding

complexes.[69] For example, at room temperature, HMTTF:TCNQ (Table 1, Entry 3) has the same conductivity as TTF:TCNQ whereas the conductivity of HMTSeF:TCNQ (Table 1, Entry 8) is three times higher than that of its parent compound's (Table 1, Entry 10).

The first synthetic approach to 58 made use of the classical route utilized in the synthesis of TCNQ[8] (Figure 27). Surprisingly, the attempted condensation of 1,4-cyclohexanedione with nitroacetonitrile has failed, due

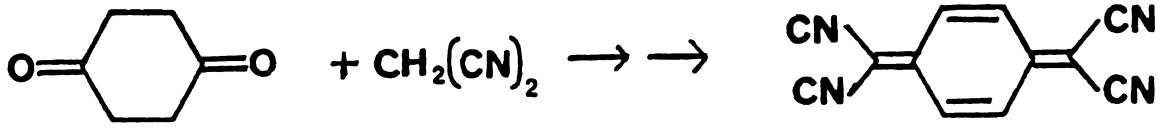


Figure 27. Classical route to TCNQ

mostly to the instability of nitroacetonitrile, which was generated in situ by the dehydration of methazoic acid.[70,71] A search in the literature revealed that the condensation of nitroacetonitrile with some similar systems e.g., 2,6-dimethyl-γ-pyrone and 2,6-dimethyl-γ-thiapyrone have been reported[71], but only in very low yields (8.5% and 4% respectively). The failure of this bifunctional condensation prompted us to consider a stepwise introduction of cyano and nitro groups (Figure 28). The reaction of an alkyl nitrate with an active methylene compound in the

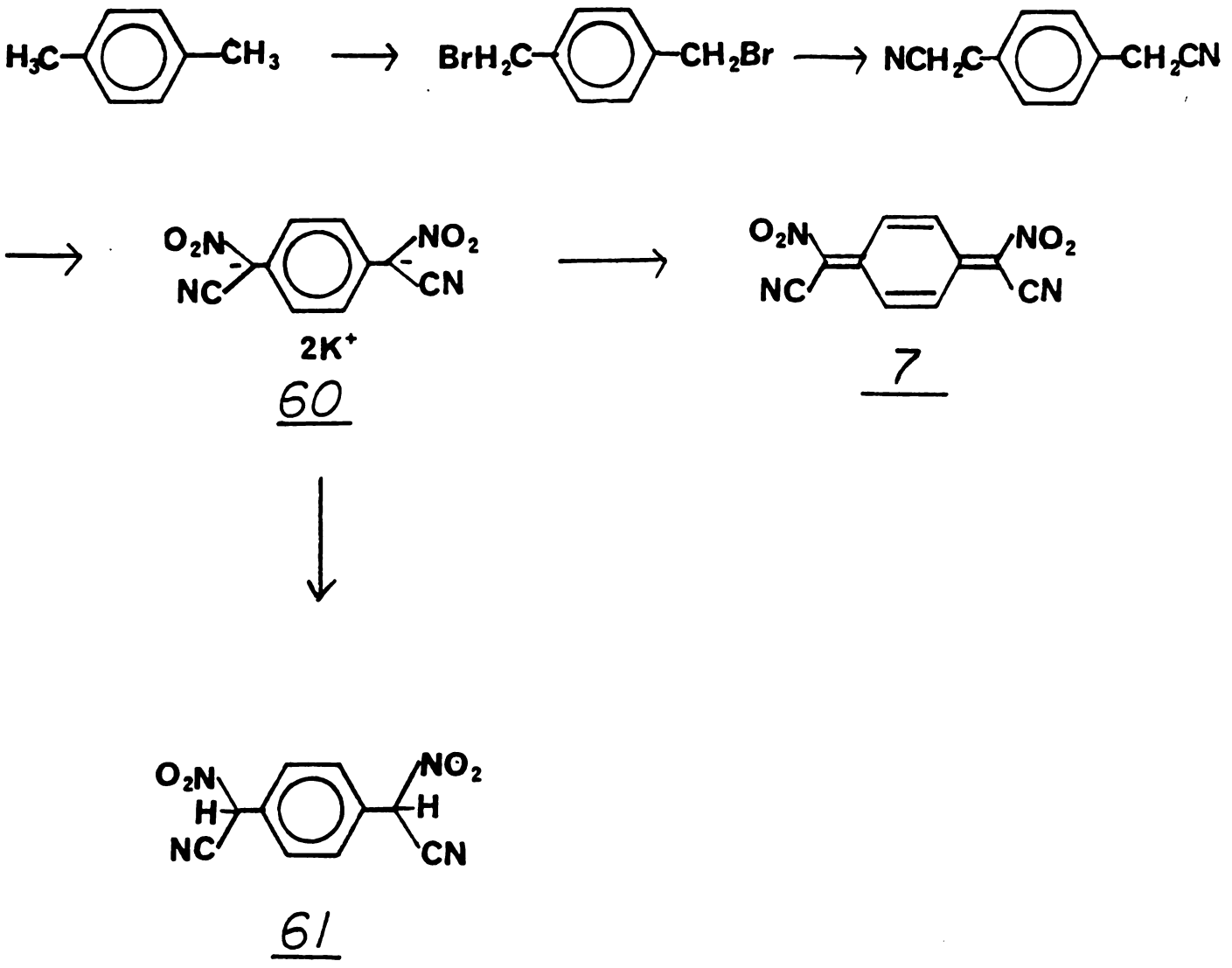


Figure 28. Projected synthesis of TCNQ analog 7

presence of an alkali metal alkoxide to give the salt of a nitro compound with the nitro group attached to the active methylene group have been known for many years. The reaction is generally applicable for aryl acetonitrile,[72] aryl acetic ester[72], fluorene[73], cyclic ketones[74,75], aliphatic nitriles and ketones[76]. However, no application

of this reaction to p-bis(cyanomethyl)benzene or 2,6-bis-(cyanomethyl)-naphthalene has been reported. By following the procedure of Feuer and Savide[76], p-bis(cyanomethyl)-benzene was treated with potassium alkoxide at -78° followed by the addition of amyl nitrate. The dipotassium salt of p-bis(cyanonitromethyl)benzene 60 was isolated as a stable yellow solid in ~95% yield. A strong IR absorption at 1250 cm^{-1} ($-NO_2^-$) and the absence of the NO_2 absorption (1560 cm^{-1}) indicate that the negative charge resides mainly on the oxygen of the nitro group.

In considering the most probable reaction path for the nitration as illustrated below (Figure 29), it would be expected that the presence of a strong base would be extremely important, for it favors the formation of the

$$R\text{-}CH_2CN + RO^- \rightleftharpoons [RCHCN]^- + ROH \qquad (1)$$

$$[RCHCN]^- + R'ONO_2 \longrightarrow R(CN)H\text{-}C(-O^-)\text{-}N(=O)\text{-}OR'$$

$$\longrightarrow RCH(CN)NO_2 + R'O^- \qquad (2)$$

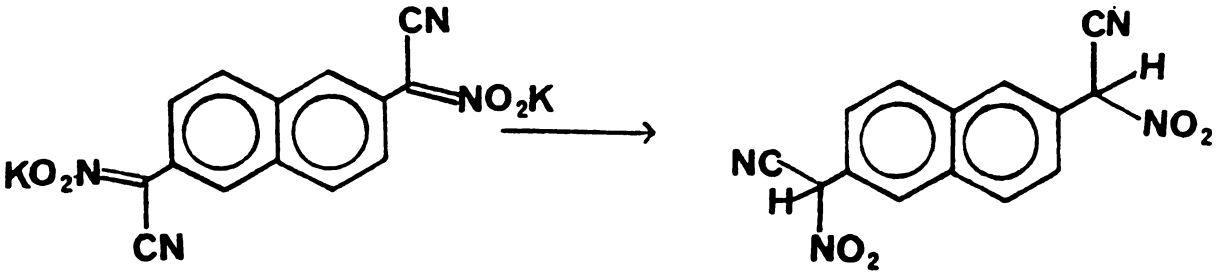
$$RCH(CN)NO_2 + R'O^- \longrightarrow [RC(CN)=NO_2]^- + R'OH$$

Figure 29. Nitration of active methylene compound

carbanion of the active methylene compound (step 1). On the other hand, it has been pointed out that alkyl nitrates undergo several reactions with strong alkaline reagents.[77,78] This becomes especially important in di-nitration reactions. If it is assumed that the nitration of compounds possessing two active methylene groups occurs stepwise. The presence of excess base required for the formation of the carbanion of the second methylene group would enhance the decomposition of the alkyl nitrate. Fortunately, for our purposes, both potassium t-butoxide and potassium ethoxide worked equally well. Amyl nitrate was found to be a satisfactory nitrating agent and was used throughout.

Upon consideration of step 1, it is suspected that the presence of hydroxylic solvents would not favor the formation of the carbanion of active methylene compounds. However, in nitration of p-bis(cyanomethyl)benzene with potassium ethoxide, we have used as much as ten times excess of ethyl alcohol but did not suffer any loss in yield.

Under identical reaction condition, the dipotassium salt of 2,6-bis(cyanonitromethyl)naphthalene 63 was synthesized in almost quantitative yield as a yellow plates with metallic shining. 63 exhibits the same characteristic NO_2^- absorption in IR spectra.



63 64

Figure 30. Acidification of dipotassium salt 63

Conversion of the salts 60 and 63 to the corresponding neutral cyanonitro compounds was not satisfactory, since only intractable solid were obtained after acidification. This was in accord with the observations made by Feuer and Savides[76] that most free α,α'-dinitrodinitriles were unstable at room temperature. We found that the protons on C-7 and C-8 of 61 are more acidic than acetic acid. These highly acidic protons might protonate the nitrile groups which were then attacked by the carbanionic nucleophiles. This explained the thermal instability of 61 and 64.

To further characterize the structure of 60 and to attempt the preparation of quinoid 7, the following reactions were carried out (Figure 31). Treatment of dipotassium salt 60 with bromine in CCl_4 resulted only in extensive decomposition. Acidification with concentrated HCl followed immediately by bromine water produced a yellow, water insoluble solid whose structure was presumed to be 7. However, it was observed that the C≡N stretching in

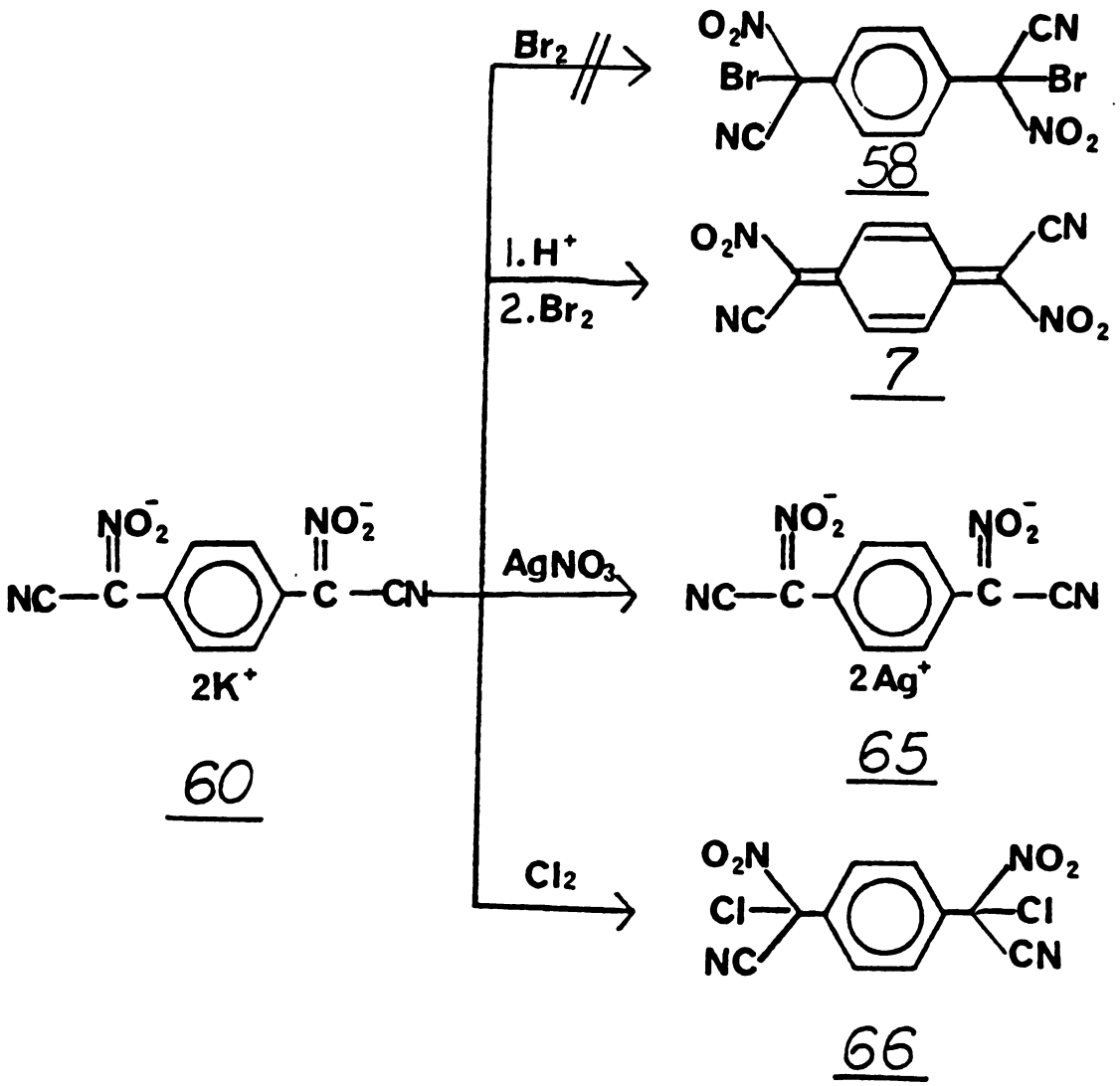


Figure 31. Reactions of salt 60

the region of 2200 cm^{-1} was very weak and could not be easily detected. A similar observation has been made by Kitson and Griffith.[79] They found that the intensity of this band decreased considerable when oxygen-containing groups were attached to the carbon atom alpha to the

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nitrile group. The C≡N band was completely absent in the spectrum of the supposed α,α'-diacetoxy-α,α'-dimethyl-succinonitrile. The lack of nitrile absorption in IR certainly did not help us in determining the structure of our product. Furthermore, this yellow solid was unstable, decomposing with the evolution of oxides of nitrogen. Therefore, further characterization were unsuccessful and inconclusive. If one considered the negative charge as mainly distributed on the oxygen of the nitro group, the difficulty in oxidation was not unexpected.

The disilver salt 65 was prepared by treating an aqueous solution of 60 with $AgNO_3$.[78] Although 65 is somewhat light sensitive, as most silver salts are, a satisfactory elemental analysis was obtained.

The dichloro derivative, 66, was prepared by the direct chlorination of 60 with chlorine gas.[78] This compound melted above 300° with a color change from yellow to white at 110°. It exhibits the characteristic nitrile absorption at 2200 cm^{-1}, nitro absorption at 1580-1620 cm^{-1} and chloride absorption at 720 cm^{-1}.

In direct support of its structure, 60 was hydrolyzed

in boiling alkaline aqueous solution, acidification led to spontaneous decarboxylation and yielded p-bis(nitromethyl)-benzene[80] (Figure 32).

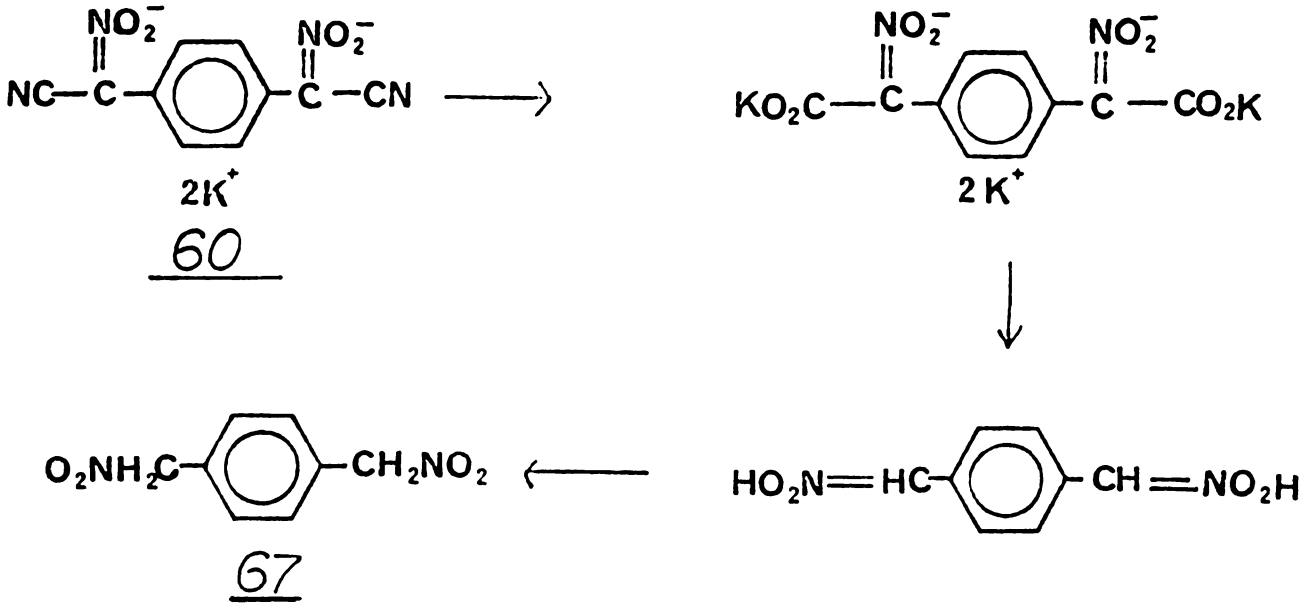


Figure 32. Hydrolysis of dipotassium salt 60

Same approaches were applied to the dipotassium salt 63. But the difficulties we encountered with 60 also occured to 63, namely, lack of strong C≡N absorption to prove the existence of nitrile; extremely low solubility limits the use of ^{13}C NMR; no parent peak in mass spectrometry due to thermal decomposition. Treatment of 63 with silver nitrate in aqueous solution did result in the precipitation of a light green disilver salt. But it was less stable than 65 and decomposed rapidly when exposed to the air.

Nevertheless, in each case, a characteristic nitro absorption appeared in the 1560-1670 cm^{-1} region and the disappearance of the original NO_2^- absorption suggested that the carbanion has been oxidized into a neutral species. Adequate condition for the oxidation of 60 and 63 to the quinoids 7 and 8 has yet to be found.

V. PREPARATION OF 4-PHENYL-5-AMINO ISOXAZOLE

To deal with the difficulties we had encountered in introducing a second nitrile into the same carbon atom[50], we searched for an alternative to replace the traditional SN-2 displacement. Two approaches we attempted but proved fruitless were a) The replacement of diazo-group by CN^- b) Reaction of enamine with sulfimide (Figure 33).

