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Synthesis of TCNE and TCNQ Derivatives and the Preparation of Conducting Polymers

Michael L. Runge

School of Arts and Sciences
Virginia Commonwealth University

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[redacted]
Codirector of Dissertation

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Codirector of Dissertation

[redacted]
Committee member

[redacted]
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May 5, 1976
Date

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A dissertation submitted in partial fulfillment of
the requirements for the degree of Doctor of
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by

Michael L. Runge

Codirectors: Dr. Raphael M. Ottenbrite

Associate Professor of Chemistry

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Abstract

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ABSTRACT

Tetracyanoethylene and tetracyanoquinodimethan were reacted with various N,N-dimethyl-α,ω-alkyldiamines to produce TCNE and TCNQ diamino and monoamino derivatives. NMR and ir spectra of the monoamino derivatives, 1-(N,N-dimethyl-α,ω-alkyldiamino)-1,2,2-tricyanoethylenes and 7-(N,N-dimethyl-α,ω-alkyldiamino)-7,8,8-tricyanoquinodimethans, indicated that these compounds exhibited strong nitrogen-hydrogen-nitrogen intramolecular hydrogen bonding. This phenomenon was corroborated by molecular weight and preliminary x-ray analyses.

The 1,1-bis(N,N-dimethyl-α,ω-alkyldiamino)-2,2-dicyanoethylene and 7,7-bis(N,N-dimethyl-α,ω-alkyldiamino)-8,8-dicyanoquinodimethan derivatives were polymerized with α,ω-alkyldibromides containing two to six methylene groups to produce the corresponding ionene polymers. Viscosity measurements of the polymers indicated that the TCNE copolymers were generally of higher molecular weight than the corresponding TCNQ copolymers.

The two polymer series were treated with lithium tetracyanoquinodimethanide to produce semiconducting polymers. Electrical measurements indicated that these materials had conductivities on the order of 10^{-7} ohm^{-1} cm^{-1}. Treatment of the polymers with neutral TCNQ resulted in increased conductivities ranging from two to five orders of magnitude.

INTRODUCTION

The ability of matter to conduct an electrical current has been investigated for many decades. The electrical conductivity of different substances varies significantly with their composition. Therefore, materials are generally classified into one of three categories: metallic conductor, semiconductor or insulator (Figure 1). Metallic conductors, such as copper and silver, have conductivities equal to or greater than 10^2 ohm^{-1} cm^{-1}. Substances having conductivities ranging from 10^2 to 10^{-10} ohm^{-1} cm^{-1} are referred to as semiconductors and include graphite, germanium and silicon. Nonconducting materials, such as nylon, sulfur and silicone glass, are insulators and have conductivities less than 10^{-10} ohm^{-1} cm^{-1}.

Although organic materials are not generally capable of conducting an electrical current, a number have been developed as semiconductors and a few have been prepared which approach metallic conductivity. Organic semiconductors have received particular interest since 1941, when it was first apparent that the transfer of π electrons from molecule to molecule might play an important role in the fundamental processes of biological systems.[1,2] Subsequent investigations into the electronic conduction mechanism have so far failed to produce a comprehensive theory of organic conduction. However, two possible transport mechanisms have emerged, the band model and the hopping model. In the band model, which is often applied to metallic conduction, there

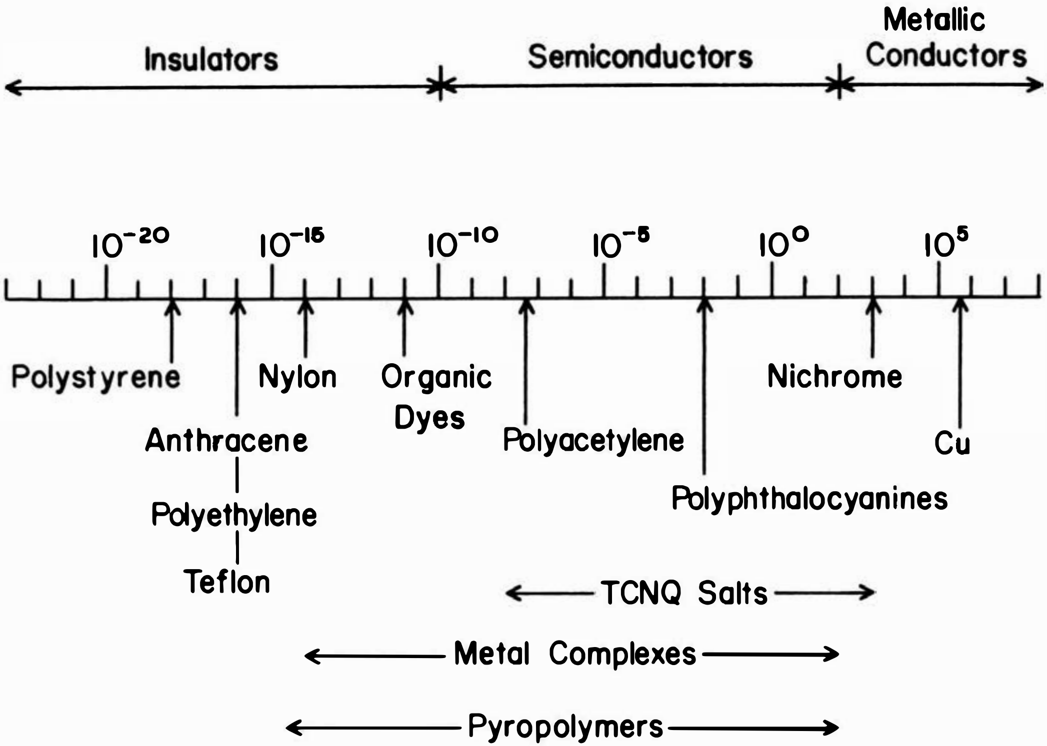


Figure 1: Examples of Conductivity at $300^{O}K$ (ohm^{-1} cm^{-1}).

are two distinct bands, conduction and valence bands, which are separated by an energy gap. When an electron is excited into the conduction band from the valence band, a hole or positive site is left in the latter. The electron in the conduction band and the hole in the valence band both act as charge carriers with high mobility as they move freely within each respective band. In the hopping model, the charge carriers are localized on the molecules themselves. In order for the electrons to pass from one molecule to the next, they must overcome an intermolecular barrier which severely lowers their mobility. Most organic molecules are appreciably separated and are held together only by van der Waals forces which results in poor electronic coupling. Therefore, electron transfer between organic molecules is generally poor. It has been established from these two models that the conductivity σ is dependent upon the concentration of charge carriers n, their charge e, and mobility μ (equation 1).

$$\sigma = ne\mu \tag{1}$$

Presently, most reliable conductivity data have been obtained from single crystals. However, many organic substances, especially polymers, are amorphous materials. Consequently, conductivity measurements are almost totally dependent upon powder techniques. The conductivity of a material in the form of a compressed powder can be obtained by measuring its resistance R (in ohms) and using equation 2;

$$\sigma = t/RA \tag{2}$$

where A is the contact area (in cm^2) of the electrode and t is the thickness (in cm) of the pellet. The conductivity, which is the reciprocal of resistivity ρ, is reported in units of $ohm^{-1}\ cm^{-1}$ or mho cm^{-1}. The conductivity of a semiconductor increases with a rise in temperature according to equation 3, where E_A is the energy of activation, k the Boltzmann constant, T the absolute temperature,

$$\sigma = \sigma_o \exp(-E_A/kT) \tag{3}$$

and σ_o a constant. The increase in conductivity may be attributed to an increase in charge carrier mobility, an increase in the concentration of charge carriers, or both. The semiconductor behavior is opposite that of a metallic conductor, whose conductivity decreases with a rise in temperature.

Measurements of the Seebeck and Hall effects have been used to elucidate the conduction mechanism of organic materials. The Seebeck effect is a thermoelectric effect measured by a coefficient whose resultant sign is the same as the sign of the majority carrier. In simple cases, the Hall effect indicates the magnitude of the mobility of the majority carrier and whether the mode of conduction is electronic or ionic. The Hall mobility for most organic materials is usually low and has been measured only in a few cases.

Specific monomeric as well as polymeric organic materials have been investigated for their potential as electrical conductors.[3,4] The polymeric systems are of particular interest since macromolecules of high conductivity (low resistivity) can be expected to possess useful mechanical and thermal properties, such as high tensile strength, variable rigidity and high softening temperature, which are lacking in the usually microcrystalline or amorphous monomeric materials. The polymeric semiconductors could be used as conductive surfaces for electroplating nonconductors, for printed circuit boards, for conversion of solar energy into electrical energy, and as photoconducting films for copying. The expected plastic properties of high molecular weight polymeric semiconductors would allow them to be fabricated into semiconducting films, filaments and molded articles.

There are several methods by which polymers with low electrical resistance can be prepared. For example, conducting materials have been obtained by doping nonconducting polymers with conducting fillers, such as a metal powder or special types of carbon black.[5] The nonconductive polymer functions as a matrix to hold the conducting filler together. These evenly dispersed particles render the polymer conductive when a sufficient number of them have been incorporated and when there exists a high degree of contact between them. Usually a high concentration of filler is required in order to achieve low resistivity. Although these materials are electrical conductors, they also have some resistance which produces heat during the passage of an electrical current. The heat causes the polymer to expand, and upon expansion the conducting particles move apart, decreasing the degree of contact and the conductivity of the material until failure occurs.