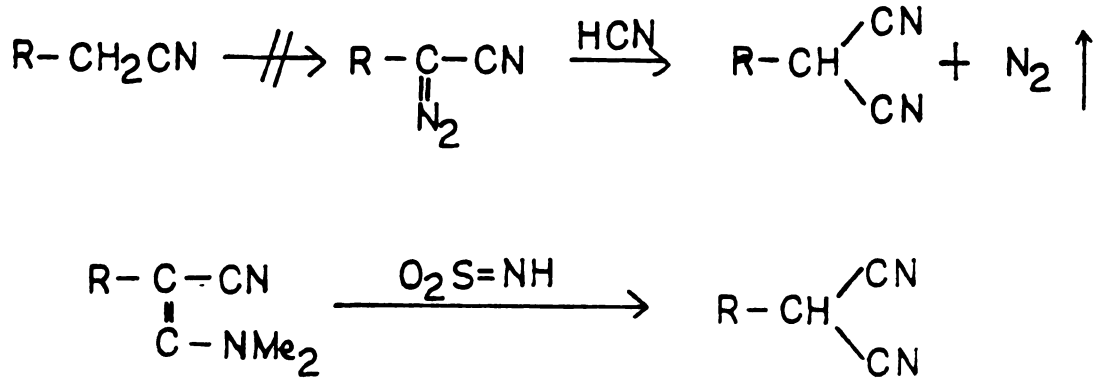


Figure 33. Proposed syntheses of α,α-dinitrile

Hydrogen halides are known to replace the diazo-group in α-diazo ketones. But when we treated phenylaceto-nitrile with tosylazide, no expected diazo-nitrile compound was obtained.

It was also well documented that reaction of free sulfimide with aldehyde provided nitriles.[81] We used enamines as hidden aldehydes, but detected no desired products.

We then turned our attention to the use of HOSA[82] (Hydroxyamine-O-sulfonic acid), since an additional

nitrile synthesis using HOSA has recently been reported[83] (Figure 34). The method would be extremely useful for us

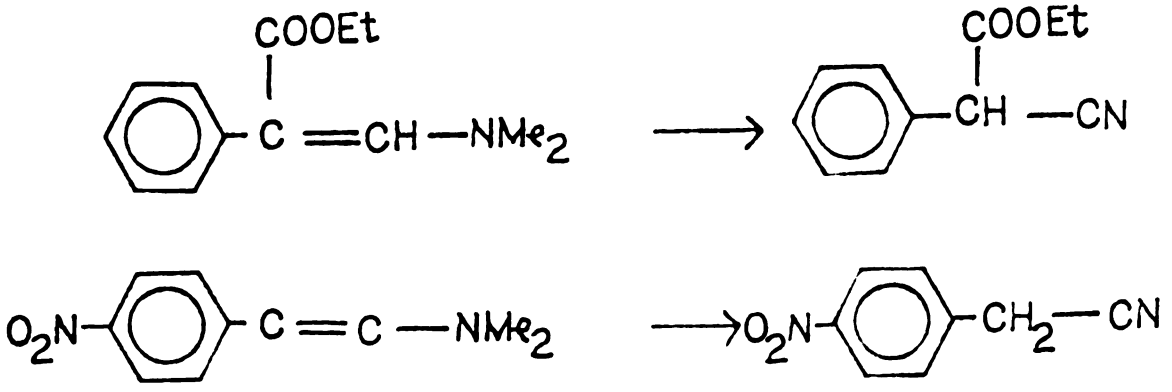


Figure 34. Synthesis of nitrile by using HOSA

since enamines could be prepared from readily available mono-cyano compounds and bis-dimethylamino-t-butoxymathane[84] (Brederek's reagent)(Figure 35).

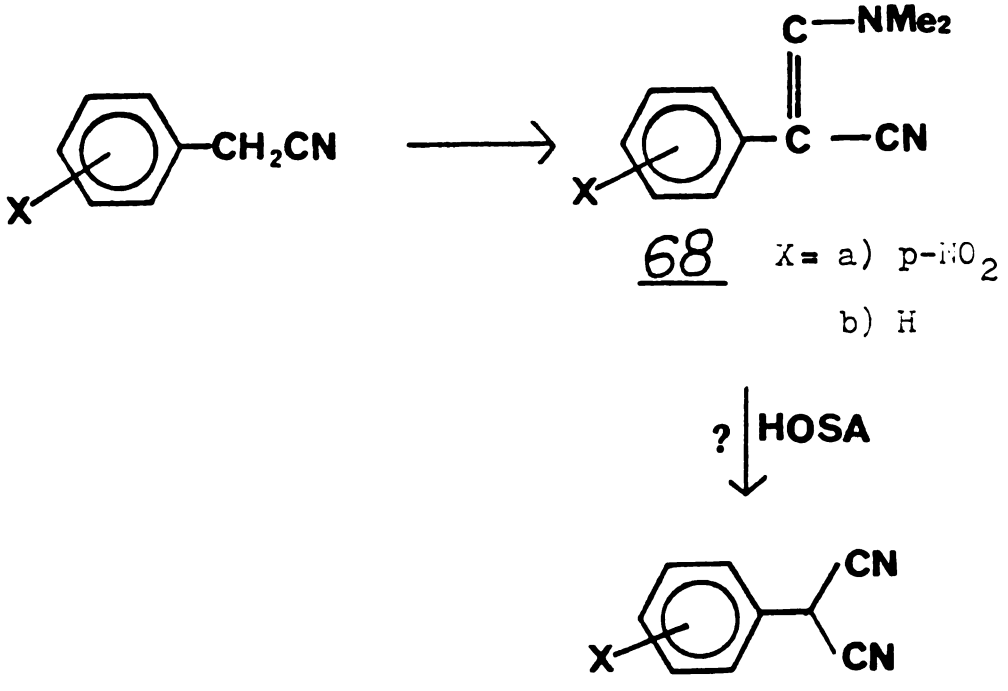


Figure 35. Synthesis of α,α-dinitrile with HOSA

Surprisingly, when this method was used on enamine 68, an unexpected reaction was observed. Treatment of p-nitrophenylacetonitrile with Brederek's reagent afforded the enamine 68a in 83% yield as a bright yellow solid, mp 184-185°. Enamine 68a when refluxed with HOSA in ethanol or isopropanol yielded an orange solid whose structure was assigned as 69a based on the spectroscopic data. When heated with acetic anhydride 69a yielded acetamide 70a in 55% yield (Figure 36).

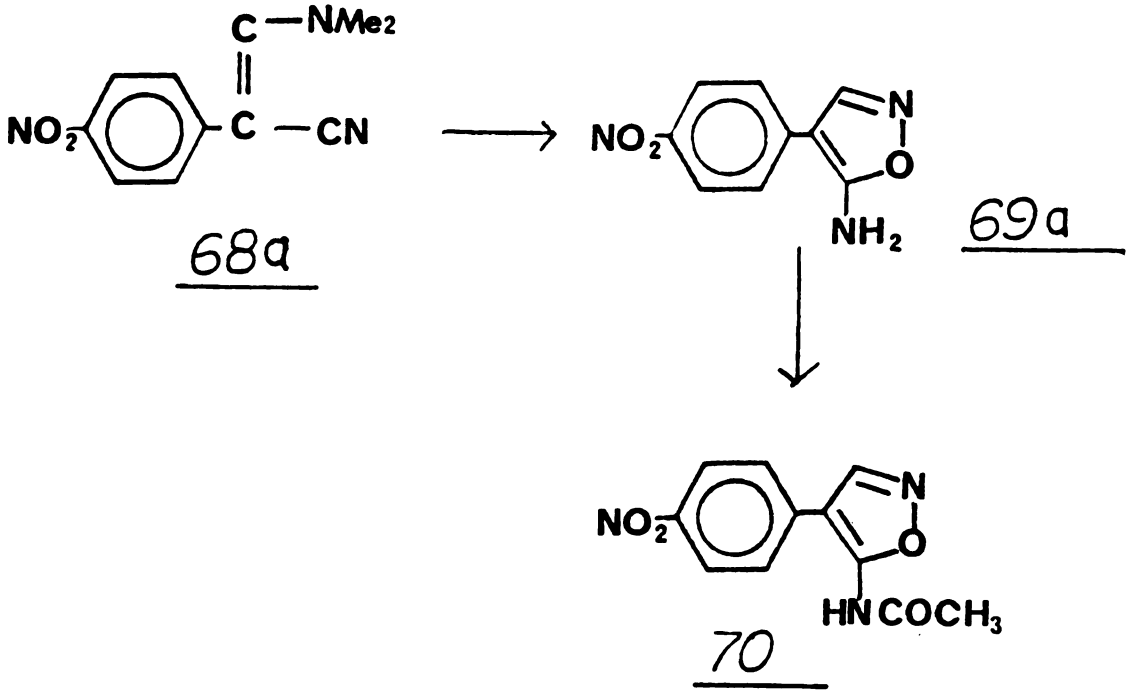


Figure 36. Cyclization reaction of 68a with HOSA

Under similar reaction condition 68b afforded 69b as a white solid in 32% yield. Literature search revealed that α-cyanoketo compound cyclized to give amino-isoxazole when reacted with hydroxylamine[85]. (Figure 37).

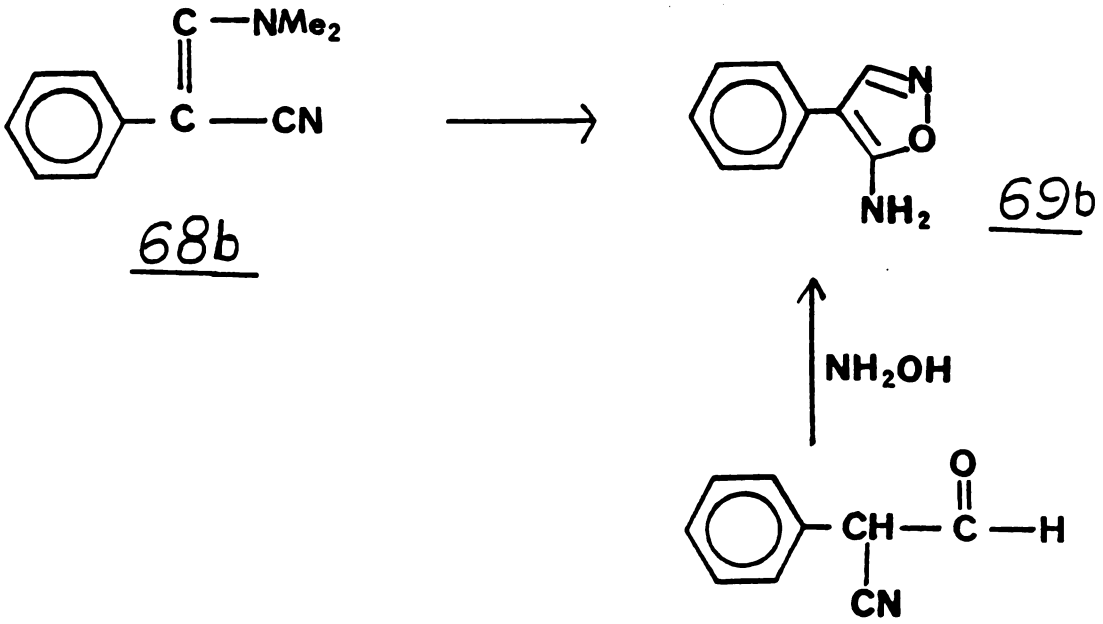


Figure 37. Cyclization of enamine 68b to isoxazole 69b

For comparison, enamine 68a was refluxed with hydroxylamine and 69a was isolated. The behavior of enamine as a carbonyl function was what we have expected. However, the detailed reaction mechanism was not clear. The reaction was run in either aqueous alcohol or in anhydrous alcohol. Both gave the same product in comparable yields. Water was involved in both cases during work-up to remove excess HOSA. One would expect HOSA to be hydrolyzed before reacted with the enamines. However, in aqueous alcohol the reaction of 68 with HOSA or $NH_2OH \cdot HCl$ required one hour at refluxing temperature to go to completion. While in anhydrous alcohol treatment of the mixture with water at room temperature after reflux generated the product

instantaneously. Based on the difference in reaction rate,

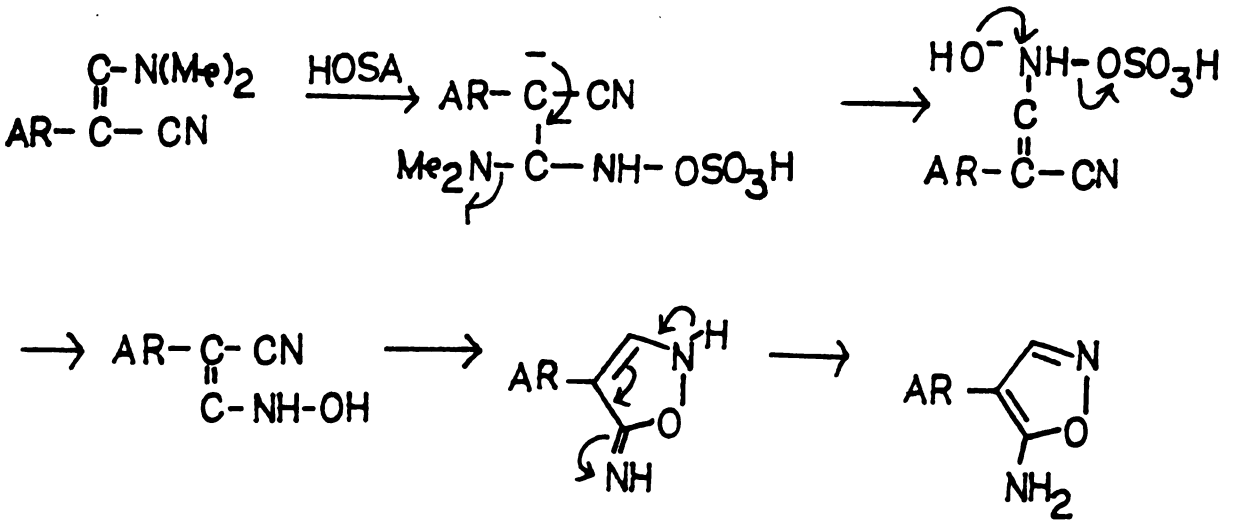


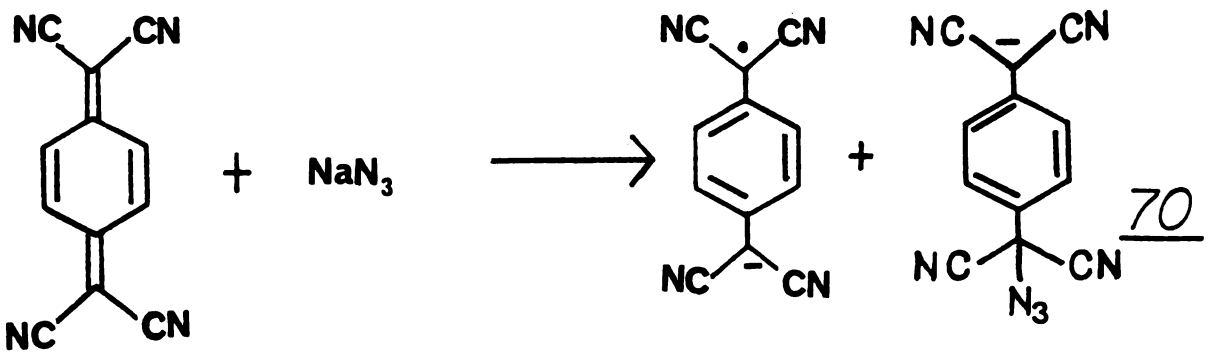
Figure 38. Mechanism of cyclization of 68

we proposed a reaction mechanism (Figure 38) in which HOSA attacks the enamine in the rate determining step followed by hydrolysis and cyclization to 5-amino-isoxazole.

Moreover, in a control experiment, when water was used as the reaction medium[87], there was recovered only the starting enamines. This appeared to be the result of low solubility of enamine in water.

VI. REDUCTION OF TCNQ WITH SODIUM AZIDE

Treatment of TCNQ with sodium azide in refluxing acetonitrile afforded a deep blue solution, from which purple crystals precipitated upon cooling. This purple product was identified as $TCNQ^{-}Na^{+}$ by IR and UV-Visible spectra analysis.[88] The deep blue acetonitrile filtrate was taken into near dryness and was purified by preparative TLC to give a deep blue solid which displayed a strong absorption at $\lambda_{max.}$ 585 nm in visible spectra with no trace of either TCNQ or $TCNQ^{-}$. This reaction demonstrated



70

the first example of the use of sodium azide as a reducing agent. We assumed the structure of the blue residue as the azide addition product 70. Although the elemental analysis of 70 was non-informative, addition of one equivalent of trifluoroacetic acid yielded 55% of $TCNQ^{-}Na^{+}$, but the formation of the blue solution was indeed completely suppressed. Instead, the filtrate was identified as unreacted TCNQ.

EXPERIMENTAL

GENERAL PROCEDURES

Melting points were determined on a Thomas Hoover Unimelt melting point apparatus and are uncorrected. ^{1}H NMR spectra were taken on a Varian T-60 or Bruker WM-250 spectrometer and are reported in parts per million from internal tetramethylsilane on the δ scale. ^{13}C NMR spectra were determined on a Varian CFT-20 spectrometer. Infrared spectra were taken with a Perkin-Elmer 237B instrument. Ultraviolet spectra were obtained on a Unicam SP-800 spectrometer. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6 or a Finnagan 4000 instrument. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan and Galbraith Laboratories, Inc., Knoxville, Tennessee.

[Bis(methylthio)methylene]malononitrile (10, R=SCH_3).

A number of similar compounds have been prepared by Gompper and Topfe[57] whose directions were followed with some modifications.

A solution of 11.2 g potassium hydroxide (0.2 moles) in 60 ml of methanol was cooled to 0°C with ice-salt bath.

To this stirred solution was added portionwise 6.6 g of malononitrile (0.1 moles) so that the temperature would not go over 0°. Six milliliter of carbon disulfide was then added in one portion. When the yellow precipitate of potassium dithiolate started forming, 13 ml of methyl iodide (0.2 moles) was added dropwise over a period of 30 minutes. After the addition was complete, the reaction mixture was allowed to warm to room temperature with stirring and diluted with 350 ml of cold water. The suspension was allowed to stand for a few hours to complete the precipitation. The yellow product was collected on a Buchner funnel and recrystallized from methanol to give 12.7 g (75%) of [bis(methylthio)methylene]malononitrile as colorless needle-like crystals; mp 79.5-80°C; PMR (acetone-d_6): δ ppm 2.8 (s); IR (nujol): 2190, 1320, 1210, 960, 925, 870 cm^{-1}; Mass spectrum m/e: 170 (parent), 155, 130, 123, 109, 98, 86, 79, 47.

Condensation of dithiooxamide with aromatic aldehydes-

Dithiooxamide (rubeanic acid) obtained from commercial sources was purified by dissolving in a large volume of hot ethanol, filtering to remove the dark, insoluble impurities. Concentration of the filtrate gave orange crystals of dithiooxamide. The aldehydes were recrystallized or redistilled before use. The condensation reaction does not appear to be particularly sensitive to small amount of impurity in either reactant.

The mixed reactants were placed in a round bottom flask fitted with a Dean-Stark apparatus to trap the small amount of water formed.

2,5-Bis(2-furyl)thiazolo[5,4-d]thiazole, 11.