Another type of conducting polymer has been made by pyrolyzing monomeric or polymeric organic substances to produce carbonaceous materials.[6] Polymers of this type are referred to as pyropolymers and are presumed to have a high degree of conjugated unsaturation. The electrical properties of pyropolymers are subject to the conditions of their preparation; for example, pyrolyzed polyacrylonitriles have conductivities ranging from 8×10^{-2} to 10^{-10} $\text{ohm}^{-1}\ \text{cm}^{-1}$, depending on the pyrolysis temperature.[7,8] This kind of material usually has the disadvantage of being nonfabricable; i.e., it is insoluble or nonsoftening. Further, since pyrolysis is a decomposition process, the products are of variable composition and intractable.

The most promising mode for producing conducting polymers is probably by direct synthesis. Since conduction in organic materials seems to be dependent on the presence of delocalized electrons to serve as charge carriers, it would be expected to be innate in polymers which have a high degree of conjugated unsaturation in the chain.[9,10] This type of polymer synthesis has met with limited success, producing materials which fall predominantly in the insulator-semiconductor region (Table 1). The low conductivity of these highly unsaturated polymers might be explained by the fact that they can undergo reactions such as proton or hydride shifts and Diels-Alder which lead to an interruption of the conjugation. These breaks in conjugation, which may take the form of crosslinking, cyclization and isolated double bonds, lower the conductivity of the system. Another approach to the synthesis of conducting polymers has been to incorporate donor-acceptor complexes into the polymer chain. This can be accomplished by linking donors to a macromolecular backbone and reacting the resulting polymer with suitable acceptors,[12-15] as has been done with the donors 10-methylphenothiazine and 4-(methylthio)anisole. Polystyrene and polyvinylnaphthalene have also been treated with acceptors, tetracyanoethylene and chloranil, to produce polymer complexes.[16] The above complexes have conductivities ranging from 3.3×10^{-8} to 5.5×10^{-15} $\text{ohm}^{-1}\ \text{cm}^{-1}$, which places them in the categories of insulators and semiconductors.

Investigations into the conductivity of organic polymers have produced many semiconducting materials. A wealth of information has

Table 1

The Conductivities of Conjugated Polymers[11]

Conjugated Polymer	σ ohm^{-1} cm^{-1} Room Temperature
Polyacetylene	
crystalline	10^{-5} to 10^{-8}
amorphous	10^{-9} to 10^{-12}
Polyphenylacetylenes	10^{-15} to 10^{-16}
Poly-ynes	10^{-15}
Pyropolymers	0.95 to 10^{-8}
Polyphthalocyanines	2.5×10^{-2} to 10^{-8}

been accumulated, but its complete interpretation has not been realized. Therefore, the conduction mechanism for such materials remains uncertain. The relationship between charge carrier mobility and macromolecular structure has yet to be determined. Nevertheless, the theoretical possibility of a polymeric superconductor has been proposed.[17,18] It has been suggested that a long unsaturated polyene chain which has highly polarizable dye molecules attached at regular intervals could act as a superconductor. The charge would resonate between the dye molecules as it moves down the polyene chain. A polymer such as the one described has not yet been synthesized, but an organic charge-transfer complex[19] has been made[20] which exhibits conductivity similar to metals at low temperatures.[21] The complex is synthesized by mixing solutions of tetrathiofulvalene and 7,7,8,8-tetracyanoquinodimethan.

The synthesis of 7,7,8,8-tetracyanoquinodimethan[22] (TCNQ) in the early sixties expanded the field of organic semiconductors. TCNQ, which forms stable charge-transfer complexes[23,24] with intermediate to high resistivities (10^3 to 10^{12} ohm cm), can also readily accept one electron to form a stable anion radical ($TCNQ^{\dot{-}}$).[24] Representative resonance structures for $TCNQ^{\dot{-}}$ are shown in Figure 2. The ability to form the stable anion radical has made possible the synthesis of highly conducting TCNQ salts, an important contribution to the area of electronic conductivity by purely organic materials.

TCNQ has been found to form two types of salt-like derivatives, each involving a complete electron transfer to TCNQ. The first are simple salts represented by $M^{+n}(TCNQ^{\dot{-}})_n$, in which M may be an organic or metal cation. These salts are characterized by intermediate to high resistivities[25] (10^4 to 10^{12} ohm cm).

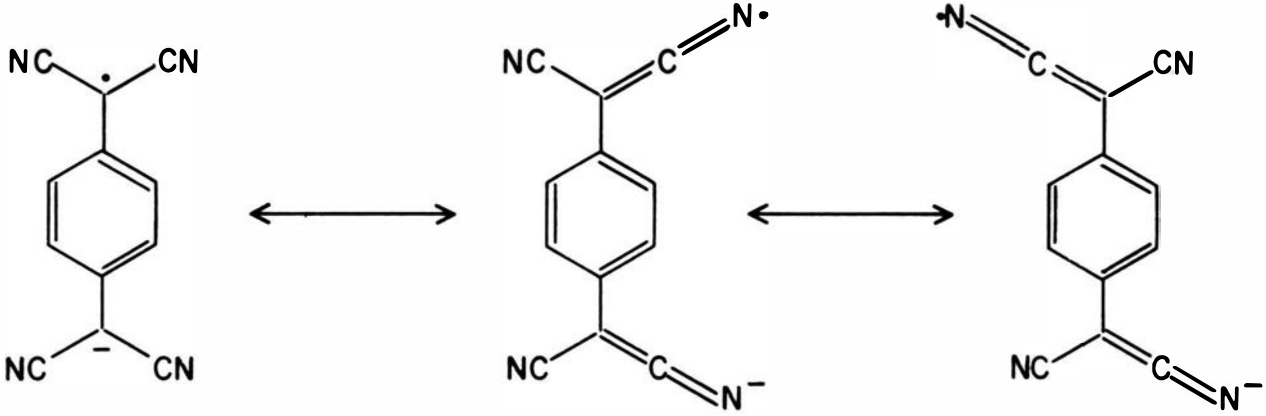


Figure 2: Representative Resonance Forms of TCNQ$^{\bar{\cdot}}$.

Although some of these salts have been synthesized by mixing a solution of TCNQ with a solution of the donor, which results in the precipitation of the desired moiety, many have been conveniently prepared using lithium tetracyanoquinodimethanide[24] (LiTCNQ). Lithium tetracyanoquinodimethanide has been prepared by the reaction of lithium iodide with TCNQ to yield the $TCNQ^{\overline{\cdot}}$, which forms an ion pair with the lithium cation.[24] LiTCNQ, upon reaction with organic compounds containing quaternary nitrogen atoms, forms dark-colored paramagnetic electrically conducting salts (Figure 3). Salts similar to tetraethylammonium tetracyanoquinodimethanide may be synthesized from the large number of ammonium, phosphonium and arsonium compounds.[24,26,27] The conductivities of these compounds are on the order of 10^{-6} ohm^{-1} cm^{-1}. However, the conductivity can be increased by the addition of the non-paramagnetic neutral tetracyanoquinodimethan ($TCNQ^{o}$). The complexes formed in this manner are represented by $R^{+}(TCNQ^{\overline{\cdot}})_{x}(TCNQ^{o})_{y}$, where R^{+} represents an organic molecule containing an ammonium, phosphonium or arsonium cation; x and y are the number of paramagnetic and neutral TCNQ molecules, respectively. The conductivities of these $TCNQ^{o}$-$TCNQ^{\overline{\cdot}}$ complexes approach 1 ohm^{-1} cm^{-1}. The N-methylquinolinium TCNQ salts are an example of this phenomenon (Table 2).

Polymeric analogs of the TCNQ salts have also been prepared.[28] This has been accomplished by synthesizing polymers of known structure from which polymeric cations can be created. Polymeric amines are one possibility since they could then be quaternized using an alkyl halide or sulfate. Treatment of the quaternized polymer with LiTCNQ produces the polymeric TCNQ salt (Figure 4). Lupinski and coworkers[28] prepared this type of polymer using 4-vinylpyridine, 2-vinylpyridine, 4-dimethyl-

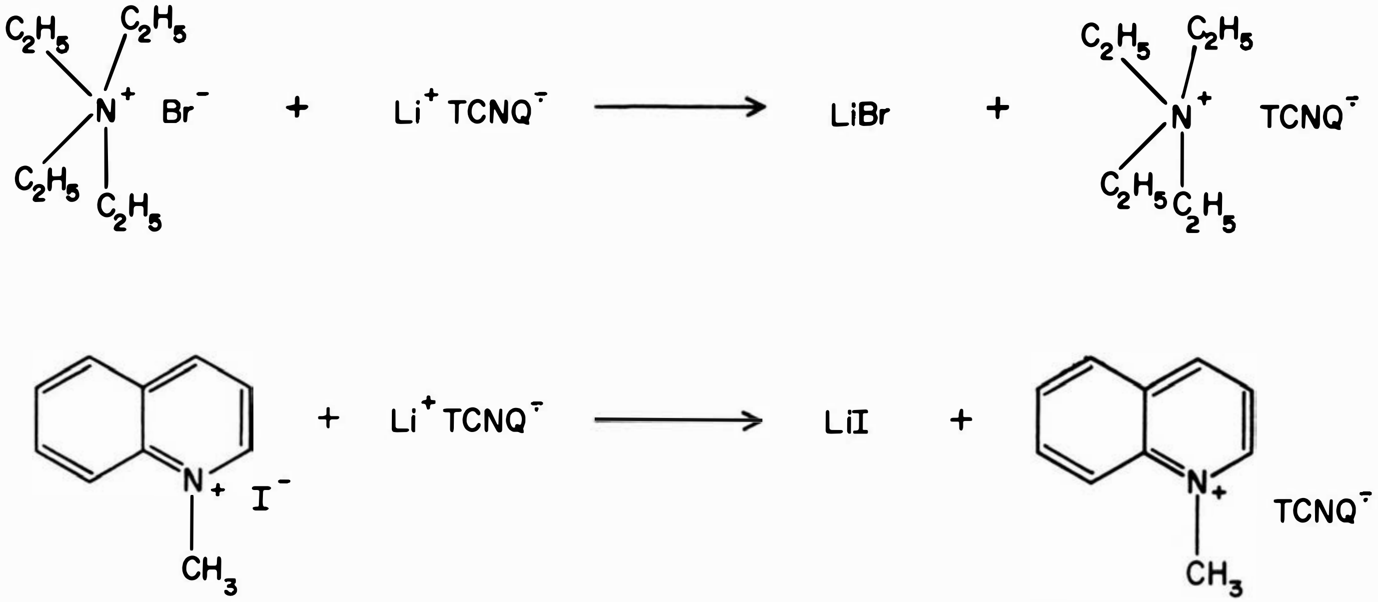
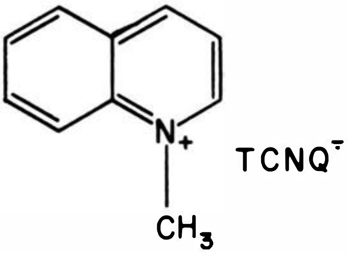


Figure 3: Formation of Ammonium Tetracyanoquinodimethanide Salt.

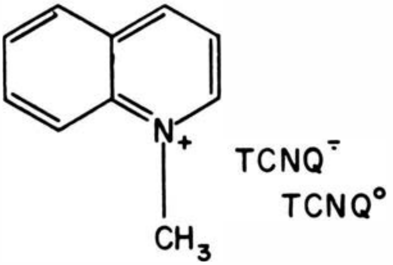
Table 2

The Conductivities of the Simple and Complex TCNQ Salts of N-Methylquinoline[24]



σ ohm^{-1} cm^{-1}

10^{-7}



σ ohm^{-1} cm^{-1}

0.3

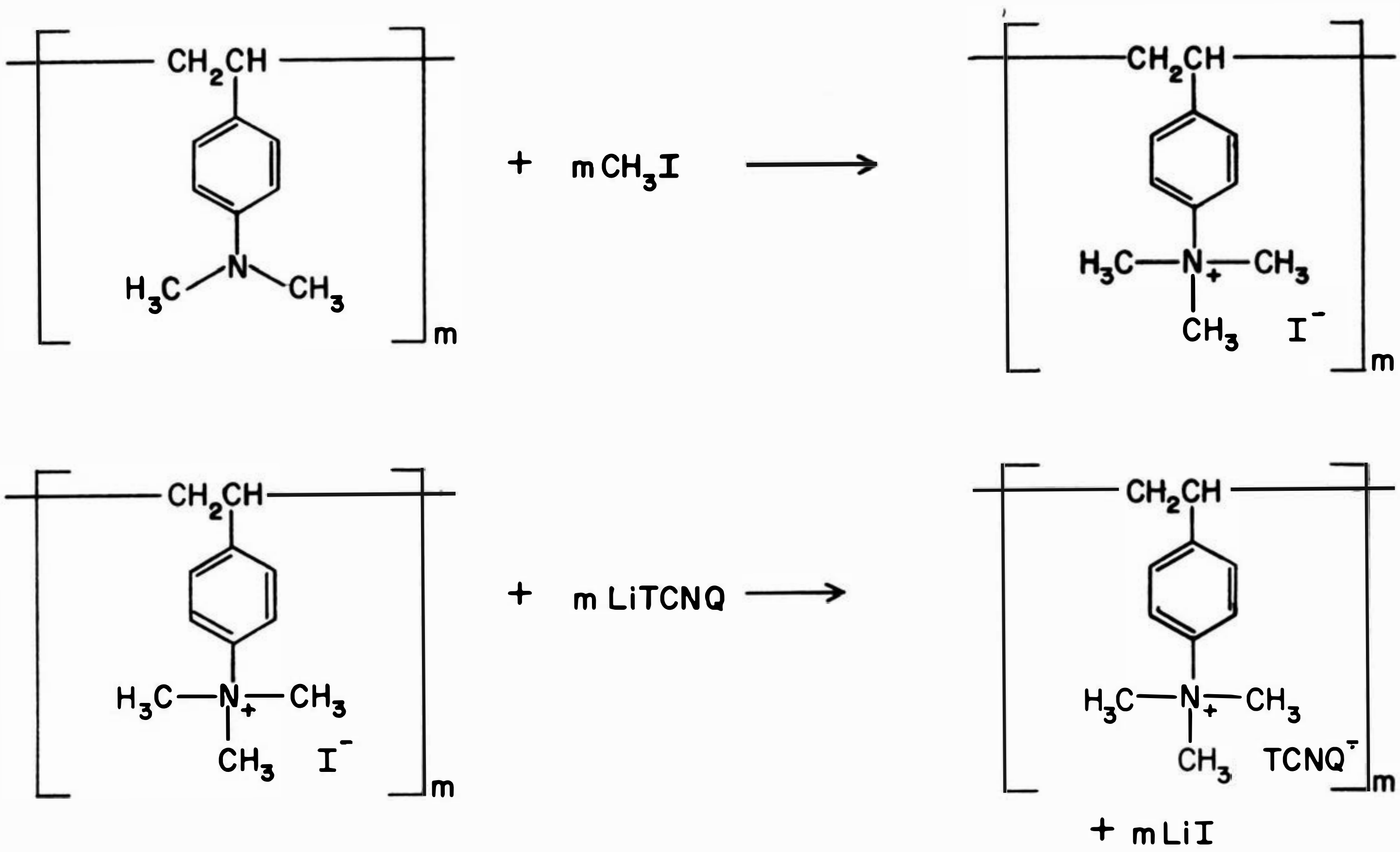


Figure 4: Formation of a Polymeric Tetracyanoquinodimethanide Salt from Poly-4-dimethylaminostyrene.

aminostyrene and N-vinylimidazole. A significant increase in the conductivity was observed with addition of $TCNQ^o$ (Table 3).

Ionene polymers, another class of quaternary ammonium polymers which can be converted to conducting TCNQ salts, have been reported[29-32] by Rembaum. The polymers are synthesized by utilizing the Menschutkin reaction,[33] which is a well-known process for the formation of quaternary ammonium salts from tertiary amines. Examples of the reaction involved in the formation of polymeric ionenes are shown in Figure 5. The solution properties[34] as well as the kinetics[35] for the formation of aliphatic ionene polymers have been studied.

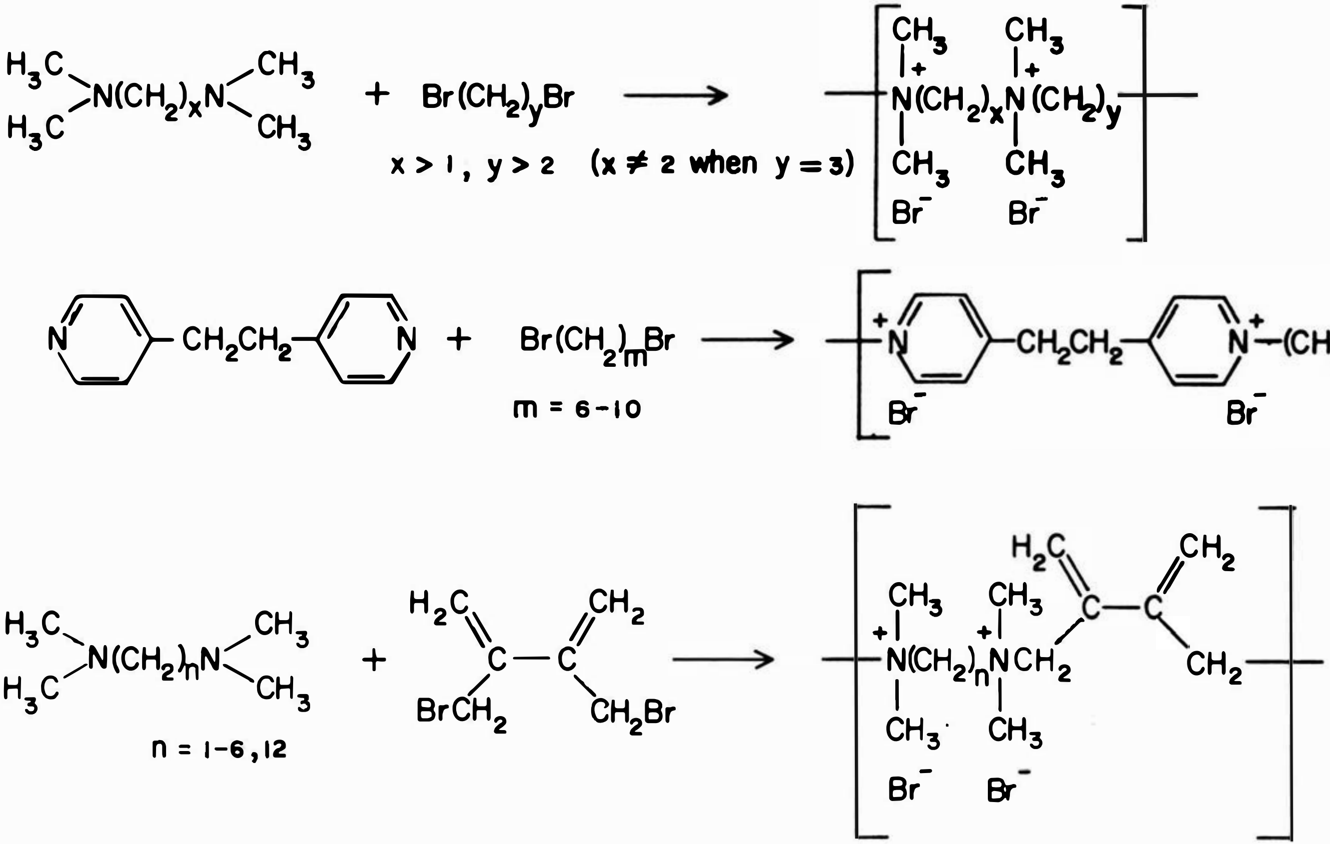
Electrically conducting polymers have been prepared from the aliphatic ionenes by their reaction with LiTCNQ in the presence and in the absence of $TCNQ^o$. Representative monomeric units of the ionene polymers have also been synthesized (Figure 6) and treated with LiTCNQ and LiTCNQ with $TCNQ^o$. The conductivity of these polymeric and monomeric $TCNQ^{\overline{\cdot}}$ salts increased with the addition of $TCNQ^o$ (Tables 4 and 5).