Dithiooxamide (20 g, 0.167 moles), 60 g of phenol, and 200 g (2.08 moles) of freshly distilled furfural were heated in an oil bath at 180-200° for 45 min. After standing overnight the dark crystalline product was collected with suction and washed with several portions of ethanol, ether, and hexane. The crude product was heated under reflux with 1 l. of chloroform and the filtered solution was taken to dryness on rotory evaporator to yield 16 g (40%) of greenish yellow needles; mp 238-239° (lit. mp 238-240°)[41].

Diphenylthiazolo[5,4-d]thiazole

A mixture of 2 g of dithiooxamide (0.017 moles) and 17.7 g of benzaldehyde (0.17 moles) was heated in an oil bath to ca. 200° for 45 min. The reaction mixture was cooled to room temperature and diluted with acetone. The crude product was collected and recrystallized from benzene to give 3.3 g (77%) of faintly yellow crystals; mp 208-209°. (lit. mp 209-210°)[54].

2,5-Bis(2-hydroxy-1-naphthyl)thiazolo[5,4-d]thiazole, 20.

This compound was prepared in the same manner as diphenylthiazolo[5,4-d]thiazole but using DMF (dimethylformamide) as solvent. Recrystallization from pyridine gave 65% yield of light yellow crystals; mp 335-337° (lit. mp 339-342°).

2,5-Bis(4-hydroxyphenyl)thiazolo[5,4-d]thiazole, 16.

A mixture of 1 g of dithiooxamide (8.3 mmoles) and 2.48 g of p-hydroxybenzaldehyde (20.3 mmoles) in 10 ml DMF (dimethylformamide) was refluxed for 15 hours then allowed to cool to room temperature. The resulting dark solution was diluted with water and the precipitate collected on Buchner funnel. The dark crystalline product was washed extensively with ethanol, recrystallized from cyclohexanone and washed with ethanol again to give 0.8 g (31%) of the desired product as yellow solid; mp 365-370° (lit. mp 369-373°)[40].

2,5-Bis(3,5-di-tert-butyl-4-hydroxyphenyl)thiazolo[5,4-d]-thiazole, 19.

Dithiooxamide (1.2 g) and 3,5-di-tert-butyl-4-hydroxybenzaldehyde (4.7 g) were refluxed in 50 ml of ethylene glycol (oil-bath temperature 200°) for 15 min. After cooling, the reaction mixture was poured into 300 ml of

water. The precipitates which formed were collected on a Buchner funnel and washed with methanol and hexane. One recrystallization from chloroform/petroleum ether gave 3.1 g (56%) of light yellow crystals; mp 313-314° (lit. mp 314-315°).[53] This compound oxidezed to a pale-green solid when exposed to the air; PMR ($CDCl_3$): δ ppm 1.5 (s, 18 H), 5.4 (s, 1 H), 7.6 (s, 2 H).

2,5-Thiazolo[5,4-d]thiazoledicarboxylic acid, 12.

A suspension of 17 g of 2,5-bis(2-furyl)thiazolo-thiazole (0.062 moles) and 475 ml of pyridine were heated on a steam bath with rapid stirring until the solid had dissolved. After cooling to 70°, 75 ml of water was added to produce an uniform suspension of fine crystals. The mixture was cooled to 15-20° and held at this temperature while 104 g (0.66 moles) of powdered potassium permanganate and 70 ml of water were added, with continued rapid stirring. After the permanganate had been added, the temperature of the mixture was allowed to rise slowly to 40° and maintained there for 12 hours. Caution has to be taken to avoid overheating immediately after the removal of the cooling bath. The mixture was then cooled and 1 g of sodium bisulfite and 100 ml of water were introduced. The brown precipitate was collected with suction on a large filter, washed sparingly with water, and squeezed dry

with a filter dam. The filtrate might be discarded with little loss of product since the sparingly soluble potassium salt of the acid was effectively salted out by the high concentration of potassium ions in the system. The filter cake was boiled with 1 l. of water and the extract filtered hot with suction. Two further extractions of the residual manganese dioxide were made with smaller volumes of hot water. The colorless filtrates were acidified with concentrated HCl through addition funnel and the precipitated acid was collected. The air-dried material weighted 7.6 g (50%): mp 212-213° (dec) (lit. mp 214° dec); IR (nujol): 3450, 3350, 1690, 1410, 1320, 1310, 1280, 1112, 750 cm^{-1}; Mass spectrum m/e: 230 (parent), 186, 142, 115, 88, 70, 44. This compound was shown to exist as a dihydrate[41].

Thiazolo[5,4-d]thiazole

2,5-Thiazolothiazoledicarboxylic acid dihydrate (600 mg, 2.3 mmoles) was heated under reflux with 100 ml of absolute ethanol for 14 hours. The suspension turned clear after 30 minutes of heating and the product reprecipitated gradually. The solvent was removed by rotory evaporator. There remained 298 mg (91%) of crystals of thiazolothiazole. The analytical sample was purified by recrystallization from ethanol: mp 150-151° (lit. mp 150°)[41]; Mass spectrum m/e:

142 (parent), 115, 100, 88, 70, 44.

Dimethyl 2,5-thiazolo[5,4-d]thiazoledicarboxylate

This dimethyl ester was prepared by the method of Johnson's[41] in 87.6% yield; mp 248.5-249.5° (lit. mp 249-250°); Mass spectrum m/e: 258 (parent), 227, 200, 114, 88, 70, 59. The diethyl ester was prepared in the same manner but in lower yield (42%, mp 139-140°; lit. mp 140-141°) due to the facile decarboxylation of 2,5-dicarboxylic acid into its parent compound, thiazolothiazole; ^{13}C NMR ($CDCl_3$): δ ppm 162.05, 159.36, 154.22, 63.22, 14.00.

2,5-Bis(hydroxymethyl)thiazolo[5,4-d]thiazole, 13.

Into a three-neck round bottom flask equipped with condenser, addition funnel and thermometer was charged 0.572 g (2 mmoles) of diethyl 2,5-thiazolothiazoledicarboxylate in 25 ml dry tetrahydrofurane and cooled in ice-bath until it reached 10°. To this stirred solution, 8 ml of 1 M Super-Hydride (lithium triethylborohydride, 8 mmoles) was added dropwise so that the temperature was kept below 15°. After the addition was complete, the brown solution was further stirred at 10° for one hour. Five milliliters of water and 15 ml of 3 N HCl were added slowly to quench the

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excess hydride. The resulting brown solution was distilled under vacuum (bath temperature 35°) to remove triethylborane and tetrahydrofurane. After the volatiles were removed, the dark brown residue was diluted with ethyl ether and treated with 25% potassium carbonate aqueous solution. The organic layer was separated and the aqueous layer was extracted with more ether. The combined ether extracts was dried ($MgSO_4$) and evaporated on rotory evaporator to give 0.278 g of the diol 13 (69%) as a yellow solid; mp 167-169°; IR (nujol): 3200 (broad), 1350, 1160, 1060, 720; PMR (DMSO-d_6): δ ppm 4.8 (d, 4 H), 6.2 (t, 2 H). When D_2O was added: 4.8 (s); ^{13}C NMR (DMSO-d_6): δ ppm 175.52, 148.39, 61.33. Mass spectrum m/e: 202 (parent), 173, 143, 114, 102, 88, 84, 70, 57, 45, 31. This compound could also be prepared from the dimethyl ester but in lower yield (47%).

2,5-Bis(chloromethyl)thiazolo[5,4-d]thiazole, 14.

Diol 13 (0.202 g, 1 mmole) was refluxed with 5 ml of thionyl chloride for two hours. After cooling, the reaction mixture was poured carefully into 25 ml of cold water with stirring. The precipitates formed were collected on Buchner funnel and washed with water to give 0.23 g of the bis-(chloromethyl) derivative (96%) as brown plates; mp 123-125°; PMR ($CDCl_3$): δ ppm 4.8 (s); Mass spectrum m/e: 238 (parent), 203, 168, 88, 84. Anal. Calcd. for $C_6H_4N_2S_2Cl_2$:C, 30.13%;

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H, 1.69%. Found: C, 30.27%; H, 1.72%.

2,5-Bis(2,5-cyclohexadiene-3,5-di-t-butyl-1-diylidene-4-oxo)thiazolo[5,4-d]thiazole, 2b (R = t-butyl).

To a stirred solution of 0.5 g of 2,5-bis(3,5-di-t-butyl-4-hydroxyphenyl)thiazolothiazole 19 (0.9 mmoles) in 100 ml of methylene chloride was added 2.2 g (9 mmoles) of lead peroxide. The mixture was refluxed for 5 hours affording a deep blue solution. The solvent was removed in vacuo and the residue treated with 50 ml of chloroform and filtered. The solvent of the filtrate was removed to give 0.3 g of the deep blue quinoid compound 2b (60%); mp 289.5-290.5°; PMR ($CDCl_3$): δ ppm 1.33 (s, 18 H), 7.8 (d, 2 H); IR (nujol): 1630, 1600, 1375, 1250, 1150, 1080, 1030, 910, 830 cm^{-1}; Mass spectrum m/e: 548 (parent), 533, 493, 275, 260, 246, 216, 105; UV-Visible (CH_2Cl_2): $\lambda_{max.}$ 555nm (ϵ: 9.1×10^4), 602 nm (ϵ: 3.0×10^5).

Oxidation of 2,5-Bis(2-hydroxy-1-naphthyl)thiazolo[5,4-d]-thiazole 20.

This compound was oxidized in the same manner as above using benzene as the solvent to give the quinoid 3 as a green solid; UV-Visible ($CHCl_3$): $\lambda_{max.}$ 675 nm. Compound 3 became discolored without the presence of excess lead peroxide. Therefore, further characterization was not possible.

Oxidation of 2,5-Bis(p-hydroxyphenyl)thiazolo[5,4-d]thiazole 16.

This compound was not soluble in most organic solvents and consequently the oxidation with lead peroxide in organic solvent failed. Instead, 0.25 g of 16 (0.77 mmoles) was dissolved in 30 ml of diluted NaOH aqueous solution and treated with 1.0 g of $K_3Fe(CN)_6$ (3.08 mmoles). After 2 hours of stirring at room temperature, this suspension of fine green solid was centrifuged and the precipitate collected on a Buchner funnel to give 0.17 g (69%) of the corresponding quinoid compound 2a. Very insoluble for spectroscopic determinations; Mass spectrum m/e: 324 (parent). Without the presence of excess $K_3Fe(CN)_6$ this compound was in equilibrium with the "phenol" form 16, as shown by the increasing intensity at m/e 326.

N,N'-Dimethyl-2,5-diphenylthiazolo[5,4-d]thiazole trifluoromethanesulfonate salt, 24a.

2,5-Diphenylthiazolothiazole (1 g, 3.4 mmoles) and 5 ml of methyl trifluoromethanesulfonate were placed in a sealed tube and heated on a steam bath overnight, until the dissolution was complete. The contents in the tube were cooled to room temperature and diluted with ethyl ether to precipitate a white solid. The solid product was collected

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and washed with ethyl ether and alcohol. Recrystallization from trifluoroacetic and ethyl acetate afforded 1.96 g of the product as white shining crystals (92.5%); mp 260° (dec); PMR (CF_3COOH): δ ppm 4.53 (s, 6 H), 7.8 (s, 10 H); IR (nujol): 3050, 1600, 1520, 1485, 1275, 1225, 1150, 1030, 1000, 945, 880, 855, 760, 700. Anal. Calcd. for $C_{20}H_{16}N_2S_4F_6O_6$: C, 38.58%; H, 2.59%. Found: C, 38.62%; H, 2.62%. The fluorosulfonate salt 24b was similarily prepared by treatment with methyl fluorosulfonate in 90% yield.

N,N'-Dimethylthiazolo[5,4-d]thiazole trifluoromethanesulfonate salt 25a

Thiazolo[5,4-d]thiazole (200 mg, 1.4 mmoles) and 3 ml methyl trifluoromethanesulfonate were sealed in a glass tube and heated on steam bath for 1 hour. Starting material dissolved and a white plate-like crystal formed. After cooling, the product was collected on Buchner funnel and washed with dry ether. Caution should be taken not to draw too much air through the funnel for the product 25a appeared to be air sensitive. The product was dried under vacuum to give 300 mg (45.3%) of 25a; mp 258-260°(dec); PMR (CF_3COOH): δ ppm 4.2 (s, 6 H), 10 (s, 2 H). The corresponding fluorosulfonate salt 25b was prepared in the same manner but was extremely air sensitive and decomposed rapidly.

N,N-Dimethylamino-triphenoxymethane, 32[56b]

A mixture of 1.625 g (0.01 moles) of phosgene immonium chloride and 1.88 g of phenol (0.02 moles) in 10 ml of methylene chloride was refluxed for 1 hour over the steam bath until the evolution of hydrogen chloride gas had ceased. The solvent was removed under vacuum to afford an oil which precipitated upon addition of ethyl ether; PMR (acetone-d_6): δ ppm 2.95 (s, 6 H), 6.6-7.3 (m, 15 H). mp > 300°(dec).

2,6-Diphenyl-N1(3)H, 5(7)H-benzo[1,2-d:4,5-d']-diimidazole, 35

In a 50 ml round bottom flask heated with oil bath (bath temperature 190-200°) was refluxed 1.42 g of 1,2,4,5-tetraaminobenzene·4HCl (5 mmoles) in 10.6 g of benzaldehyde (0.1 moles) for 3 hours. After cooling to room temperature the reaction mixture was diluted with large quantity of ethanol and a yellow solid precipitated. The solid was collected on Buchner funnel and washed with water, ethanol and ether to give 0.3 g (20%) of the title compound 35; mp > 350°; IR (nujol): 3675, 1610, 1570, 1500, 1250, 1000, 855 cm^{-1}; Mass spectrum m/e: 310 (parent), 155, 122, 105, 91, 77.

2,6-Bis(3,5-di-tert-butyl-4-hydroxyphenyl)-benzo[1,2-d:4,5-d']diimidazole, 36.

1,2,4,5-Tetraaminobenzene·4HCl (1.42 g, 5 mmoles) and 2.34 g of 3,5-di-t-butyl-4-hydroxybenzaldehyde (10 mmoles) were mixed in 25 ml of ethylene glycol and heated under reflux for 30 minutes. The cooled reaction mixture was poured into 200 ml of water and the precipitate formed was collected and washed with water to give 1.1 g of off-white solid 36 (36%); mp > 360°. IR (nujol): 3400, 1610, 1420, 1245, 1115, 890 cm^{-1}; Mass spectrum m/e: 566 (parent), 555, 499, 382, 338, 298, 218, 103, 161, 82.

Oxidation of 2,6-Bis(3,5-di-t-butyl-4-hydroxyphenyl)-benzo[1,2-d:4,5-d']diimidazole, 36

A solution of compound 36 in dimethyl sulfoxide was treated with excess lead peroxide. A deep green solution of quinoid 4 was obtained. Excess lead peroxide was filtered and the UV-Visible spectrum of the green filtrate was taken; $\lambda_{max.}$(DMSO): 750 nm. However, the solution lost its color gradually. Addition of PbO_2 regenerated the color.

Reaction of 1,2,4,5-tetraaminobenzene with bisdithiomethyl-dicyanoethylene.

Under a blanket of nitrogen, 2.84 g (10 mmoles) of tetraaminobenzene·4HCl in cool, boiled oxygen-free water was treated with ice-cold 15% sodium hydroxide solution. The precipitate was filtered with suction under nitrogen, washed with ice-cold ethanol and suspended in 30 ml of dry n-butanol. To this stirred suspension was added 3.4 g of bis(dithiomethyl)-dicyanoethylene (20 mmoles) and heated under reflux for 60 minutes. The hot reaction mixture was filtered to collect 1.9 g of slightly yellow solid (89.6%), mp >300°; IR (nujol): 3405, 2210, 2170, 1635 cm^{-1}; Mass spectrum m/e: 212 (parent), 170, 94, 79, 66.

2,6-Bis(bromomethyl)naphthalene

A mixture of 50 g (0.32 moles) of 2,6-dimethylnaphalene, 120 g (0.675 moles) of recrystallized N-bromosuccinimide, 800 ml of carbon tetrachloride, and 200 mg of benzoyl peroxide was stirred at reflux under nitrogen for 4 hours. Then 500 mg of azobisisobutyronitrile was added, and the mixture was further stirred and reflux for 24 hours. The resulting thick mixture was cooled and filtered. The filter cake was washed well with water. One recrystallization from dioxane gave 59 g of white crystals (58%);

mp 181-183° (lit. mp 182.5-184°)[49]. Brown[89] suggested the use of a sun lamp as the source of irradiation and heat. His method was found to give more by-products as brown residues and was satisfactory.

2,6-Naphthalenedicarbodithioic acid, dipiperidinium salt 44b

To a solution of sodium methoxide (0.08 moles) in 60 ml dry methanol was added 2.56 g (0.08 moles) of elemental sulfur and refluxed for two hours. 5.8 g of 2,6-bis(bromomethyl)naphthalene (0.0185 moles) was then added to the above refluxing mixture during a period of one hour through a solid addition funnel. The resulting mixture was further refluxed for 7 hours. The reaction mixture, which contained the disodium salt of the tetrathio acid 44a was cooled and the solvent was removed by rotory evaporator. The residue was dissolved in water and filtered to remove any undesirable impurities. The deep violet filtrate was acidified with 10% HCl. The solid which precipitated upon acidification was dissolved immediately in 1.5 l. of chloroform and filtered. The resulting red solution was treated with 3.15 g of piperidine (0.037 moles) and taken to near dryness in vacuo to give, after suction filtration, 4.8 g of olive-colored dipiperidinium salt 44b (yield 57.8%); mp 154-156°; IR (nujol): 1000 cm^{-1}(CSS^-).

Diphenacyl 2,6-naphthalenedicarbodithioate 45

To a stirred suspension of 0.45 g of dipiperidinium salt of 2,6-naphthalenedicarbodithioic acid 44b (1 mmole) in 100 ml of methylene chloride was added dropwise a solution of 0.398 g of phenacyl bromide (2 mmoles) in 25 ml of methylene chloride at room temperature. After 1 hour of stirring the suspension turned to a clear red solution and the product began forming thereafter. The solvent was removed *in vacuo* after a total of 3 hours reaction time. Recrystallization from chloroform-hexanes yielded 0.45 g of 45 as a red crystals (87.2%); mp 198-100°; IR (nujol): 1690 (C=O), 1205 (C=S), 1050, 880. Anal. Calcd. for $C_{28}H_{20}O_2S_4$: C, 65.08%; H, 3.90%. Found: C, 64.93%; H, 3.86%.

Bis(1-methyl-2-oxopropyl) 2,6-naphthalenedicarbodithioate 46

To a stirred suspension of 0.45 g (1 mmole) of the dipiperidinium salt of 2,6-naphthalenedicarbodithioic acid, 44b in 100 ml of dry ethanol was added 0.21 g (2 mmoles) of 3-chloro-2-butanone in 10 ml of ethanol. The brown suspension dissolved with spontaneous precipitation of orange crystals. After 1 hour of stirring at room temperature, the solvent was removed by rotory evaporator and the residue was recrystallized from chloroform to give 0.13 g of red crystals 46 (30%); mp 180-181°; IR (nujol):

1700 (C=O), 1325, 1220 (C=S), 1175, 1150, 1130, 1045, 925, 880, 815, 800 cm^{-1}; UV ($CHCl_3$): $\lambda_{max.}$ 345, 505 nm; PMR ($CDCl_3$): δ ppm 1.65 (d, 6 H), 2.4 (s, 6 H), 4.9 (q, 2 H), 7.6-8.4 (m, 6 H). Anal. Calcd. for $C_{20}H_{20}S_4O_2$: C, 57.11%; H, 4.79%. Found: C, 57.14%; H, 4.93%.