The electrical conductivities of the above compounds are attributed to the TCNQ molecules. This has been substantiated by the fact that the highly conjugated cyanine dyes do not yield TCNQ salts with higher conductivities than the aliphatic ammonium salts.[36] X-ray techniques were used to determine that the TCNQ molecule forms stacked columns.[27,37] The direction of highest conductivity was perpendicular to the plane of the molecule.[37] The mode of conduction is considered to be electronic. This has been corroborated by temperature and pressure dependence[38] studies as well as by experiments in which a current was passed for prolonged periods without change in conductivity or observable polarization effects.[28] The conductivity of the simple salts was generally

Table 3

Conductivities of the Polyquaternary Ammonium TCNQ Salts Produced by Lupinski and Coworkers[28]

Monomer	Molecular Weight	Quaternizing Agent	Mole % Quaternized	$\sigma_{300^\circ k}$ ohm^{-1} cm^{-1}	
				TCNQ$^{\cdot}$ only	with 15% TCNQ^{o} by wt.
4-Vinylpyridine	122,000	C_4H_9I	87	$<10^{-10}$	3.2×10^{-5}
2-Vinylpyridine	2.2×10^6	$(CH_3)_2SO_4$	100	5×10^{-10}	1.0×10^{-4}
	2.2×10^6	CH_3I	60	10^{-10}	2.0×10^{-6}
	2.2×10^6	CH_3I	15	10^{-10}	3.6×10^{-4}
4-Dimethylaminostyrene	730,000	CH_3I	75	10^{-10}	2.1×10^{-3}
Styrene-1-vinylpyridine	730,000	C_4H_9I	80	10^{-10}	1.1×10^{-3}
N-Vinylimidazole	730,000	CH_3I	100	10^{-10}	9.5×10^{-3}



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29

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Figure 5: Formation of Ionene Polymers.

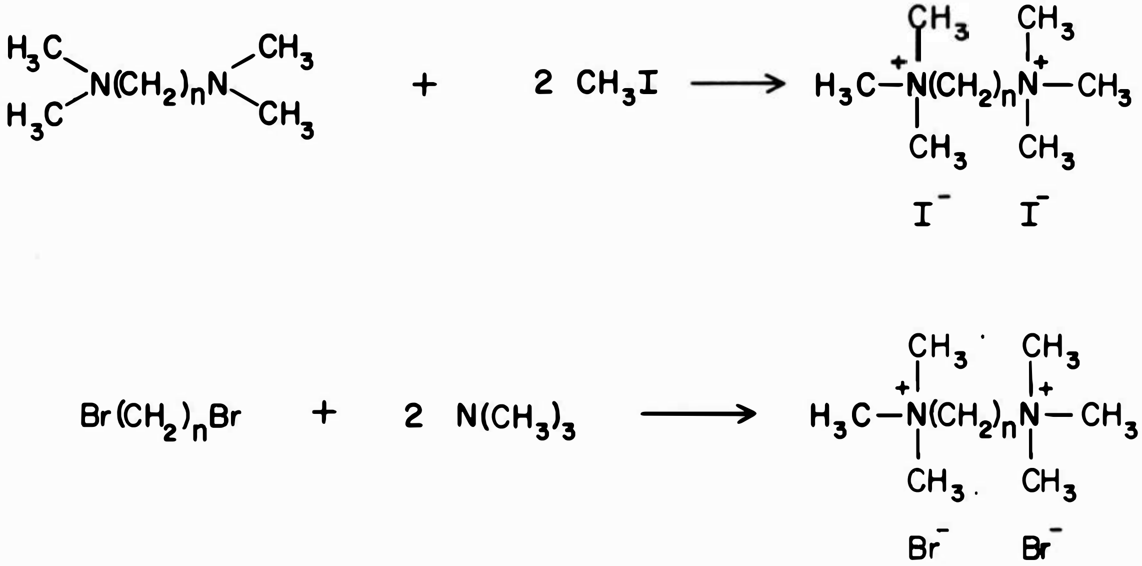


Figure 6: Synthesis of Model Monomeric Units of Aliphatic Ionenes.[27]

Table 4

Conductivities of TCNQ Salts of the Ionene Polymers[27]

Number of CH_2 Groups	Conductivity σ ohm^{-1} cm^{-1} One Unit Segment To:	
x - y	Two TCNQ$^{\bar{\cdot}}$	Two TCNQ$^{\bar{\cdot}}$, Two TCNQ^{0}
3 - 4	3.6×10^{-5}	6.7×10^{-4}
6 - 3	1.1×10^{-6}	2.9×10^{-4}
6 - 5	6.7×10^{-9}	1.3×10^{-2}
6 - 6	3.1×10^{-9}	1.3×10^{-8}
6 - 8	1.4×10^{-8}	7.1×10^{-8}
6 - 10	3.3×10^{-7}	1.4×10^{-5}
6 - 16	1.0×10^{-7}	2.1×10^{-3}

Table 5

Conductivities of TCNQ Salts of the Ionene Model Compounds[27]

	Conductivity σ ohm^{-1} cm^{-1}	
Number of CH_2 Groups	Two TCNQ$^{\bar{\cdot}}$	Two TCNQ$^{\bar{\cdot}}$, Two TCNQ^{0}
2	5.3×10^{-4}	1.1×10^{-2}
3	7.7×10^{-6}	2.4×10^{-3}
4	3.2×10^{-8}	1.5×10^{-3}
5	2.5×10^{-7}	8.3×10^{-3}
6	2×10^{-11}	1.0×10^{-2}
8	2.7×10^{-8}	1.4×10^{-1}
10	2.8×10^{-8}	2.4×10^{-6}
16	7.1×10^{-10}	6.7×10^{-3}

substantially lower than that of the complex salts. With the simple salts, in order for an electron to move along the stack, Coulombic forces have to be overcome to form the dianion. When $TCNQ^o$ is added, as in the complex salts, the formation of the dianion is not necessary (Figure 7); thus, a higher conductivity was obtained.[40]

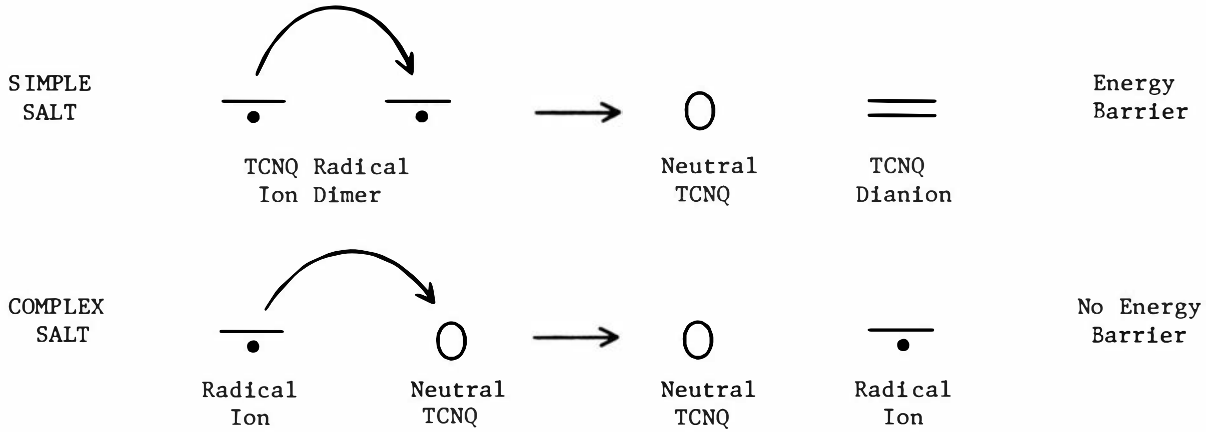
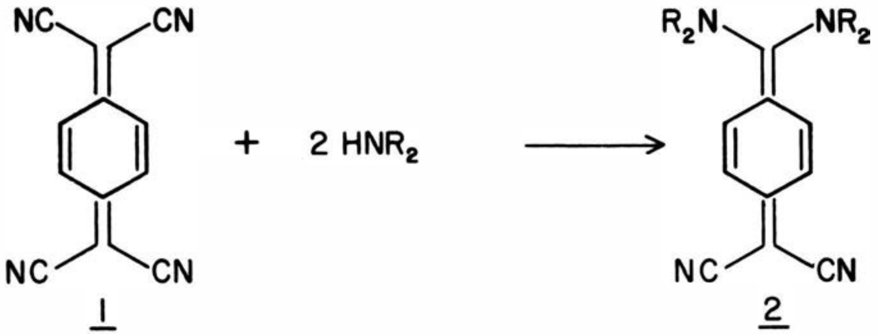


Figure 7: Coulomb Forces Which are Present for the Simple $\text{TCNQ}^{\overline{\cdot}}$ Salts are Absent for the Complex Salt.[39]

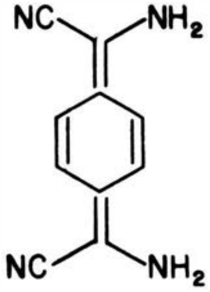
RESEARCH AIM

The purpose of this project is to develop a new polymer system capable of improved electrical conductivity. It is known that ionene polymers which have been treated with TCNQ have yielded some of the better semiconducting polymers reported. Further, the conductivities of these macromolecules have been enhanced by treatment with neutral TCNQ. It is, therefore, conceivable that if the neutral TCNQ moiety or one with similar properties was introduced into the backbone of a polymer chain and then $TCNQ^{\overline{\cdot}}$ introduced between these neutral TCNQ entities, a superior conductor could be obtained. Since ionene polymers present an easy method of introducing the $TCNQ^{\overline{\cdot}}$, the initial problem involves preparing either a dihalo-TCNQ or diamino-TCNQ monomer which can be copolymerized with the appropriate comonomer to form the corresponding ionene polymer. This would then result in an ionene polymer with the neutral TCNQ moiety fixed along the chain. Introduction of the $TCNQ^{\overline{\cdot}}$ at the quaternized positions would produce a polymer which contained repeating units of $TCNQ^{\overline{\cdot}}/TCNQ^{o}/TCNQ^{\overline{\cdot}}$.

Many derivatives[41-43] of TCNQ have been prepared since it was first synthesized by Acker and Herther.[22] For example, by reacting two moles of a primary or secondary amine with one mole of TCNQ[41,42] (<u>1</u>), two geminal cyano groups are replaced by amines. It has been established



that structure 2, rather than the cis (3) or trans (4) isomer, is the product.[41] Upon the base hydrolysis followed by acidification of



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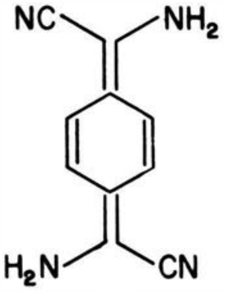

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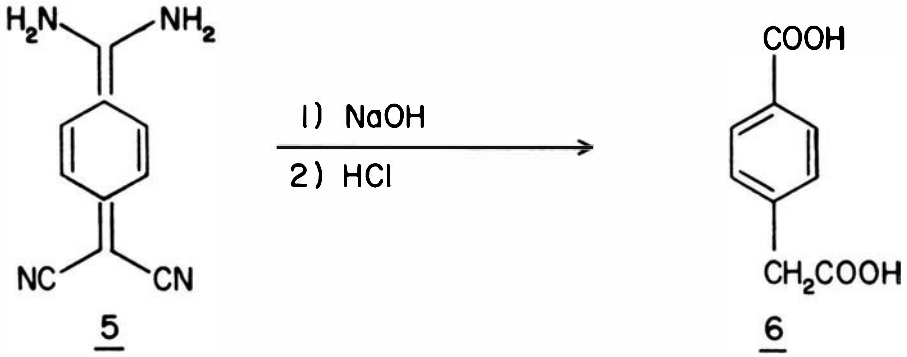
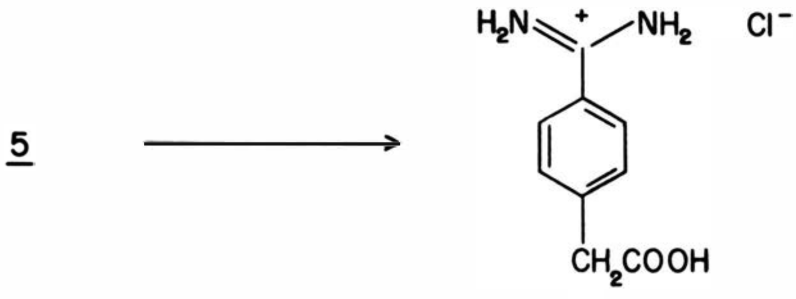
7,7-diamino-8,8-dicyanoquinodimethan (5), homoterephthalic acid (6) was obtained. Homoterephthalic acid could easily arise from 5 but



not from either the cis or the trans isomers. Furthermore, acid hydrolysis of 5 with hydrochloric acid gives p-toluamidine-α-carboxylic acid hydrochloride (7). The transient carbanion (8) would obviously



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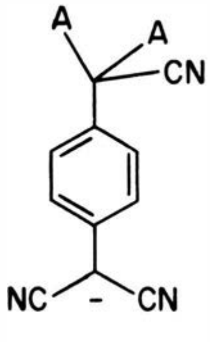
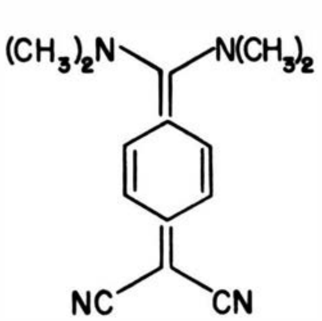
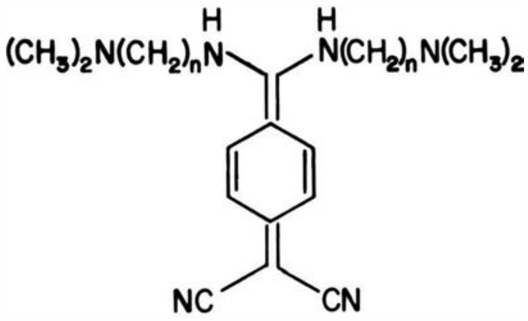
achieve maximum delocalization by two adjacent nitrile groups, as would be the case if attack by the two amine molecules occurred at the same carbon atom.



8

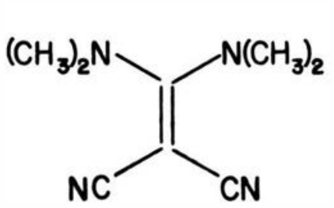
The TCNQ bisamino derivatives could be visualized as monomers in the synthesis of new polymeric ionenes. If these derivatives affect

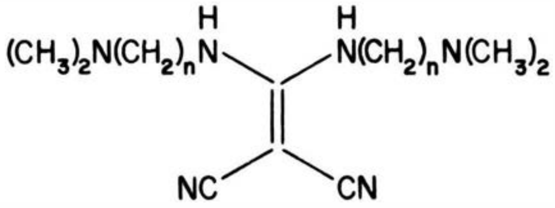




the conduction process in a manner similar to TCNQ^{0}, then the neutral species would, essentially, already have been incorporated into the ionene polymer. It would also have the added advantage of being located at specific and regular intervals along the polymer chain.

Another good electron acceptor, tetracyanoethylene (TCNE) (9), forms π-complexes[44,45] which have been reported to have semiconductor properties.[46] TCNE can accept an electron to form an anion radical (TCNE$^{\dot{-}}$). Therefore, if derivatives of TCNE, which inherited all or part of these characteristics, could be prepared and incorporated into a polymer chain, this polymer would also be expected to have enhanced electrical properties. Bisamino derivatives of TCNE, which are analogous to the corresponding TCNQ derivatives, can be prepared[48,49] and then incorporated into an ionene-type polymer.



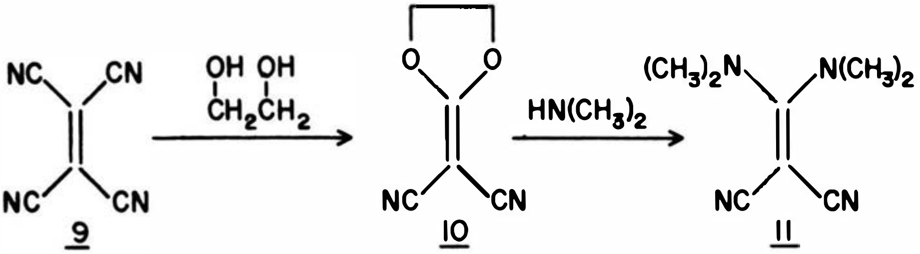


The objectives of this work are: (1) to synthesize a series of bisamino TCNE and TCNQ derivatives which would serve as appropriate monomers in an ionene polymerization; (2) to polymerize these bisamino TCNE and TCNQ monomers with various α,ω-alkyldibromides to form ionene polymers; (3) to treat the ionene polymers with LiTCNQ; and (4) to determine the conductivity of the ionene polymers which have been treated with LiTCNQ.

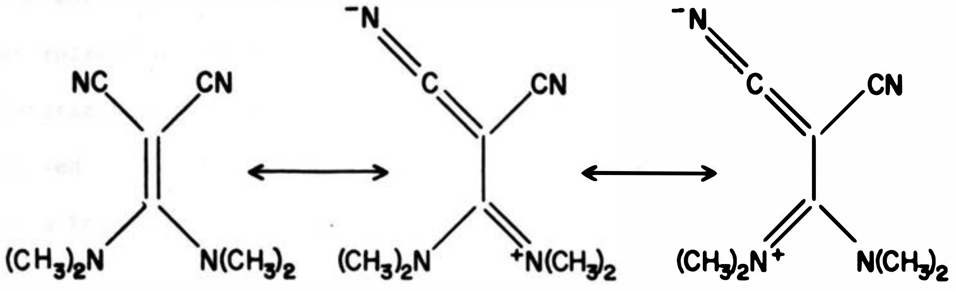
RESULTS AND DISCUSSION

Synthesis of TCNE Derivatives and Related Compounds

The bis(dimethylamine) derivative of TCNE, 1,1-bis(dimethylamino)-2,2-dicyanoethylene (11), was synthesized according to the method reported by Middleton and Engelhart.[48] In this procedure, dicyanoketene ethylene acetal (10) was prepared from TCNE (9) which was then reacted with dimethylamine to obtain 1,1-bis(dimethylamino)-2,2-dicyanoethylene (11).