Bistrifluoromethanesulfonate salt of diphenyl-TTNQ, 48b

Into 10 ml cold concentrated trifluoromethanesulfonic acid carefully dissolved 0.1 g of phenacyl 2,6-naphthalene-dicarbodithioate 45. The cold solution was poured into 50 ml of ethyl acetate to give, after washing with ethyl acetate, 0.11 g (84%) of the bis-trifluoromethanesulfonate salt 48b. mp 246-249°(dec). IR spectra indicated the disappearance of C=O and C=S bands; PMR (CF_3COOH): δ ppm 8.8 (s, 2 H), 8.1-8.8 (m, 6 H), 7.6-8.0 (m, 10 H); UV (CH_3CN): $\lambda_{max.}$ 465, 340, 250, 225 nm. Anal. Calcd. for $C_{30}H_{18}F_6S_6O_6 \cdot H_2O$: C, 45.10%; H, 2.52%. Found: C, 45.08%; H, 2.62%. The bisfluorosulfonate salt 48c, bisbisulfate salt 48a and bischlorosulfoante salt 48e were similarly prepared by dissolving the ester in the corresponding cold acids.

Bisfluoroborate salt of diphenyl-TTNQ, 48d

Phenacyl ester 45 (1.2 g, 2.3 mmoles), 0.95 ml of fluoroboric acid (48% aqueous solution) and 0.6 g of

P_2S_5 (2.7 mmoles) were refluxed in 14 ml of glacial acetic acid for 20 hours. An orange suspension was obtained at the end of the heating period. The solvent was removed in vacuo and the residue was diluted with 50 ml of ethanol to yield 1.3 g (86.2%) of 48d as orange solid; mp 250°(dec).

Bisbisulfate salt of tetramethyl-TTNQ, 47a.

Carefully dissolved 0.1 g of the di-butanone ester of the 2,6-naphthalenedicarbodithioic acid 46 in the cold sulfuric acid. The solution formed was then poured into a beaker of 50 ml ethyl acetate with stirring to precipitate the salt 47a in 72.5% yield. mp > 350°; PMR (CF_3COOH): δ ppm 2.82 (s, 12 H), 8.0-8.6 (m, 6 H); UV (CH_3CN): $\lambda_{max.}$: 442 nm. Anal. Calcd. for 47a $C_{20}H_{20}S_6O_8 \cdot H_2SO_4$: C, 35.39%; H, 3.27%. Found: C, 35.32%, 35.19%; H, 3.51%, 3.64%. The bistrifluoromethanesulfonate salt 47b and bischlorosulfonate salt 47c were similarly prepared (see Table 3).

Reaction of 48b with sodium methoxide in methanol

To a solution of 0.1 g of trifluoromethanesulfonate salt 48b (0.13 mmoles) in sufficient dry methanol was treated with a solution of 0.26 mmoles sodium methoxide in methanol.

The orange color of the original salt faded away immediately. After 2 hours stirring at room temperature, the solvent was removed by rotory evaporator. The white solid obtained was collected, recrystallized from methanol and dried to give 0.05 g (72%) of the dimethoxy derivative 49: mp 175-180°; IR (nujol): 1550, 1165, 1130, 1080, 730 cm^{-1}; PMR ($CDCl_3$): δ ppm 3.5 (s, 6 H), 6.4 (s, 2 H), 7.1-7.5 (m, 10 H), 7.6-8.3 (m, 6 H).

Reaction of 47a with sodium methoxide in methanol

To a solution of 50 mg bisulfate salt 47a (0.086 mmoles) in 50 ml of dry methanol was added 3 equivalents of sodium methoxide in 20 ml methanol. The yellow color of the salt solution disappeared completely in 10 minutes at room temperature with the formation of a white solid. The reaction mixture was taken to near dryness in vacuo and filtered to give a quantitative yield of the dimethoxy derivative 50: mp >350°; PMR ($CDCl_3$): δ ppm 1.95 (s, 12 H), 3.47 (s, 6 H), 7.67-8.17 (m, 6 H).

Reaction of the dimethoxy derivative 50 with HI

To a suspension of 0.45 g (1 mmole) of 50 in 10 ml of water was added 15 ml of 48% HI aqueous solution. The

resulting brown suspension was further stirred for an hour at room temperature and the precipitate was filtered on a Buchner funnel. There was obtained a dark brown solid, 54. The corresponding bisulfate salt 47a could be regenerated by simply dissolving 54 in concentrated sulfuric acid.

Reduction of 48b with tetrabutylammonium iodide

To a solution of 50 mg (0.064 mmoles) of trifluoromethanesulfonate salt 48b in 100 ml of dry acetonitrile was added dropwise with stirring a solution of 2 equivalents of tetrabutylammonium iodide in acetonitrile at room temperature. The color of the solution changed from orange to green and the precipitated black microcrystalline solids. The black solid was collected with suction filtration, washed with acetonitrile and dried under vacuum to give 37 mg (80%) of the iodine complex 51: mp 301-302°; UV (CH_3CN): $\lambda_{max.}$ 675 nm. Anal. Calcd. for $C_{28}H_{18}S_4I_{1.96}$: C, 45.98%; H, 2.48%; I, 34.01. Found: C, 46.19%, H, 2.57%; I, 34.25%. Reduction with lithium was similarily carried out. The salts 48 could be recovered from the complex by dissolving 51 in the concentrated, cold acids.

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Complex of 48b with $Li^{+}TCNQ^{-}$

To a solution of 0.1 g (0.128 mmoles) of trifluoromethane sulfonate salt 48b in large amount of acetonitrile (ca. 250 ml) was added 0.055 g (0.256 mmoles) of $Li^{+}TCNQ^{-}$. After stirring overnight, a brownish green solution was obtained. UV spectra indicated a strong absorption of neutral TCNQ plus $TCNQ^{-}$. Analysis of the UV spectra suggested the formation of $(TCNQ)^{+}TCNQ^{\circ}(TCNQ)^{-}$ mix-valence complex.

Bis-1,2-dithioethane acetal of terephthaldehyde, 57

To a three-neck round bottom flask equipped with magnetic stirrer, Dean-Stark trap, reflux condenser and addition funnel was charged with 5.66 g (0.06 moles) of 1,2-ethanedithiol, 60 ml benzene and a catalytic amount of p-toluenesulfonic acid. This solution was brought to refluxing and a solution of 4.02 g (0.03 moles) of terephthaldehyde in 15 ml of benzene was added dropwise over a period of one hour. The reaction was nearly 90% complete in 30 minutes. After 1.5 hours of reflux the reaction mixture was cooled to room temperature and the solid that has deposited was collected on a Buchner funnel and washed first with water and then sparingly with ethanol. Recrystallization from chloroform yielded 8.2 g of 57 (95.6%) as colorless crystals: mp 207-208°; IR (nujol);

1425, 1280, 870, 820, 730 cm^{-1}; Mass spectrum m/e: 286 (parent), 258, 225, 197, 181, 166, 153, 121, 105, 89, 69, 60, 45.

Dipotassium p-bis(cyanonitromethyl)benzene 60

Potassium t-butoxide or potassium ethoxide (0.034 moles) was formed *in situ* from 1.34 g (0.034 g atom) of potassium and 10 ml of t-butanol or ethanol. Dry THF (tetrahydrofurane) was added during this stage to help solubilize the alkoxides. To this solution at -78° was added a solution of 1.56 g (0.01 mole) of p-bis(cyanomethyl)benzene in 15 ml of THF, followed by the addition of 2.93 g (0.022 moles) of amyl nitrate. The dry-ice bath was then removed and the reaction mixture was allowed to reach room temperature and stirred overnight. The resulting brown slurry was filtered with suction filtration and was washed, successively, with 20 ml portions of THF, absolute ethanol and 30 ml of anhydrous diethyl ether, and dried *in vacuo* to yield 3.0 g (93%) of the dipotassium salt 60: mp 359-361 (dec); IR (nujol); 2210, 1500, 1390, 1350, 1275, 1250, 1150, 1020, 987, 820 cm^{-1}; PMR (D_2O): δ ppm 7.6 (s); ^{13}C NMR (D_2O): δ ppm 128.73, 125.76, 118.04, 102.30; UV (D_2O): $\lambda_{max.}$ 375, 225 nm. Anal. Calcd. for $C_{10}H_4N_4O_4K_2$: C, 37.25%; H, 1.25%. Found: C, 36.85%; H, 1.41%.

Disilver salt of p-bis(cyanonitromethyl)benzene, 65

The disilver salt was precipitated from solution when silver nitrate was added to an aqueous solution of the dipotassium salt. The light green disilver salt was light sensitive. The yield was quantitative: mp 200-202°; IR (nujol): 2200, 1230, 1150, 975 cm^{-1}. Anal. Calcd. for $C_{10}H_4N_4O_4Ag_2$: C, 26.12%, H, 0.88%. Found: C, 25.02%; H, 1.01%.

p-Bis(chlorocyanonitromethyl)benzene 66

Dipotassium p-bis(cyanonitromethyl)benzene (1 g) was suspended in 50 ml of anhydrous ether and cooled in ice-bath to 0°. Chlorine was bubbled in slowly until the suspension dissolved and the solution turned yellow. The reaction mixture was filtered to remove small amount of brown solid and the filtrate was concentrated by means of rotory evaporator. The yellow solid which was collected by suction filtration was washed with water and dried under vacuum. The yield was 0.59 g (61%): mp $>$ 300°; IR (nujol): 2200, 1610, 1420, 1330, 1060, 920, 825, 730 cm^{-1}; PMR ($CDCl_3$): δ ppm 7.9 (s).

Dipotassium salt of 2,6-bis(cyanonitromethyl)naphthalene, 63

Potassium t-butoxide (8 mmoles) was formed *in situ* by refluxing 0.31 g of freshly cut potassium and 0.60 g of t-butanol in 15 ml of dry THF until all of the metal was dissolved. To this solution at -78° was added dropwise a solution of 0.412 g (2 mmoles) of 2,6-bis(cyanomethyl)-naphthalene[31] in THF, followed immediately by 0.59 g (4.4 mmoles) of amyl nitrate. The reaction mixture was allowed to warm to room temperature and stirred at that temperature overnight. The precipitate which formed were then suction filtered and washed extensively with THF, absolute ethanol and anhydrous ether. A light brown water soluble solid was obtained in quantitative yield: mp > 320°. An analytically pure sample was prepared by recrystallization from hot water to give yellow shining crystals: IR (nujol): 2200, 1380, 1320, 1270, 1250, 1160, 1130, 1010, 890, 875, 800 cm^{-1}; PMR (DMSO-d_6): δ ppm 8.328 (s, 2 H), 7.762, 7.728, 7.672 and 7.637 (AB quartet, 4 H), determined by Bruker WM-250 NMR. ^{13}C NMR (DMSO-d_6): δ ppm 130.29, 129.65, 126.76, 122.96, 120.13, 119.61, 97.1; UV (DMSO): $\lambda_{max.}$ 380, 295, 285, 227 nm. Anal. Calcd. for $C_{14}H_6N_4O_4K_2$: C, 45.15%; H, 1.63%. Found: C, 44.86%; H, 2.04%.

p-Bis(nitromethyl)benzene 67

To a boiling solution of 3 g of potassium hydroxide in 15 ml water was added, in small portions, 2 g of dipotsssium salt 60. Caution has to be taken to avoid excess foaming. Boiling was continued for at least 24 hours until the evolution of ammonia ceased (negative to wet litmus paper). The hot alkaline solution was cooled and stirred with 20 g of ice. With the help of the external ice-salt bath, the solution was cooled down to -5°. Acidified with concentrated HCl gave a yellow solid precipitate which was collected and triturated with 50 ml of water to yield 0.8 g (65.7%) of compound 67: mp 123-125°; IR (nujol): 1550, 1425, 1320, 895, 890, 680 cm^{-1}; PMR (DMSO-d_6): δ ppm 5.67 (s, 1 H), 7.4 (s, 1 H); Mass spectrum m/e: 150 (parent - NO_2), 104, 78.

Reaction of p-nitrophenylacetonitrile with bis-dimethylamino-t-butylmethane (Brederek's reagent)

To a stirred solution of 6.5 g (0.04 moles) of p-nitrophenylacetonitrile in 30 ml of DMF (dimethyl formamide) was added dropwise 7.0 g of bis(dimethylamino)-t-butoxymethane in 15 ml of DMF. A deep green solution was obtained immediately. After stirring overnight at room temperature, the solvent was removed under vacuum. The brown residue was collected

with a suction funnel and washed with ether to give 7.3 g of the corresponding enamine 68a (83%). An analytically pure sample was obtained by column chromatography (Silica gel, CH_2Cl_2). The bright yellow solid melted at 184-185°; Mass spectrum m/e: 217 (parent), 187, 171, 156, 130; IR (nujol): 2200, 1625, 1585, 1120, 855, 845, 750 cm^{-1}; PMR (DMSO-d_6): δ ppm 3.3 (s, 6 H), 7.6 (s, 1 H), 7.2, 7.4; 7.8, 8.0 (AB quartet, 4 H); ^{13}C NMR ($CDCl_3$): δ ppm 151.02, 144.51, 143.76, 124.18, 122.89, 119.50, 76.14, 42.91.

Reaction of phenylacetonitrile with Brederek's reagent

A 100 ml round bottom flask was charged with 4.7 g of phenylacetonitrile (0.04 moles) and 7.0 g of bis(dimethylamino)-t-butoxymethane (0.04 moles). After stirring at room temperature for 12 hours a white solid precipitated. This was collected on a Buchner funnel and dried under vacuum to yield 6.5 g of the enamine 68b (94.5%): mp 77-78.5° (lit. mp 79-80°)[86]; IR (nujol): 2180, 1625, 1140, 990, 770 cm^{-1}; PMR ($CDCl_3$): δ ppm 3.0 (s, 6 H), 6.7 (s, 1 H), 7.2 (broad s, 5 H); Mass spectrum m/e: 172 (parent), 157, 144, 130, 117, 103, 91, 86, 77, 42; ^{13}C NMR ($CDCl_3$): δ ppm 149.85, 136.64, 128.67, 124.99, 123.88, 121.09, 76.55, 42.42.

Preparation of 5-amino-4-(p-nitrophenyl)isoxazole 69a

In a 100 ml round bottom flask, 1 g (4.6 mmoles) of 68a and 1.3 g of HOSA (Hydroxyamine-O-sulfonic acid, 11.5 mmoles) were refluxed overnight with 50 ml of iso-propanol under nitrogen. The reaction mixture was cooled and diluted with water. Rotory evaporation to partially remove the iso-propanol and to precipitate an orange solid. After washing with water, the product was dried under vacuum to give 0.9 g (95%) of 69a: mp 188-189°; IR (nujol): 3325, 1640, 1600, 1500, 1330, 1187, 1110, 850 cm^{-1}; PMR (CD_3COCD_3): δ ppm 6.55 (broad, 2 H), 7.5-8.1 (AB quartet, 4 H), 8.4 (s, 1 H); ^{13}C NMR (DMSO-d_6): 166.25, 150.83, 143.64, 138.72, 124.76, 124.01, 91.08; Mass spectrum m/e: 205 (parent), 189, 162, 149, 132, 116, 104, 89, 77, 63, 51.

Preparation of 5-amino-4-phenylisoxazole 69b

Enamine 68b (200 mg, 1.16 mmoles) and 330 mg of HOSA (2.9 mmoles) were refluxed in 50 ml of iso-propanol overnight. The reaction mixture was taken to near dryness on a rotory evaporator. To the resulting white, thick suspension was added 40 ml of water to obtain a clear solution. After standing for 10 minutes, the white crystals which precipitated were collected on Buchner funnel and dried

to give 60 mg of 5-amino-4-phenyl isoxazole 69b (32%): mp 144.5-146.5°; IR (nujol): 3440, 2250, 1675, 1275, 1210, 800, 760, 725, 685; PMR (CD_3COCD_3): δ ppm 4.93 (s, 1 H), 6.2 (broad, 2 H), 7.3 (broad s, 5 H); Mass spectrum m/e: 161 (parent+1), 117, 90.

5-Acetamido-4-(p-nitrophenyl)isoxazole 70a

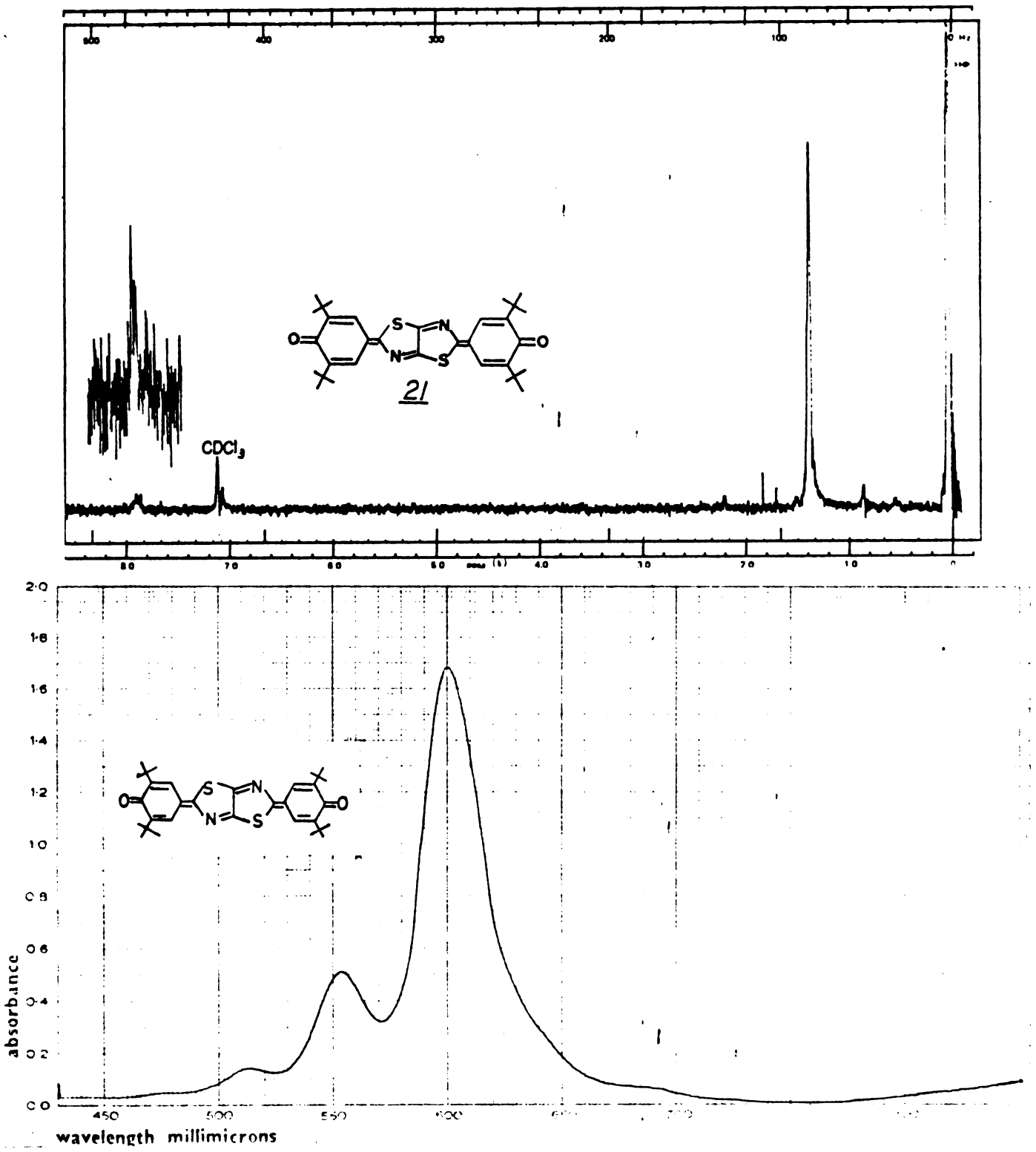
A solution of 0.5 g (2.4 mmoles) of 5-amino-4-(p-nitrophenyl)isoxazole 69a in 15 ml of acetic anhydride was refluxed for 24 hours. The hot solution was poured into 100 ml of water and cooled in the refrigerator for several days. The precipitate was collected on Buchner funnel and washed with water and dried under vacuum to give 0.33 g (55%) of 70a: mp 213-215°(dec); PMR (DMSO-d_6): δ ppm 2.1 (s, 3 H), 7.6-8.2 (AB quartet, 4 H), 8.6 (s, 1 H); IR (nujol): 3250, 1690, 1630, 1600, 1505, 1320, 1225, 1170, 1105, 1020, 990, 920, 860, 850, 750 cm^{-1}; Mass spectrum m/e: 247 (parent).