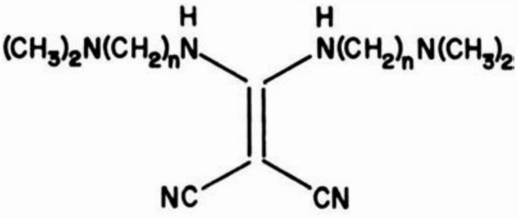


The NMR spectrum of 1,1-bis(dimethylamino)-2,2-dicyanoethylene (11) showed a singlet at δ 2.97 for the four methyl groups. The position of the peak was approximately 40 Hz downfield from the average position of tertiary amines. This large downfield shift indicated that these protons were being strongly deshielded by the rest of the molecule. The nitrile groups, which are strongly electron-withdrawing, are in conjugation with the lone pairs of electrons on the dimethylamine nitrogens and so can delocalize these nonbonded electrons as shown by the resonance forms below.

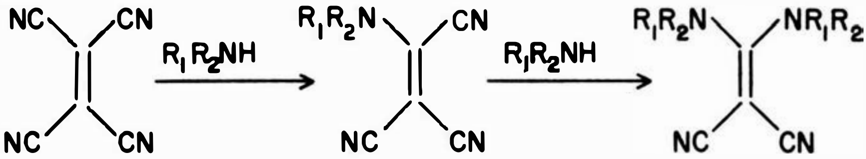


It was further observed that quaternization of these dimethylamine nitrogens with hydrochloric acid or methyl iodide was not possible. It was concluded that the nitrile groups were, in fact, delocalizing the amine electrons to such an extent that the basic and nucleophilic characteristics of the amine groups were not apparent and, further, gave rise to the NMR deshielding observed.

The inability of the amino groups of 1,1-bis(dimethylamino)-2,2-dicyanoethylene to be quaternized made this compound unsuitable to form ionene polymers directly. It was apparent that the conjugation between the nitrogen to be quaternized and the nitrile groups would have to be interrupted. It was, therefore, considered that, if an aliphatic group was placed between the nitrogen and the electron-withdrawing nitrile group, the conjugation would be broken and, thus, the nitrogen could be quaternized. Consequently, N,N-dimethyl-α,ω-alkyldiamines such as N,N-dimethyl-1,2-ethanediamine, N,N-dimethyl-1,3-propanediamine and N,N-dimethyl-1,4-butanediamine were considered to be suitable amines for the preparation of TCNE derivatives which could form ionene polymers through the Menschutkin reaction. The primary amine moiety would serve as the functional group that would participate in the displacement to form the TCNE bisamino derivative. Due to the fact that this joining amine would be in conjugation with the nitrile groups, it could not be quaternized and, therefore, would be unable to participate in the later polymerization process. The tertiary amine groups which could not be involved in the displacement reaction would serve as the functional groups through which the polymerization process could proceed.



Due to the poor yield experienced with dicyanoketene ethylene acetal (<50 percent) and the even poorer yield of 1,1-bis(dimethylamino)-2,2-dicyanoethylene (<30 percent from the acetal), it was decided that an alternative method for synthesizing TCNE amino derivatives would be attempted. TCNE has been reported to react readily with primary or secondary aliphatic amines to give 1-amino-1,2,2-tricyanoethylene derivatives[49,50] which then reacted with another amine molecule to give 1,1-diamino-2,2-dicyanoethylenes.[49]



In the reaction of the above N,N-dimethyl-α,ω-alkyldiamines with TCNE to form the 1,1-bis(N,N-dimethyl-α,ω-alkyldiamino)-2,2-dicyanoethylene compounds (Figure 8), it was found that optimum yields were obtained when an excess of the diamine was added, under a nitrogen atmosphere and with stirring, to a mixture of TCNE and tetrahydrofuran in a manner such that the temperature of the reaction did not rise above -60°C during the addition. The reaction was then allowed to warm to room temperature overnight and the product isolated (Table 6). The 1,1-bis(N,N-dimethyl-1,1-ethanediamino)-2,2-dicyanoethylene (13a) and 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b) were isolated in good yield as crystalline materials. The 1,1-bis-(N,N-dimethyl-1,4-butanediamino)-2,2-dicyanoethylene (13c) was obtained as an oil. All attempts to crystallize this latter compound were unsuccessful. Therefore, it was not used in any polymerization studies.

Monosubstituted amine derivatives, 1-(N,N-dimethyl-α,ω-alkyldiamino)-1,2,2-dicyanoethylenes, were also synthesized by reacting a 1:1 molar ratio of TCNE to diamine (Figure 8, Table 6). These compounds were readily converted to the corresponding 1,1-bis(N,N-dimethyl-α,ω-alkyldiamino)-2,2-dicyanoethylene by reacting them with additional diamine. However, if the preferred product was the 1,1-bis(N,N-dimethyl-α,ω-alkyldiamino)-2,2-dicyanoethylene, then the 1-(N,N-dimethyl-α,ω-alkyldiamino)-1,2,2-tricyanoethylene intermediate was not isolated.

It was further observed that when N,N-dimethyl-1,3-propanediamine and N,N-dimethyl-1,4-butane were reacted with TCNE in a 4:1 molar ratio and the products isolated before the reaction temperature reached -25°C, the products were 1-(N,N-dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene (12b) and 1-(N,N-dimethyl-1,4-butanediamino)-1,2,2-

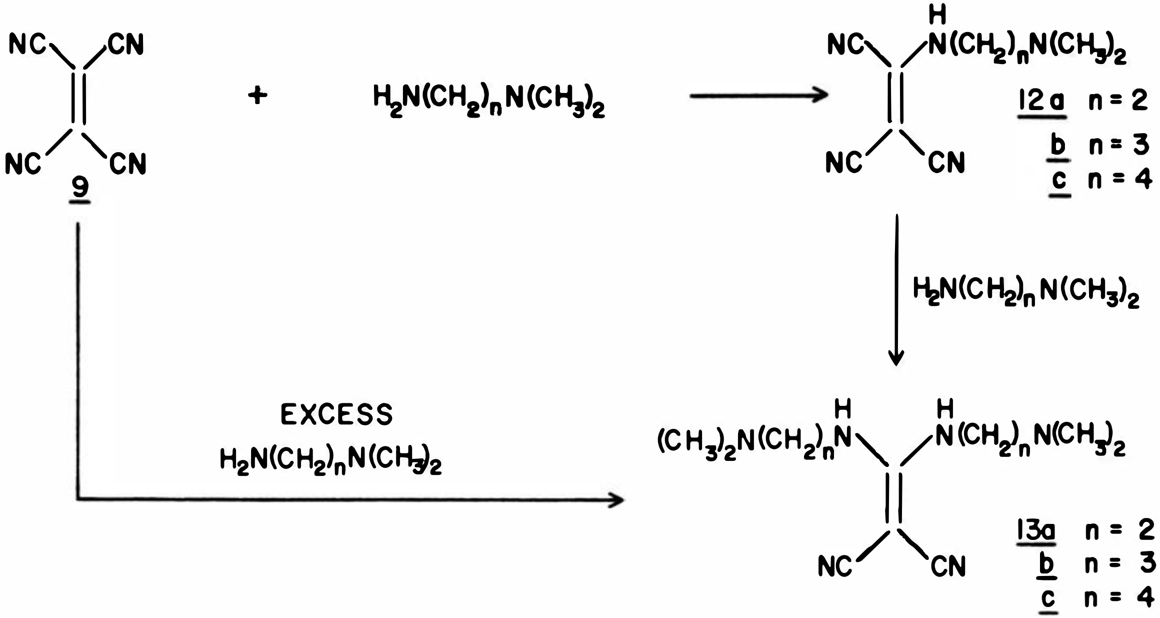


Figure 8: The Reactions of N,N-Dimethyl-α,ω-alkyldiamine with TCNE.

Table 6

N,N-Dimethyl-α,ω-alkyldiamine Derivatives of TCNE

Compound	MP (°C)	% Yield	Elemental Analysis Calculated C	H	N	Found C	H	N
1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a)	110-111	92.4	57.57	8.86	33.57	57.39	8.77	33.80
1,1-Bis)N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b)	106-107	91.6	60.40	9.41	30.19	60.32	9.38	30.32
1,1-Bis(N,N-dimethyl-1,4-butanediamino)-2,2-dicyanoethylene (13c)			Isolated as an Oil					
1-(N,N-Dimethyl-1,2-ethanediamino)-1,2,2-tricyanoethylene (12a)	191-193 dec.	91.9	57.13	5.86	37.01	57.00	5.86	37.21
1-(N,N-Dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene (12b)	197-199 dec.	71.5	59.10	6.44	34.46	59.09	6.44	34.31
1-(N,N-Dimethyl-1,4-butanediamino)-1,2,2-tricyanoethylene (12c)	162 dec.	92.9	60.81	6.96	32.23	60.90	7.00	31.99

tricyanoethylene (12c), respectively. In the case of N,N-dimethyl-1,2-ethanediamine, an intermediate was isolated which upon standing at room temperature formed 1,1-bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene, as determined by NMR spectra. This intermediate was observed to be stable at -70°C and was maintained for more than a month without any apparent change. The evolution of the intermediate to 1,1-bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene can be followed using NMR spectroscopy (Figure 9). However, determination of its structure and investigation of its mechanistic role in the formation of 1,1-bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene were not pursued.

In order to synthesize model compounds of the ensuing ionene polymers of 1,1-bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a) and 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b), these compounds were reacted with methyl iodide to produce diiodide salts (Figure 10, Table 7), which are hygroscopic. The salts were treated with LiTCNQ by adding a solution of LiTCNQ to a solution of the 1,1-bis(ω-trimethylammoniumalkylamino)-2,2-dicyanoethylene diiodide. The product, 1,1-bis(ω-trimethylammoniumalkylamino)-2,2-dicyanoethylene di(tetracyanoquinodimethanide), which precipitated from the solution, represented a model monomeric unit of an ionene polymer. These compounds were only slightly soluble in organic solvents and water.

Spectral Characteristics of the TCNE Derivatives

The NMR spectrum of 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b) (Figure 11) has a singlet at δ 2.16 for the methyl groups of the tertiary nitrogens. The methylene groups adjacent

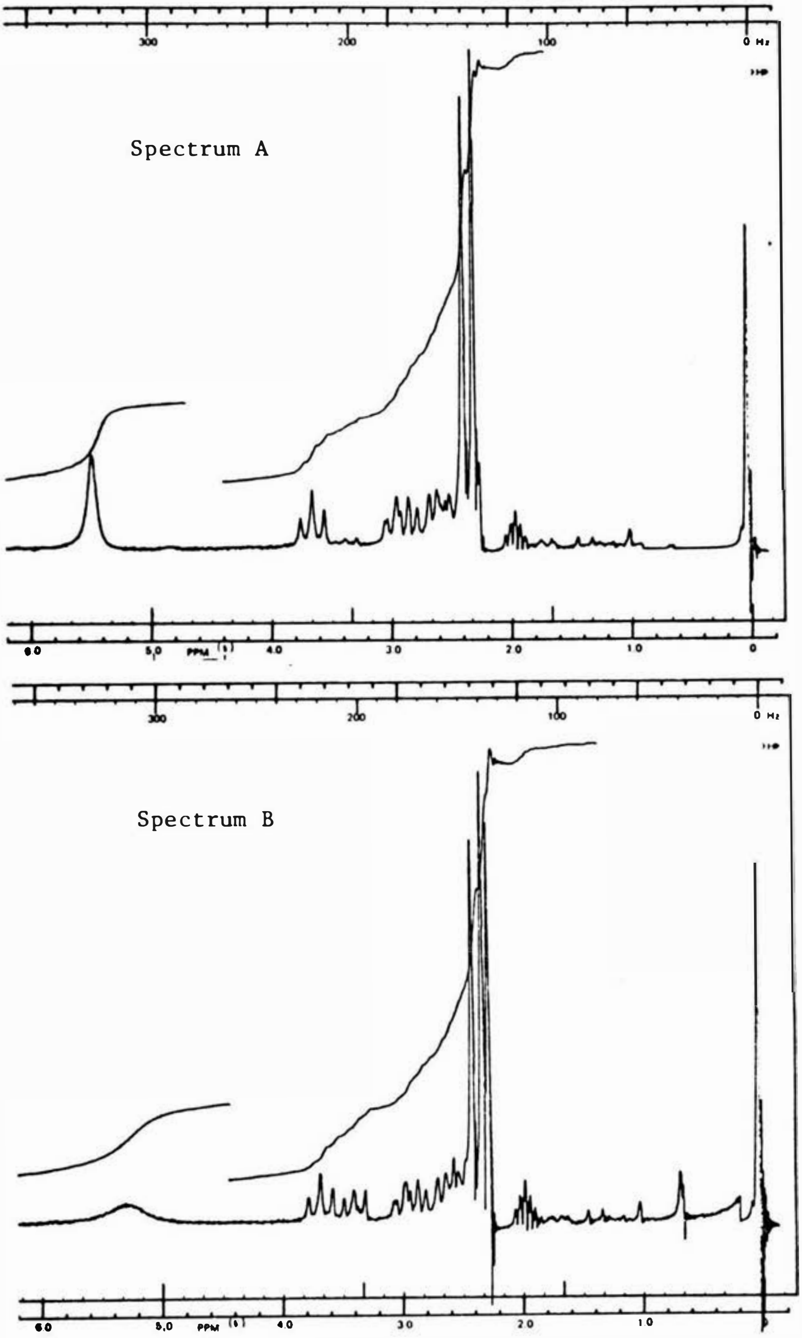
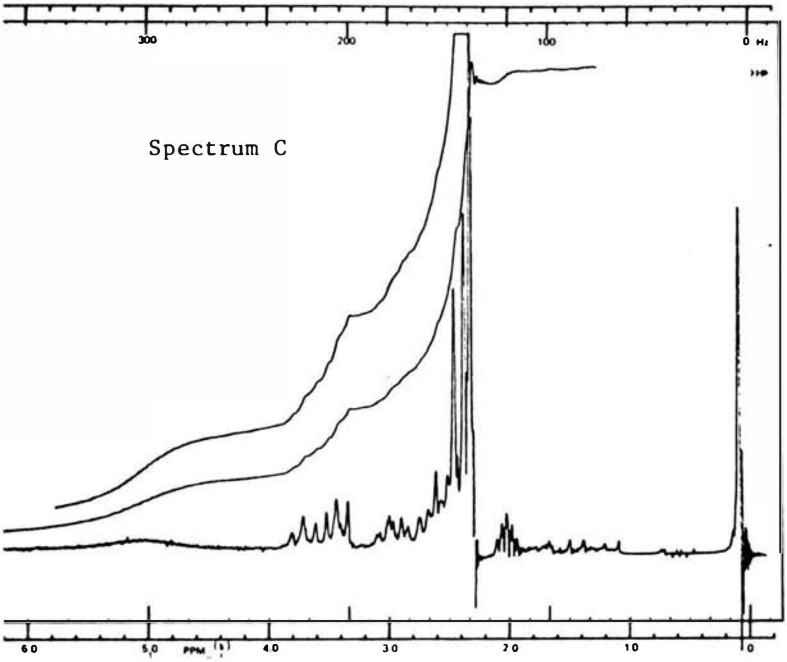
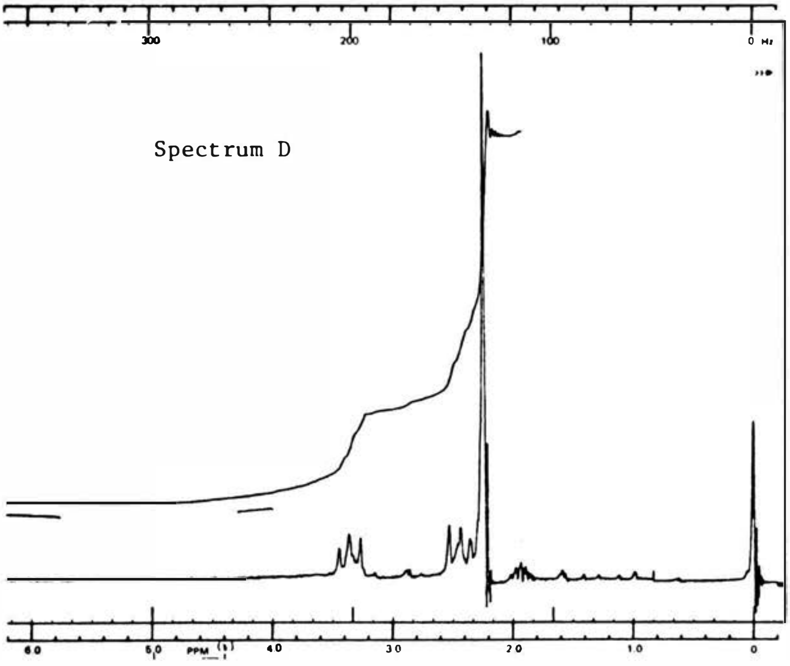


Figure 9: The Evolution of the Intermediate to Form 1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene Followed by NMR: Spectrum A, Time 0; Spectrum B, Time 0.5 Hours; Spectrum C, Time 1.2 Hours; Spectrum D, Time 11.3 Hours.



Spectrum C



Spectrum D

Figure 9 (Continued)

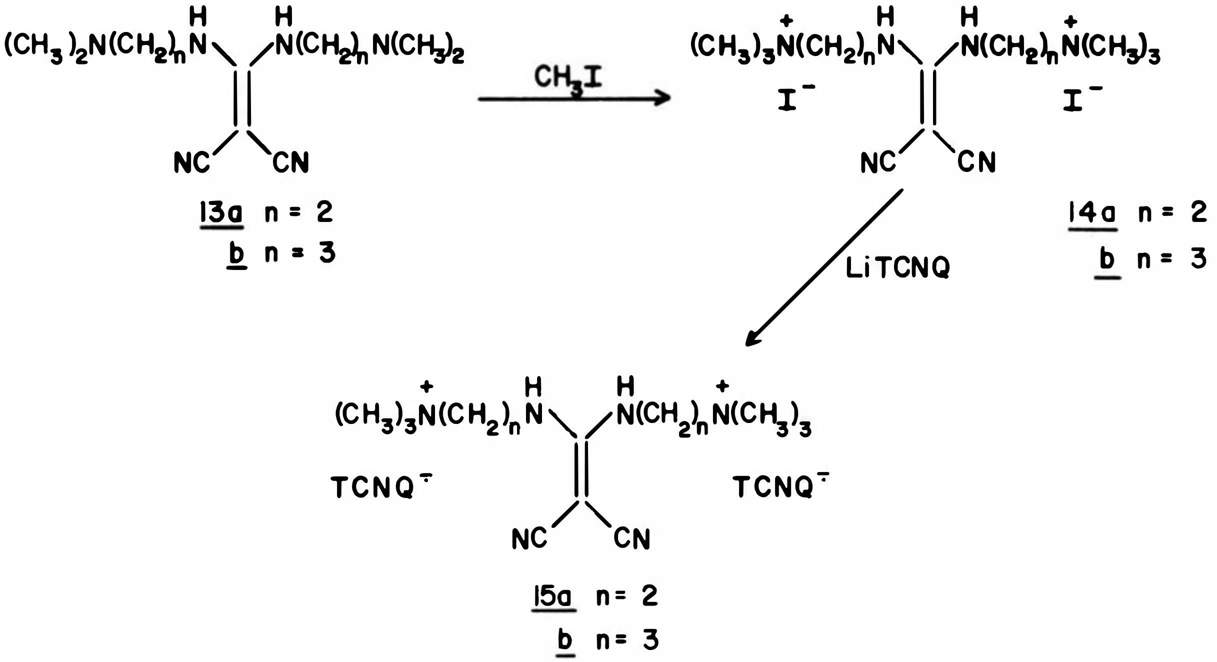


Figure 10: The Synthesis of Iodide and Tetracyanoquinodimethanide Salts of 1,1-Bis(N,N-dimethyl-α,ω-alkyldiamino)-2,2-dicyanoethylene.