Preparation of $TCNQ^{\cdot-}Na^{+}$ by TCNQ and sodium azide

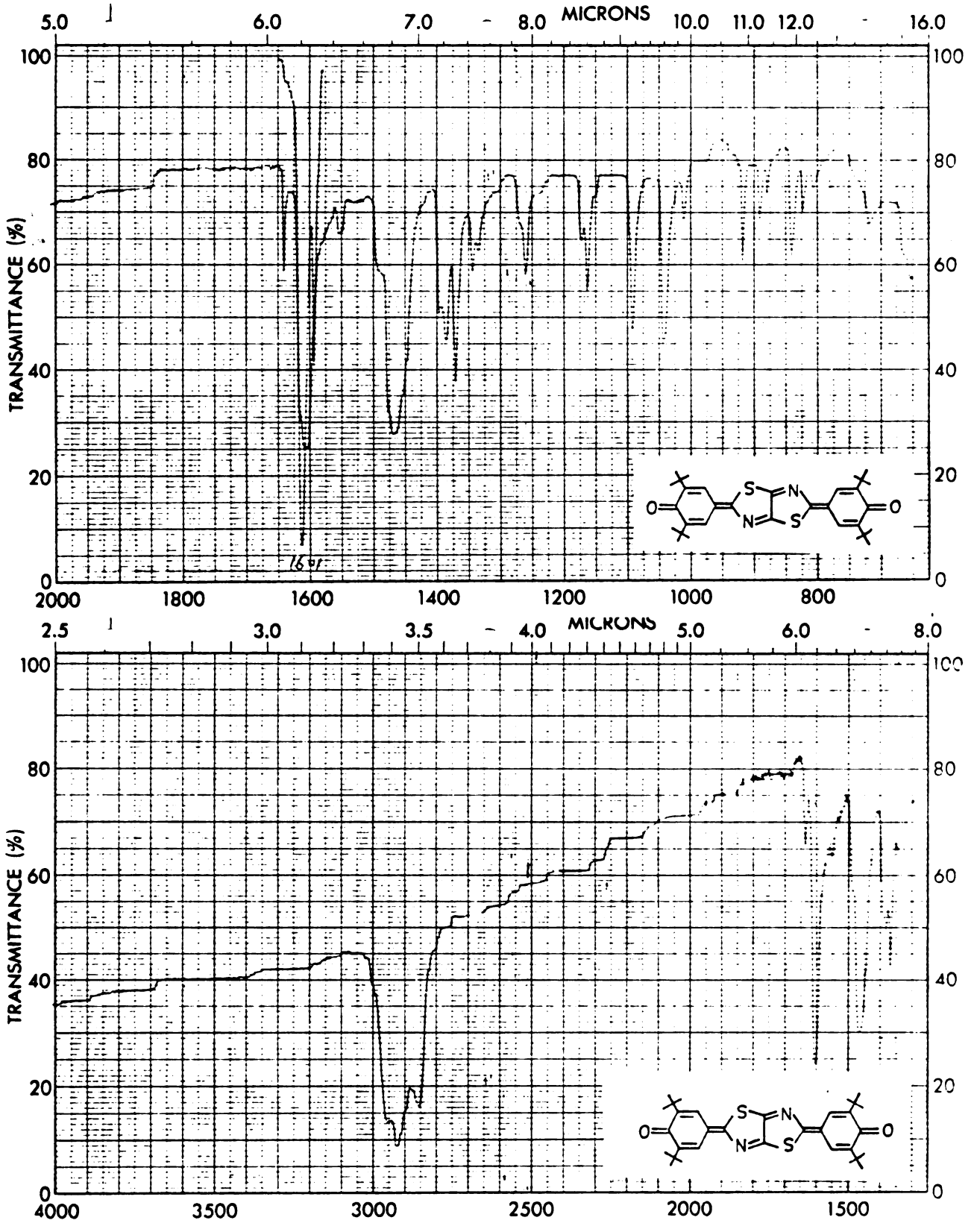
A 50 ml round bottom flask was charged with 600 mg (3 mmoles) of TCNQ, 195 mg of NaN_3 (3 mmoles) and 15 ml of acetonitrile. This mixture was refluxed for 6 hours

then cooled to room temperature. The precipitate which formed was collected on Buchner funnel, washed sparingly with acetonitrile and dried to give 0.5 g (75%) of $TCNQ^{\cdot-}Na^{+}$. IR and UV spectra of this compound were essentially identical to that of the authentic sample of $TCNQ^{\cdot-}Na^{+}$. The solvent of the blue filtrate was removed <u>in vacuo</u> and the residue purified on preparative TLC (Silica Gel; eluted by a 92.5% : 7.5% mixture of ethyl acetate : acetonitrile). The resulting blue solid melted above 300°. UV-Visible (CH_3CN): $\lambda_{max.}$ 585 nm.

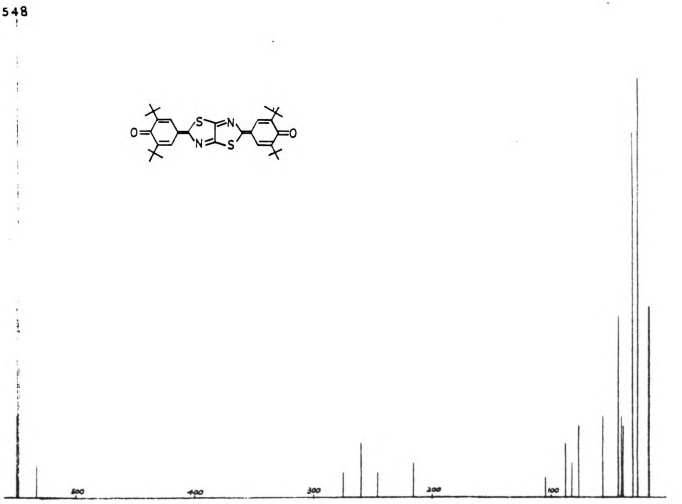
APPENDIX



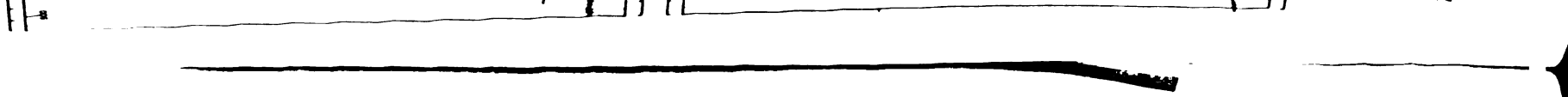
1. PMR spectrum (top) and Ultraviolet spectrum (bottom) of 2b.

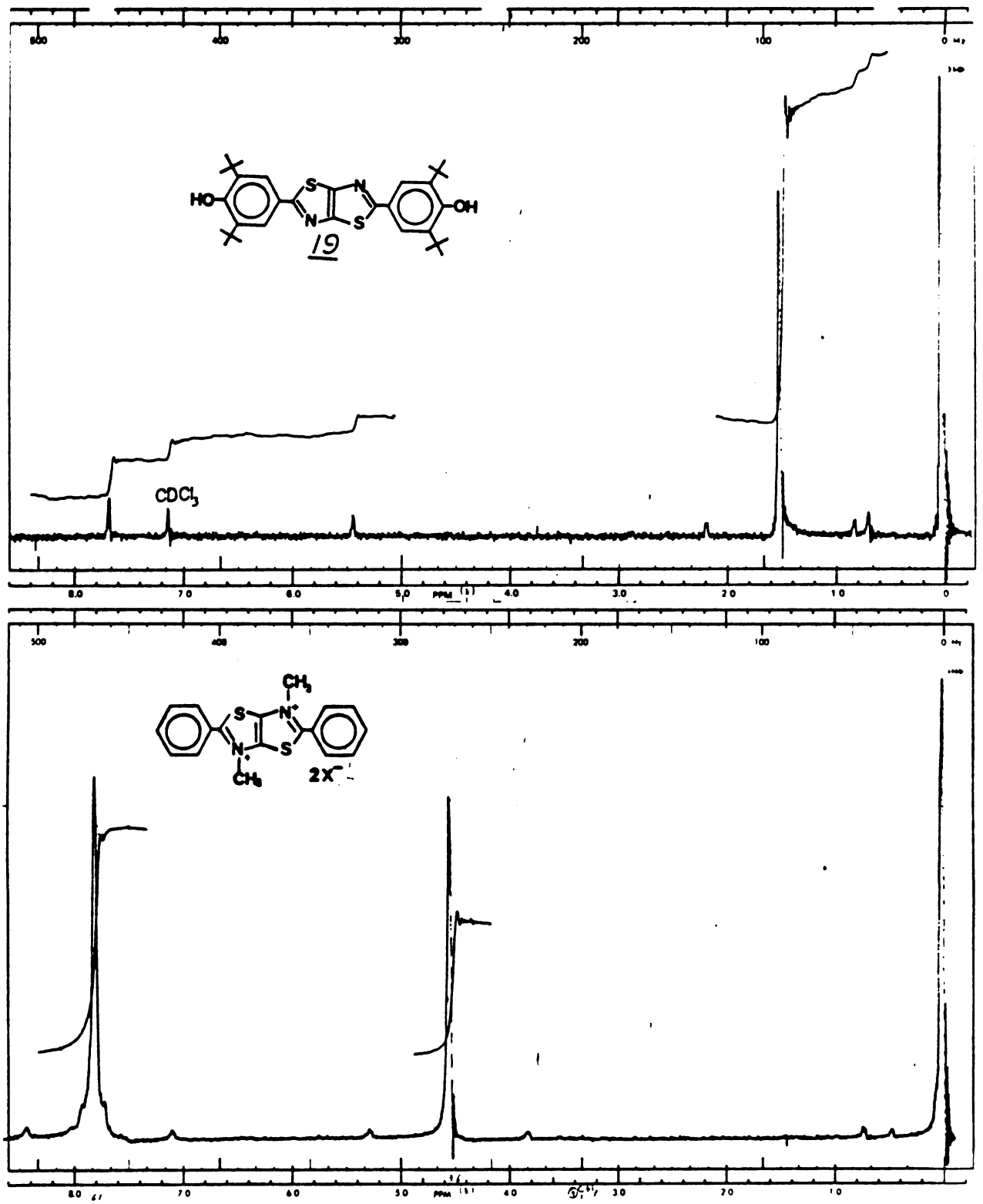


2. Infrared spectrum of 2b.

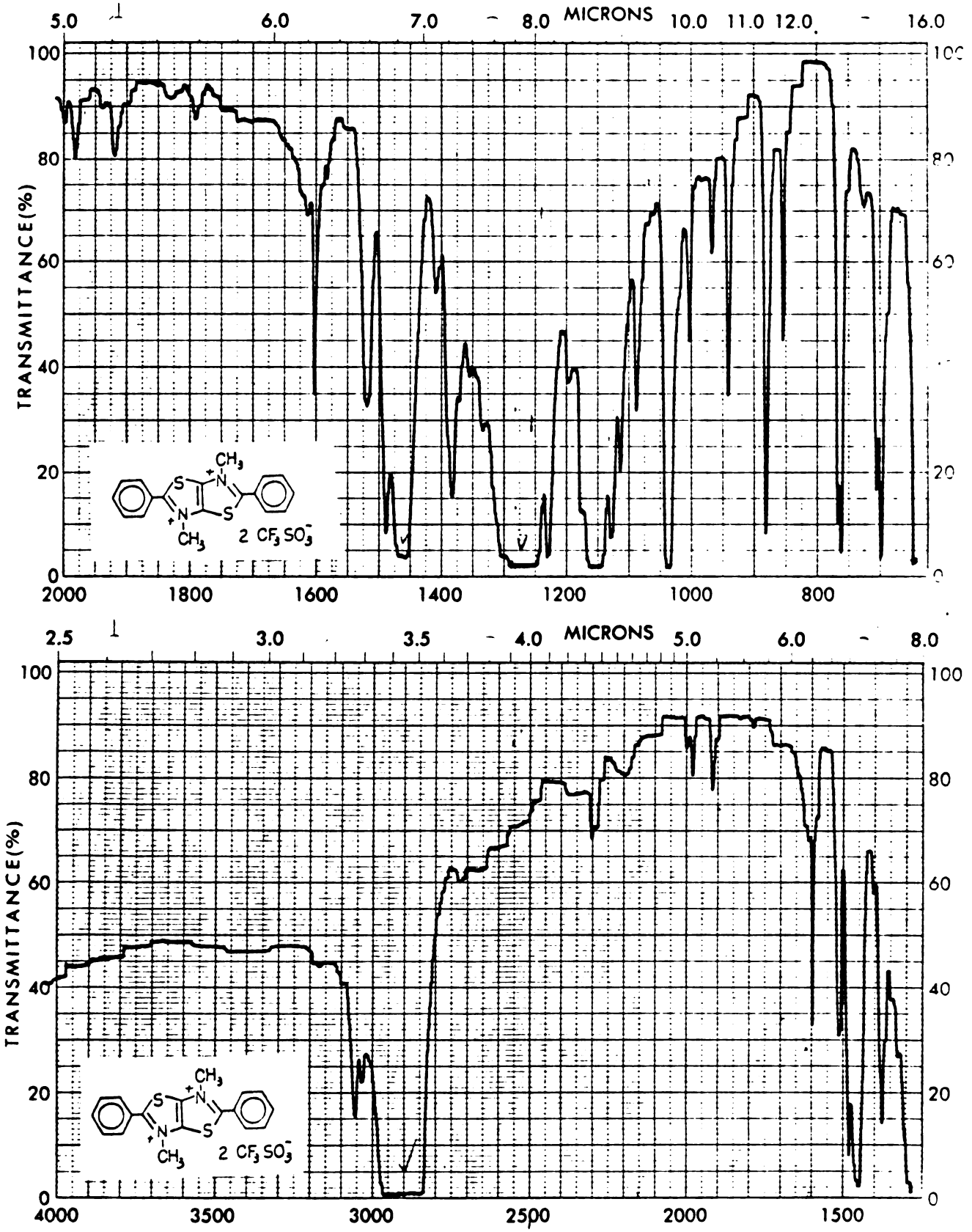


3. Mass spectrum of 2b

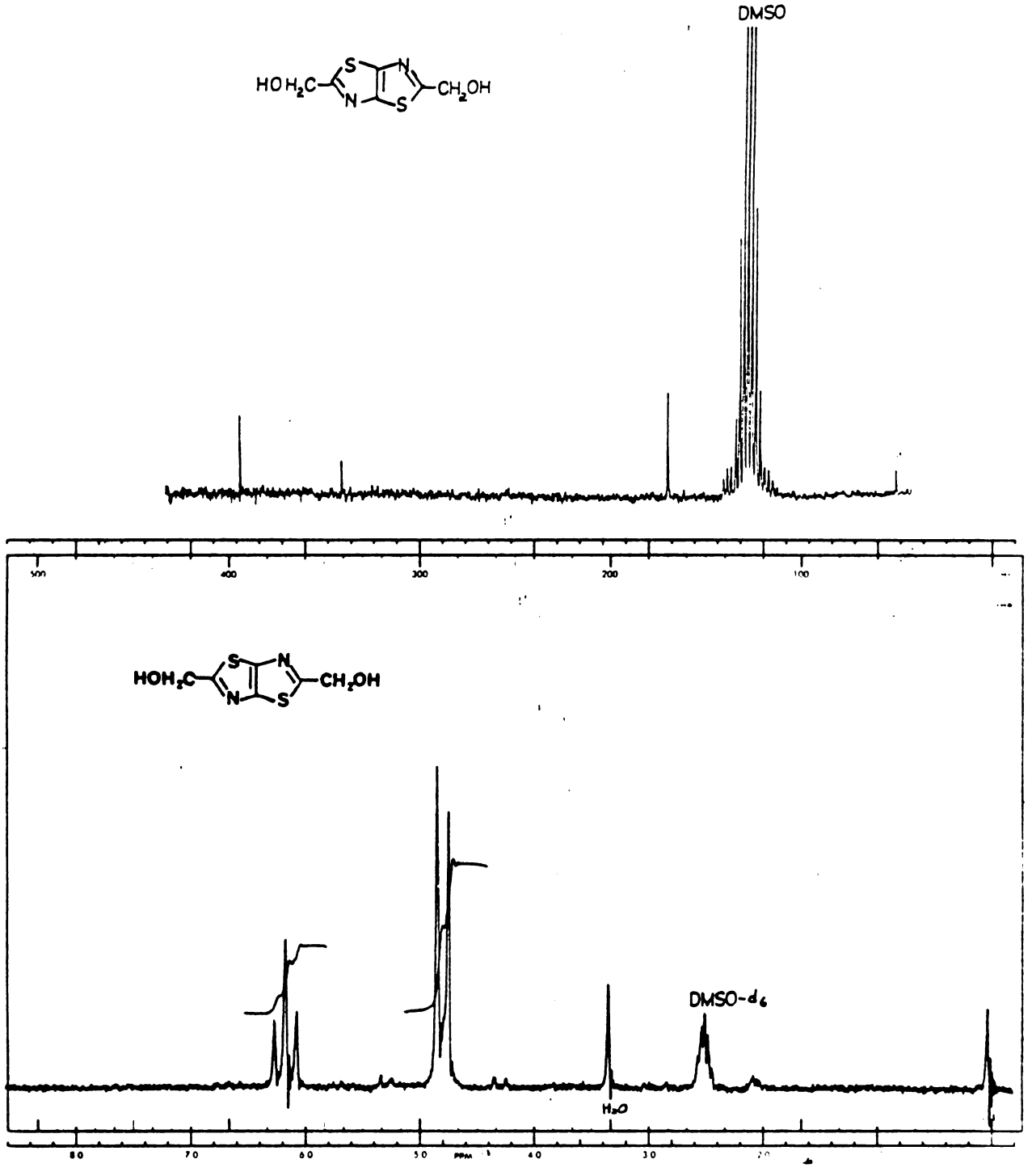




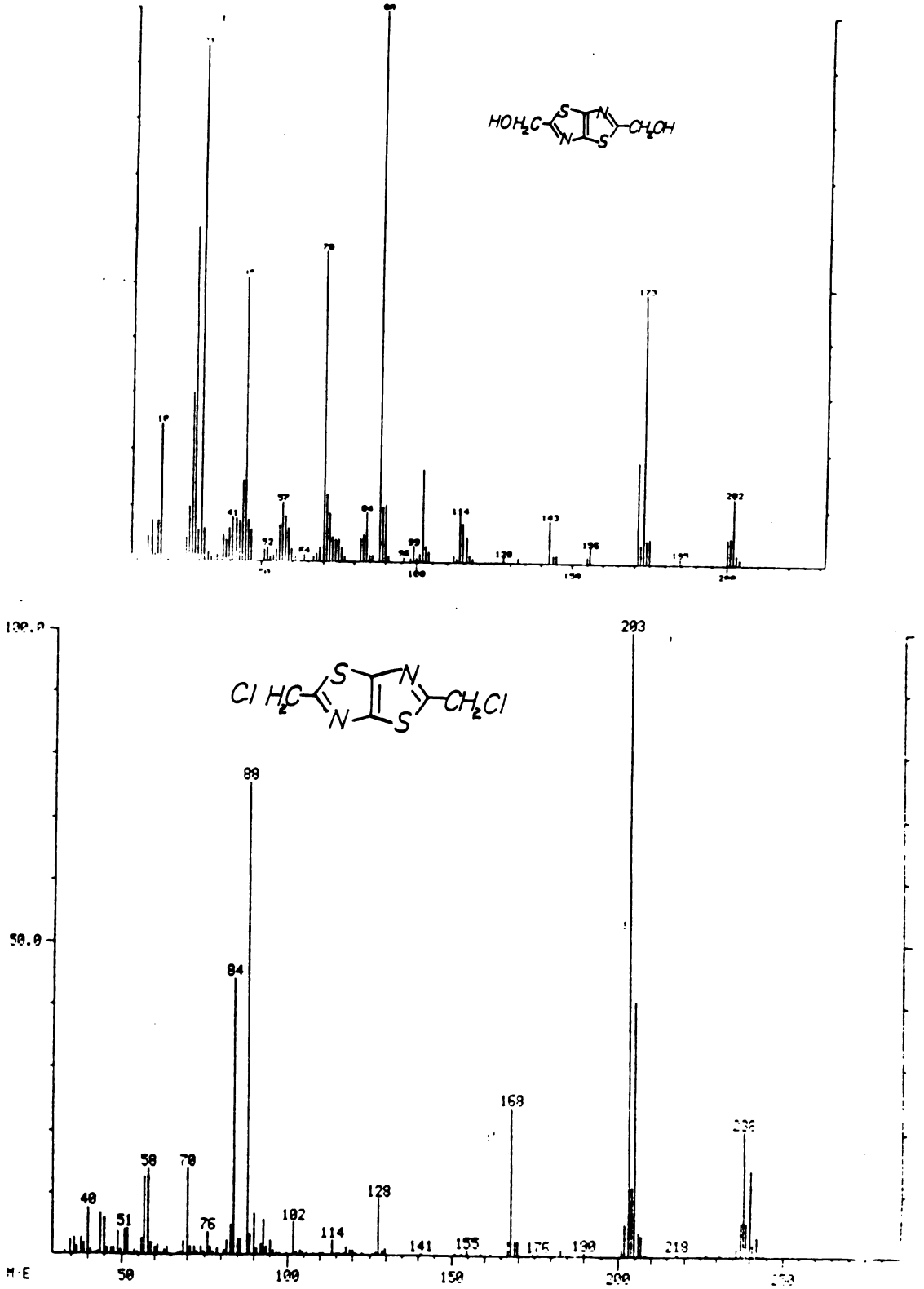
4. PMR spectrum of 19 (top) and 24 (bottom).



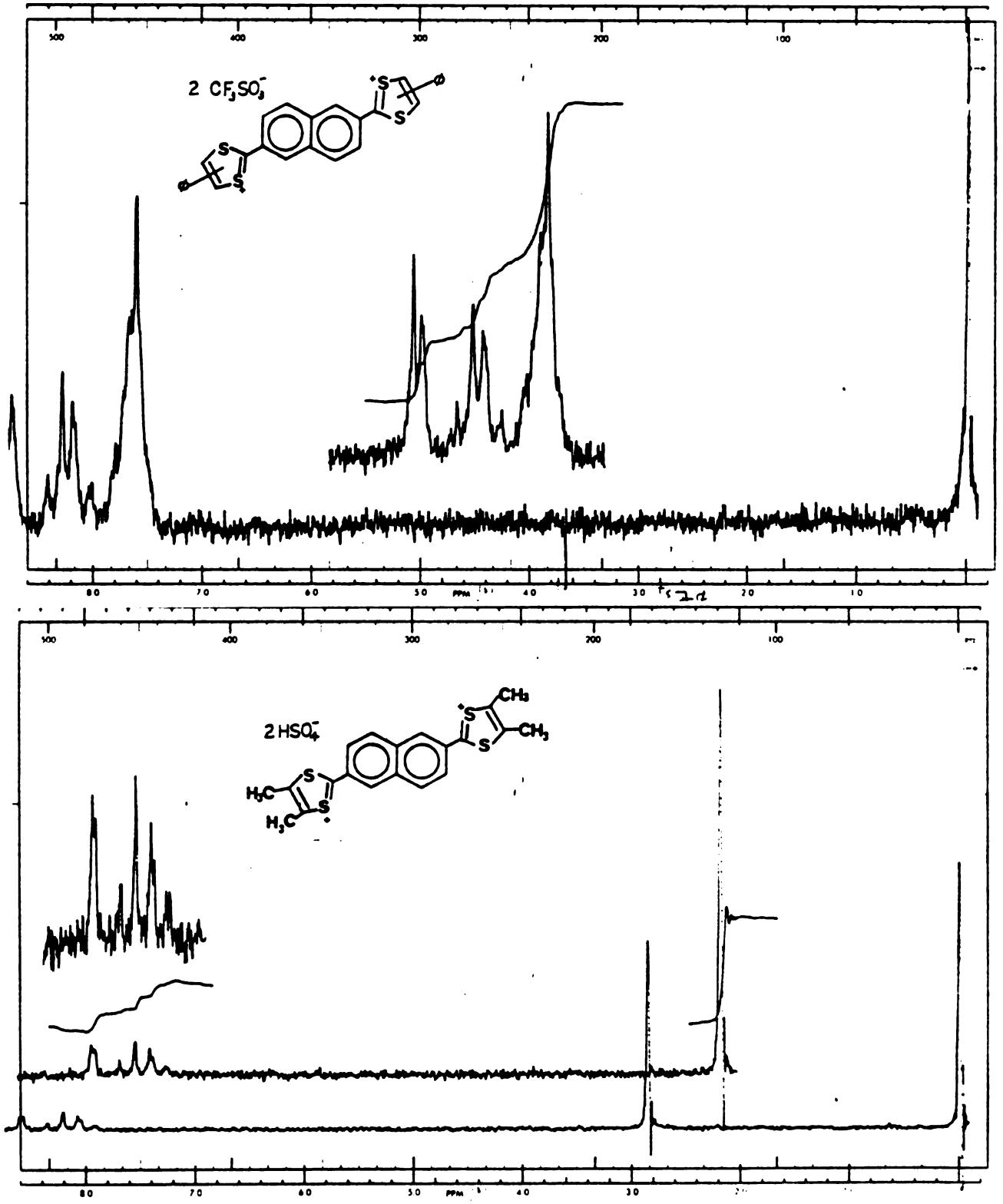
5. Infrared spectrum of 24.



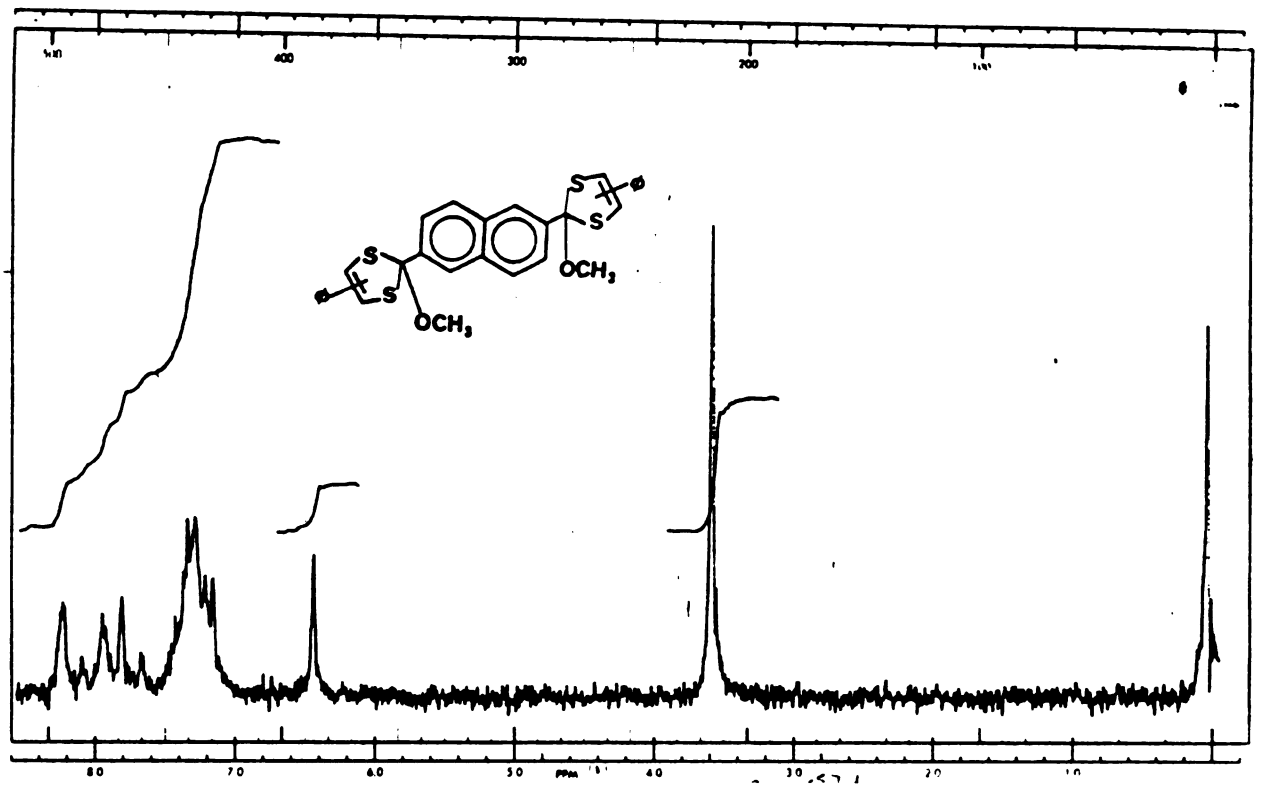
6. ^{13}C NMR (top) and PMR (bottom) of 13



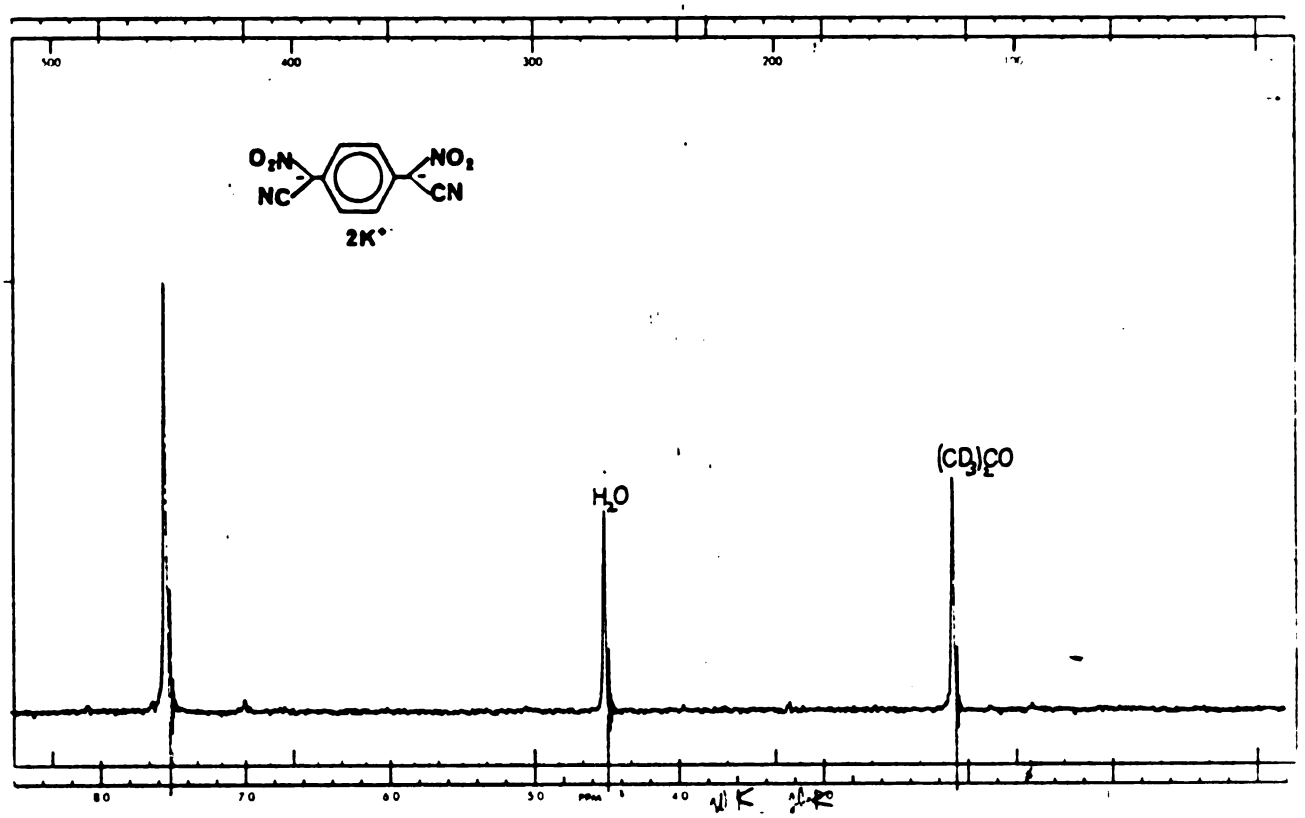
7. Mass spectra of 13 (top) and 14 (bottom)

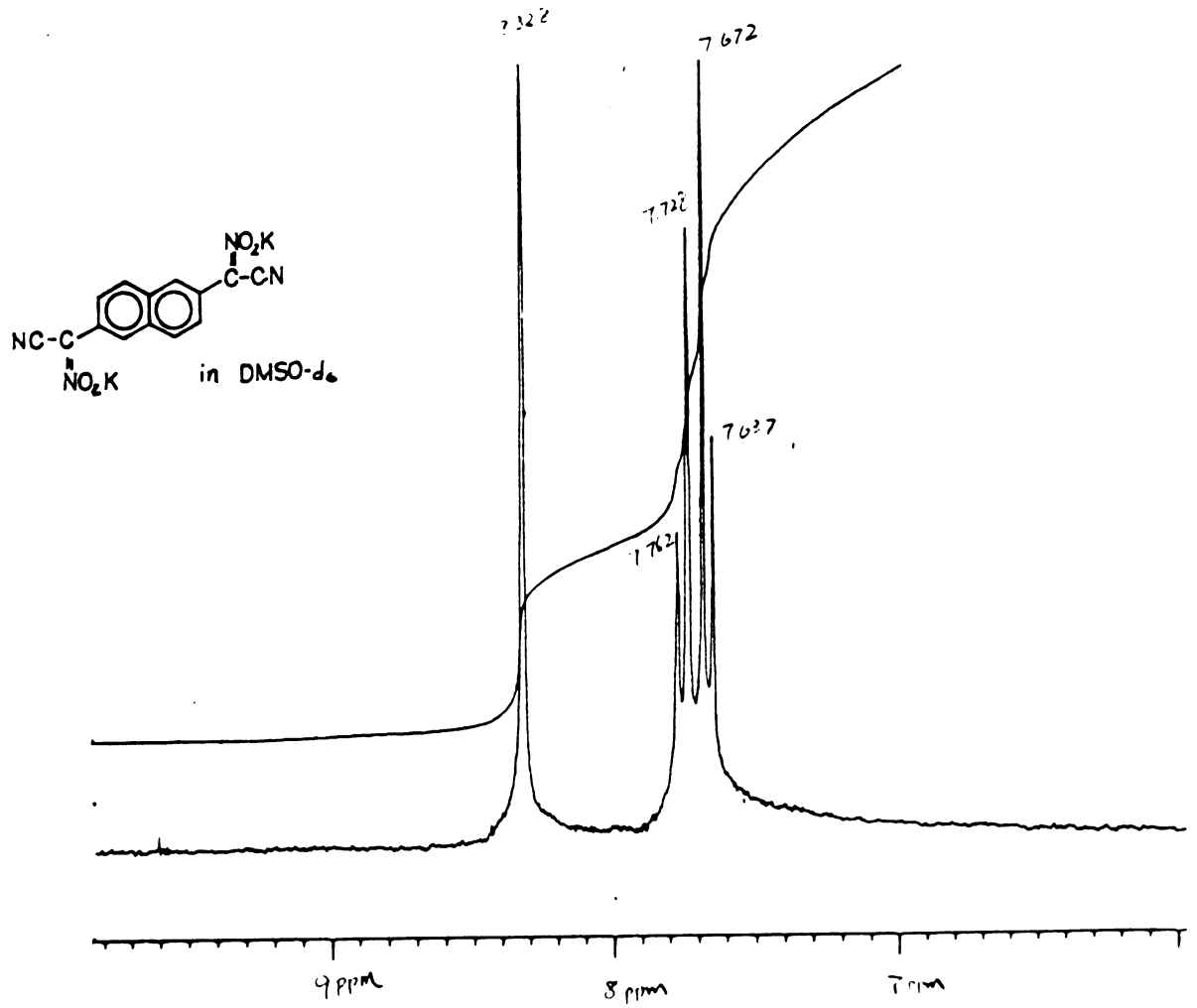


8. PMR spectra of 48b (top) and 47a (bottom)

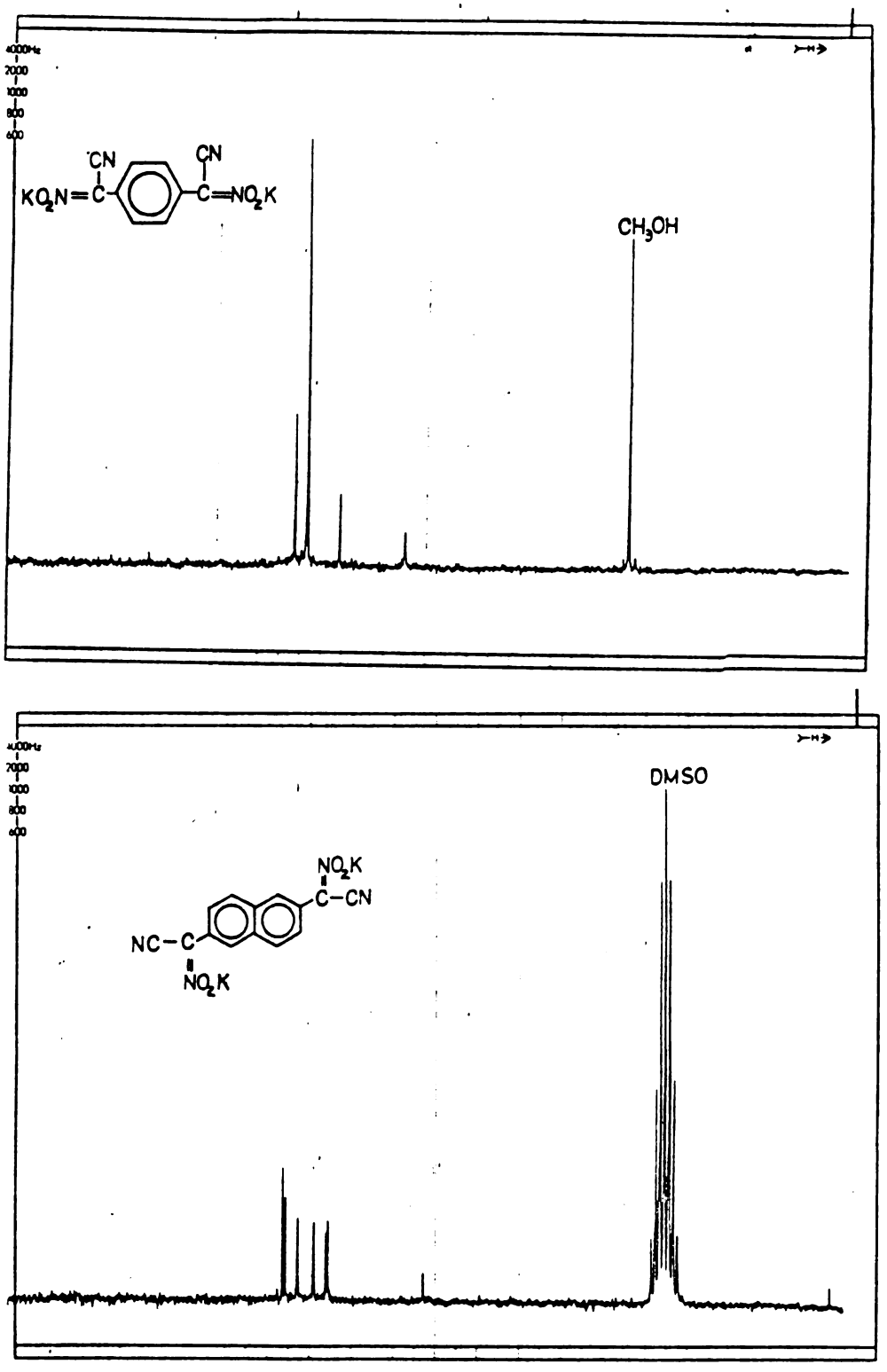


9. PMR spectrum of 49

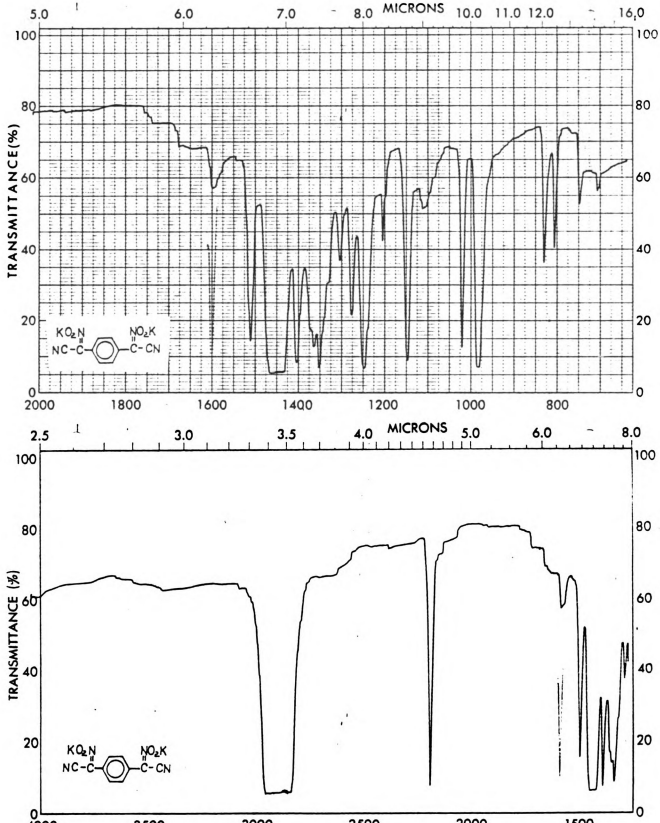




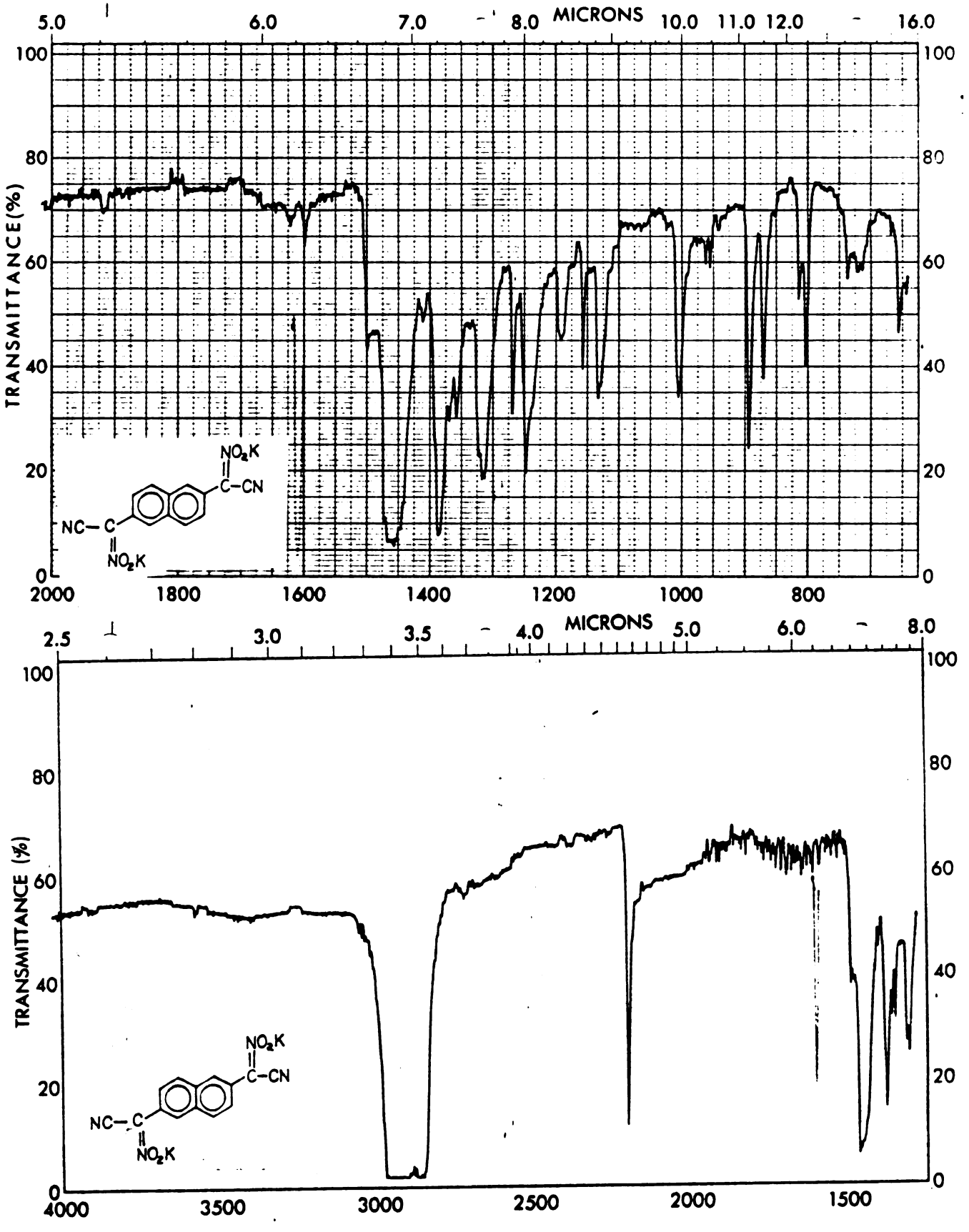
10. PMR spectra of 60 (top) and 63 (bottom)



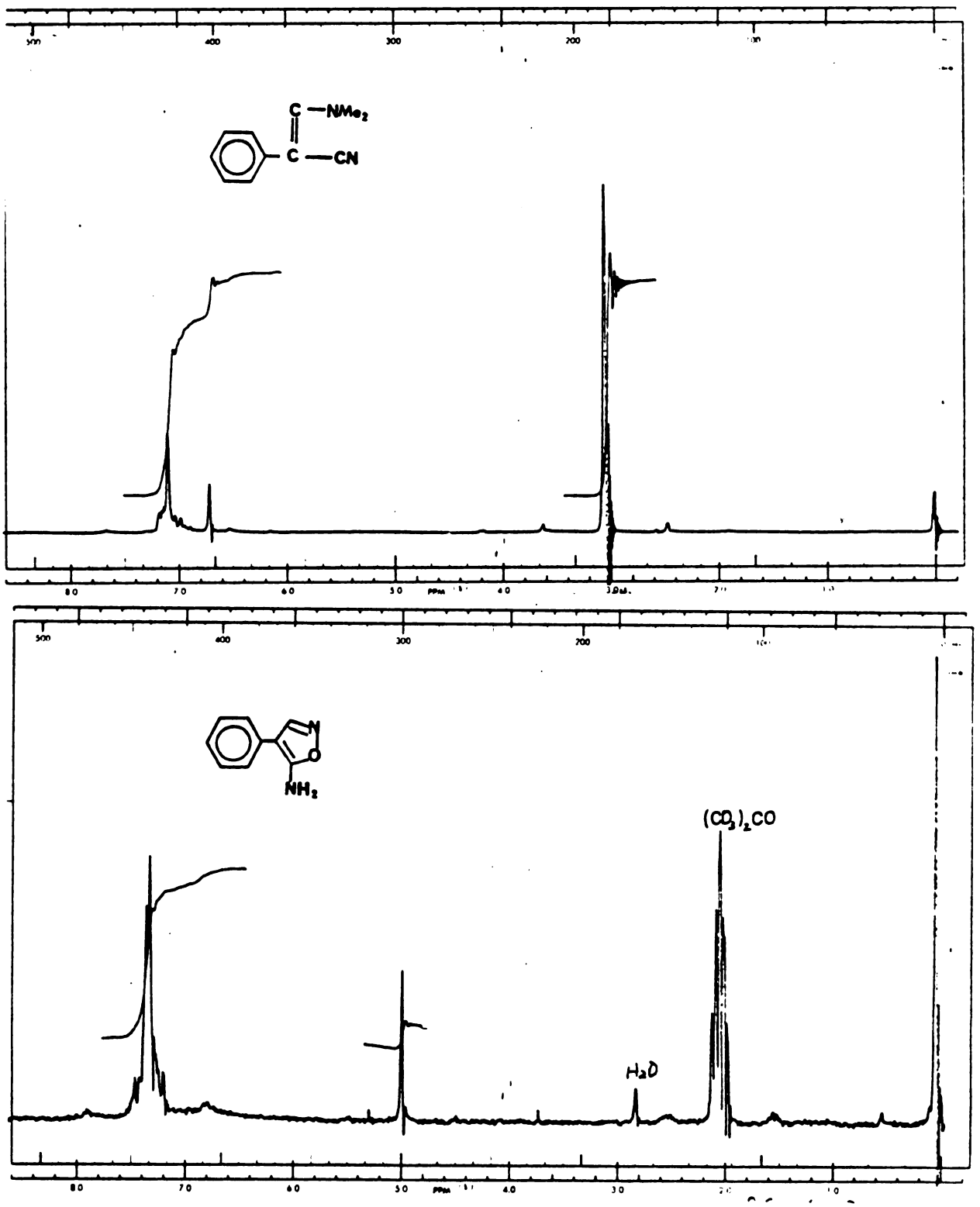
11. ^{13}C NMR spectra of 60 (top) and 63 (bottom)



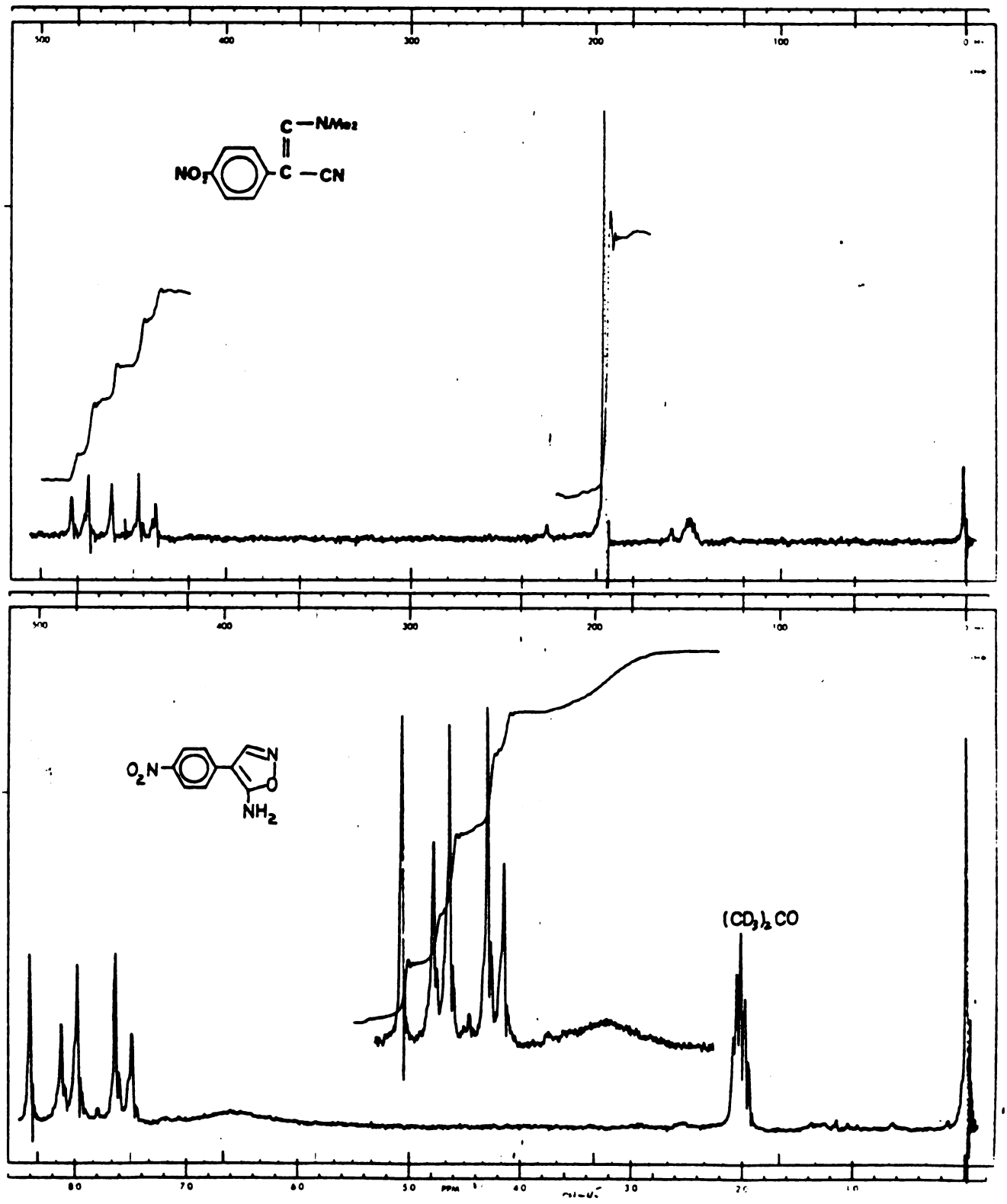
12. Infrared spectrum of 60



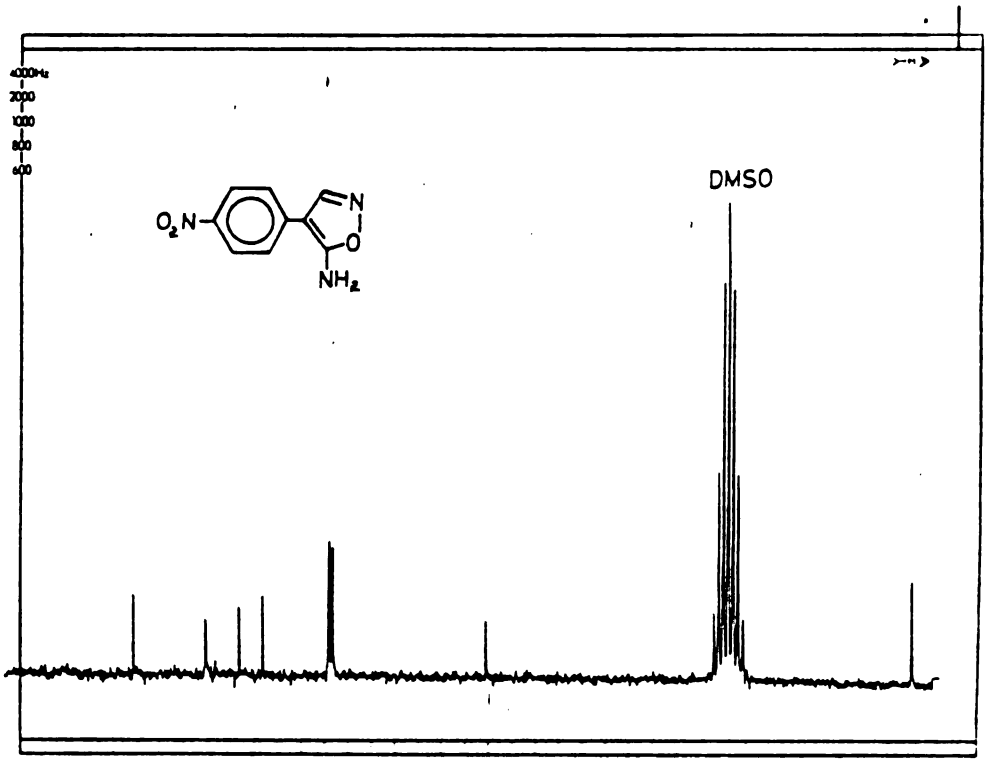
13. Infrared spectrum of 63

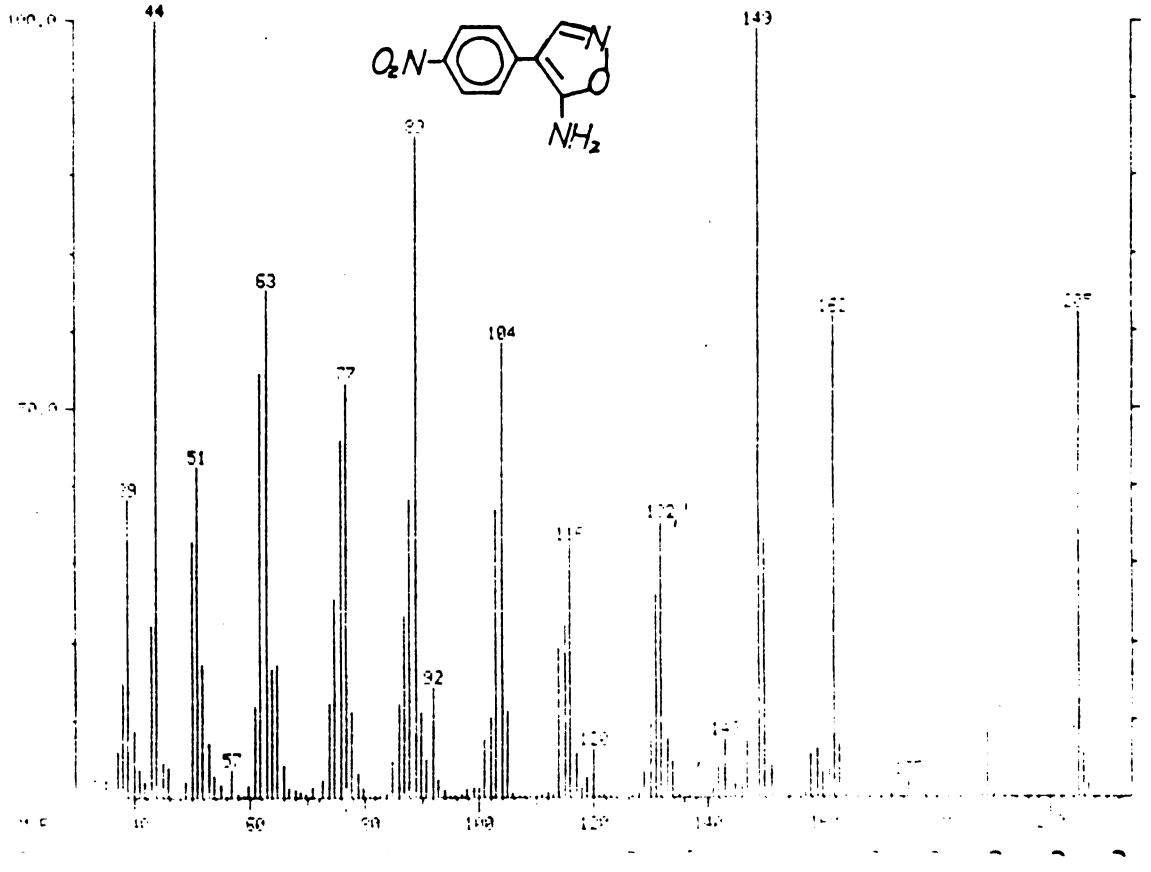


14. PMR spectra of 68b (top) and 69b (bottom)

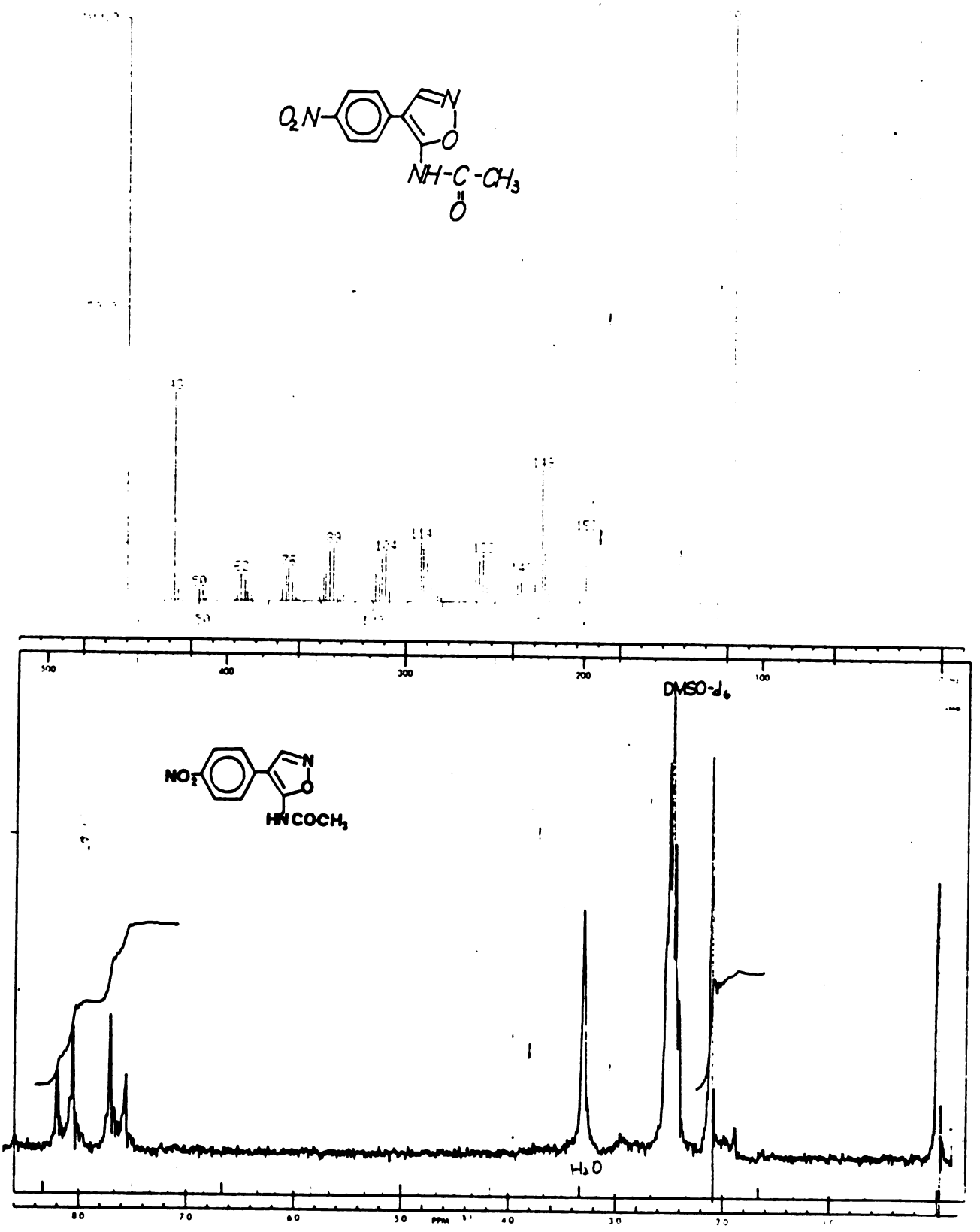


15. PMR spectra of 68a (top) and 69a (bottom)

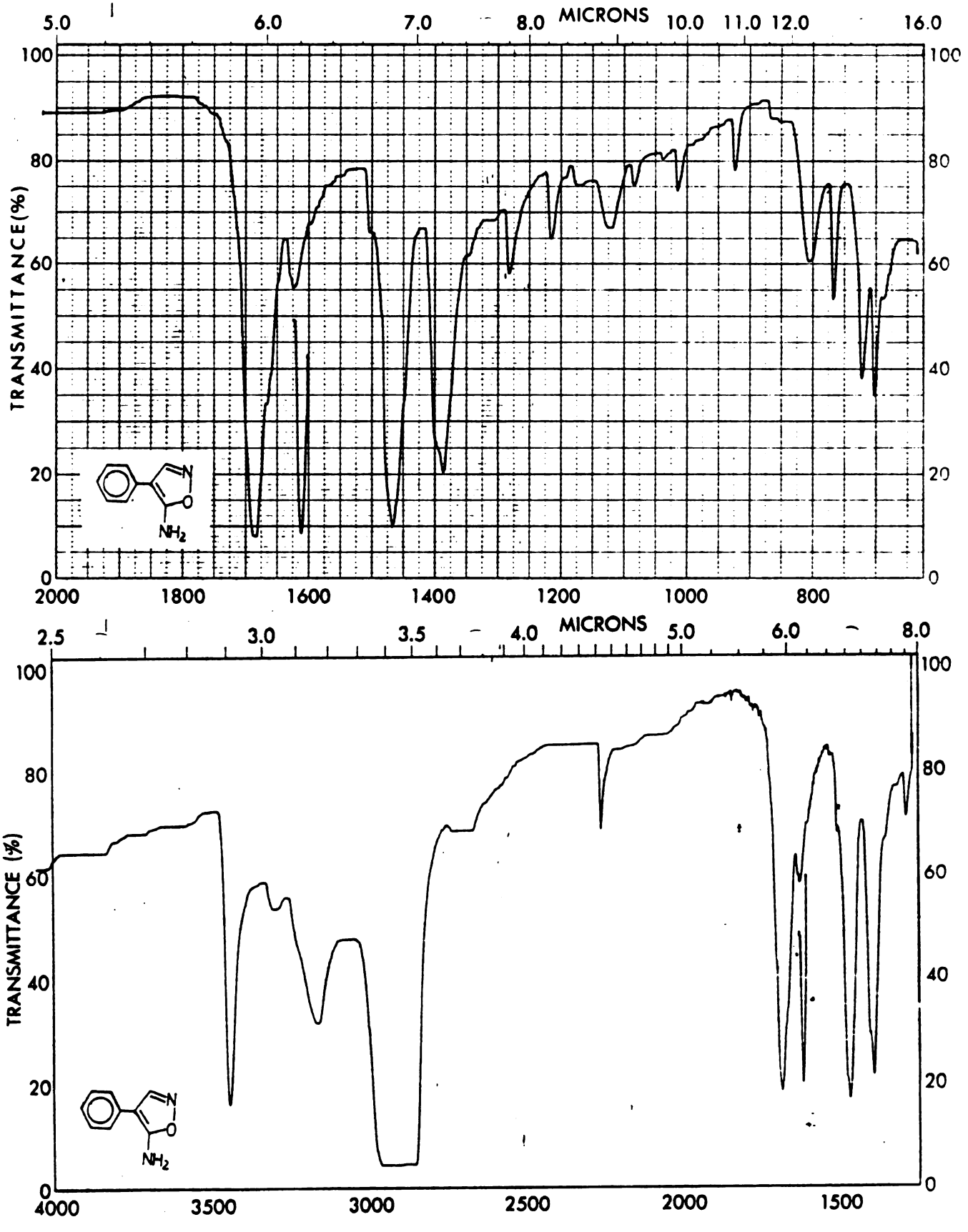




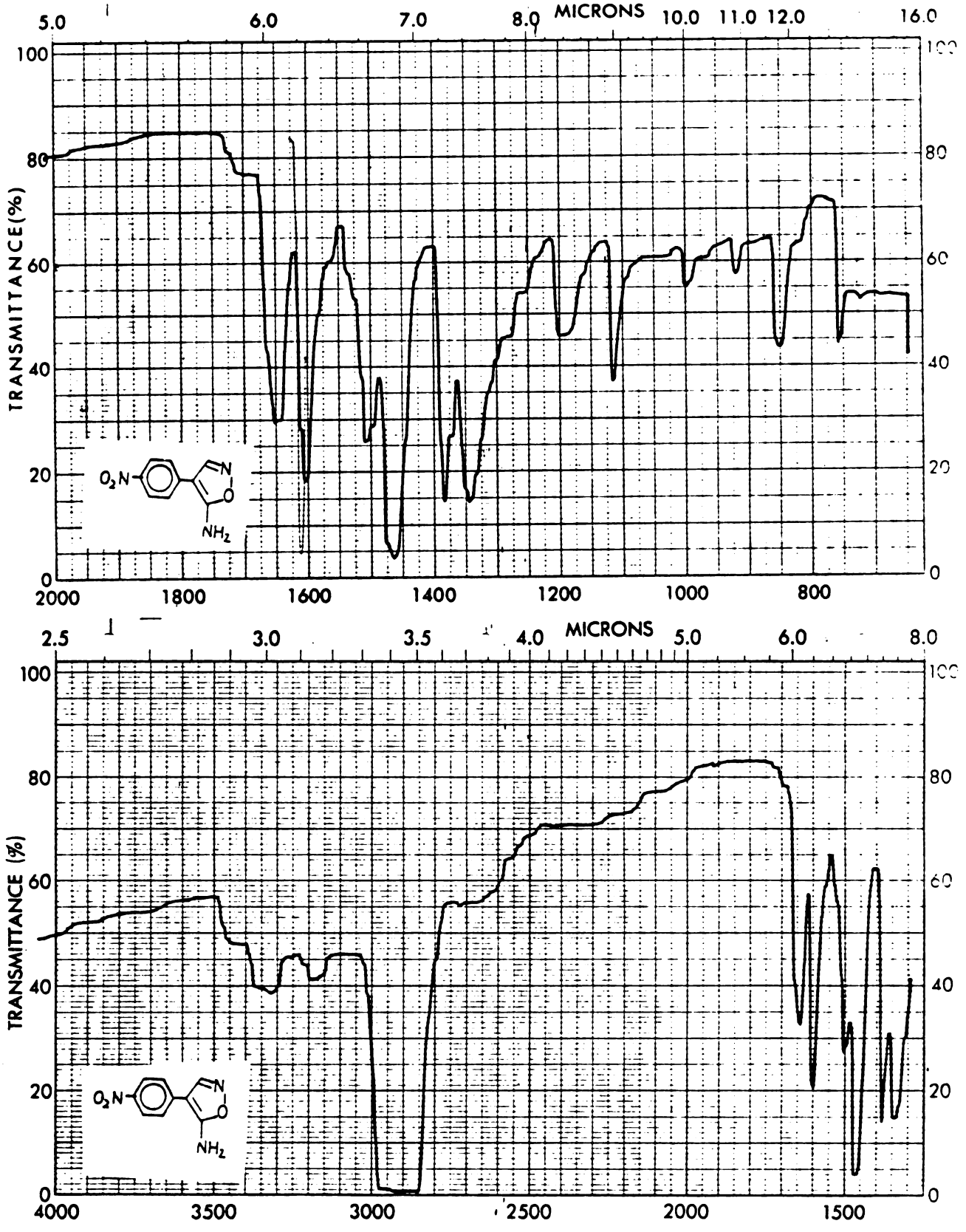
16. ^{13}C NMR spectrum (top) and Mass spectrum (bottom) of 69a



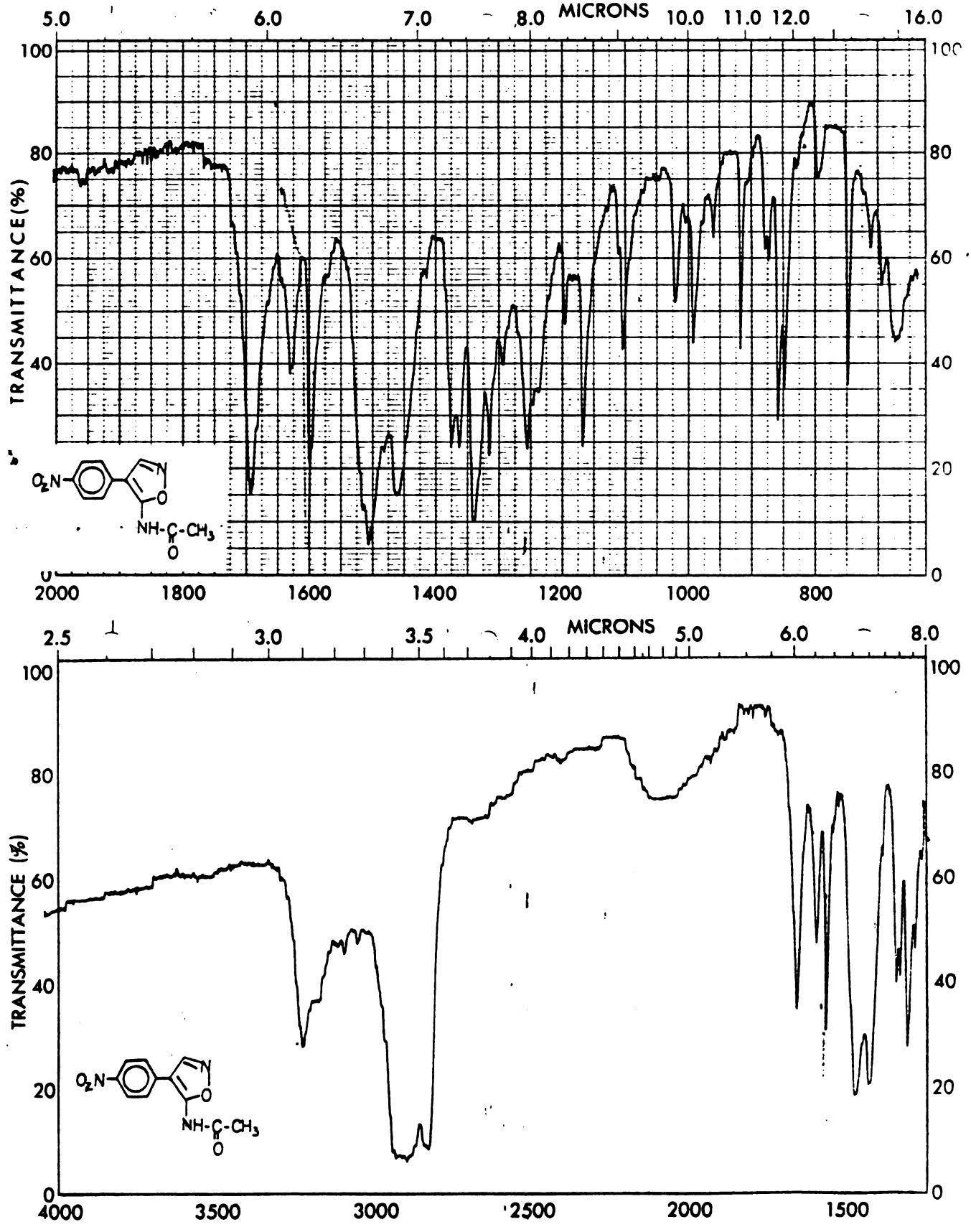
17. Mass spectrum (top) and PMR spectrum (bottom) of 70



18. Infrared spectrum of 69b



19. Infrared spectrum of 69a



20. Infrared spectrum of 70

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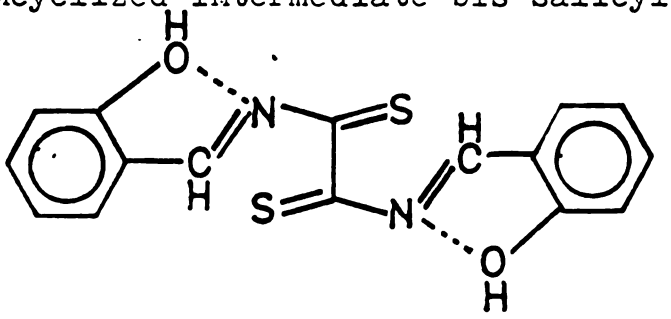

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