Table 7

Preparation of Iodide and Tetracyanoquinodimethanide Salts of
1,1-Bis(N,N-dimethyl-α,ω-alkyldiamino)-2,2-dicyanoethylene

Compound	%	Elemental Analysis							
		Calculated				Found			
	Yield	C	H	N	I	C	H	N	I
1,1-Bis(2-trimethylammoniumethylamino)-2,2-dicyanoethylene diiodide (14a)	96.6	31.48	5.28	15.73	47.51	31.54	5.39	15.39	ND[a]
1,1-Bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene diiodide (14b)	96.5	34.18	5.73	14.95	45.41	33.88	5.74	14.90	ND[a]
1,1-Bis(3-trimethylammoniumethylamino)-2,2-dicyanoethylene di(tetracyanoquinodimethanide) (15a)	38.8	66.26	5.27	28.47		66.14	5.19	28.23	
1,1-Bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene di(tetracyanoquinodimethanide) (15b)	40.1	67.02	5.62	27.36		66.94	5.66	27.18	

[a] ND = Not Determined.

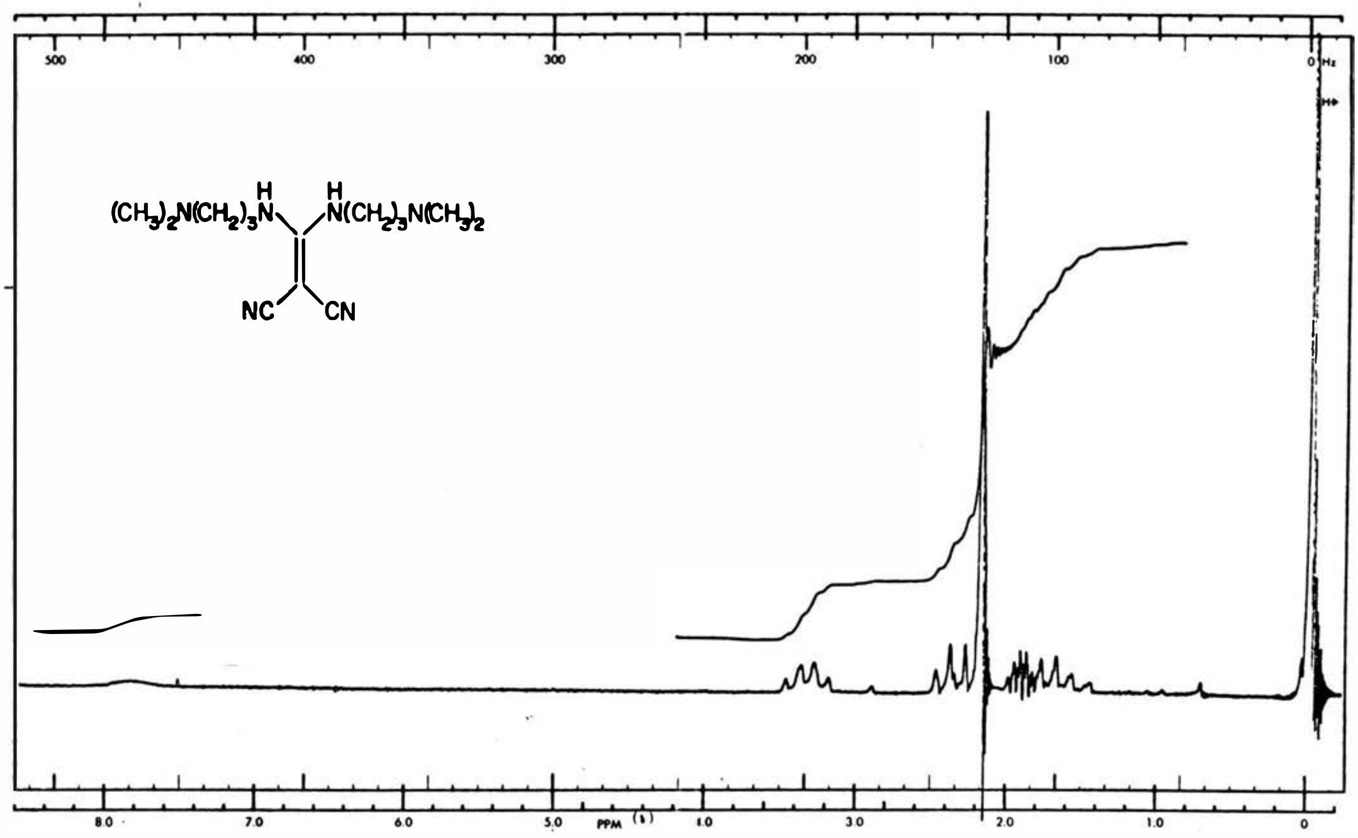


Figure 11: NMR Spectrum of 1,1-Bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b) in Deuterated Acetonitrile.

to the tertiary nitrogen atoms appeared just downfield from this singlet at δ 2.38. The methylene groups attached to the secondary nitrogen atoms came at δ 3.35 as a quartet due to coupling with the amine and methylene protons. The downfield position of this quartet has been attributed to the loss of electron density by the secondary nitrogen atoms because the lone pairs of electrons are conjugated with the electron-withdrawing nitrile groups. The methylene groups which are adjacent to two other methylene groups appeared as a multiplet at δ 1.64. The protons of the secondary amines appeared as a broad singlet at δ 7.83. This downfield position was again attributed to the deshielding effect of the nitrogen atoms. The NMR spectra of 1,1-bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a) and 1,1-bis(N,N-dimethyl-1,4-butanediamino)-2,2-dicyanoethylene (13c) were similar to (13b) (Table 8).

Upon quaternization of the tertiary amines, there was a general downfield shift of all the absorptions in the spectrum from the positions of the unquaternized compound. The absorptions most affected were those of moieties bonded directly to the quaternized nitrogen. The NMR spectrum of 1,1-bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene diiodide (14b) is shown as Figure 12. The methyl groups of the quaternary amine appeared as a singlet at δ 3.16. The two methylene groups bonded to the secondary nitrogen atoms, as well as the two adjacent to the quaternary nitrogen atoms, appeared as a quartet at δ 3.43. The methylene groups which were bonded to two methylene groups appeared as a multiplet at δ 2.08. The NMR spectrum of 1,1-bis(2-trimethylammoniumethylamino)-2,2-dicyanoethylene diiodide (14a) was very similar to the one just discussed (Table 8).

Table 8
NMR Spectral Absorptions of 1,1-Bis(N,N-dimethyl-α,ω-alkyldiamino)-2,2-dicyanoethylene, 1,1-Bis(ω-trimethylammoniumalkylamino)-2,2-dicyanoethylene Diiodide, and 1-(N,N-Dimethyl-α,ω-alkyldiamino)-1,2,2-tricyanoethylene Compounds

Compound	Solvent	Internal Standard	NMR Spectra δ
1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a)	CD_3CH	TMS	2.26(s,12H), 2.42(t,4H), 3.33 (broad unresolved t,4H), 7.70 (broad s, 2H)
1,1-Bis(2-trimethylammoniumethylamino)-2,2-dicyanoethylene diiodide (14a)	D_2O	DSS	3.23(s,18H), 3.75(broad unresolved m,8H)
1-(N,N-Dimethyl-1,2-ethanediamino)-1,2,2-tricyanoethylene (12a)	CD_3CN	TMS	2.70(s,6H), 3.12(t,2H), 3.72 (t,2H)
1,1-Bis(N,N-dimethyl-1,2-propanediamino)-2,2-dicyanoethylene (13b)	CD_3CN	TMS	1.64(m,4H), 2.16(s,12H), 2.38 (t,4H), 3.35(q,4H), 7.83 (broad s,2H)
1,1-Bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene diiodide (14b)	D_2O	DSS	2.08(m,4H), 3.16(s,18H), 3.43 (q,8HO
1-(N,N-Dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene (12b)	CD_3CN	TMS	1.91(m,2H), 2.16(s,6H), 3.28 (t,2H), 3.77(t,2H), 8.33 (broad s,1H)

Table 8
(Continued)

Compound	Solvent	Internal Standard	NMR Spectra δ
1,1-Bis(N,N-dimethyl-1,4-butanediamino)-2,2-dicyanoethylene (<u>13c</u>)	CD_3CN	TMS	1.53(m,8H), 2.20(s,12H), 2.30 (t,4H), 3.28(m,4H)
1-(N,N-Dimethyl-1,4-butanediamino)-1,2,2-tricyanoethylene (<u>12c</u>)	CD_3CN	TMS	1.80(m,4H), 2.76(s,6H), 2.96 (unresolved t,2H), 3.33 (unresolved t,2H), 6.48 (broad s,1H)

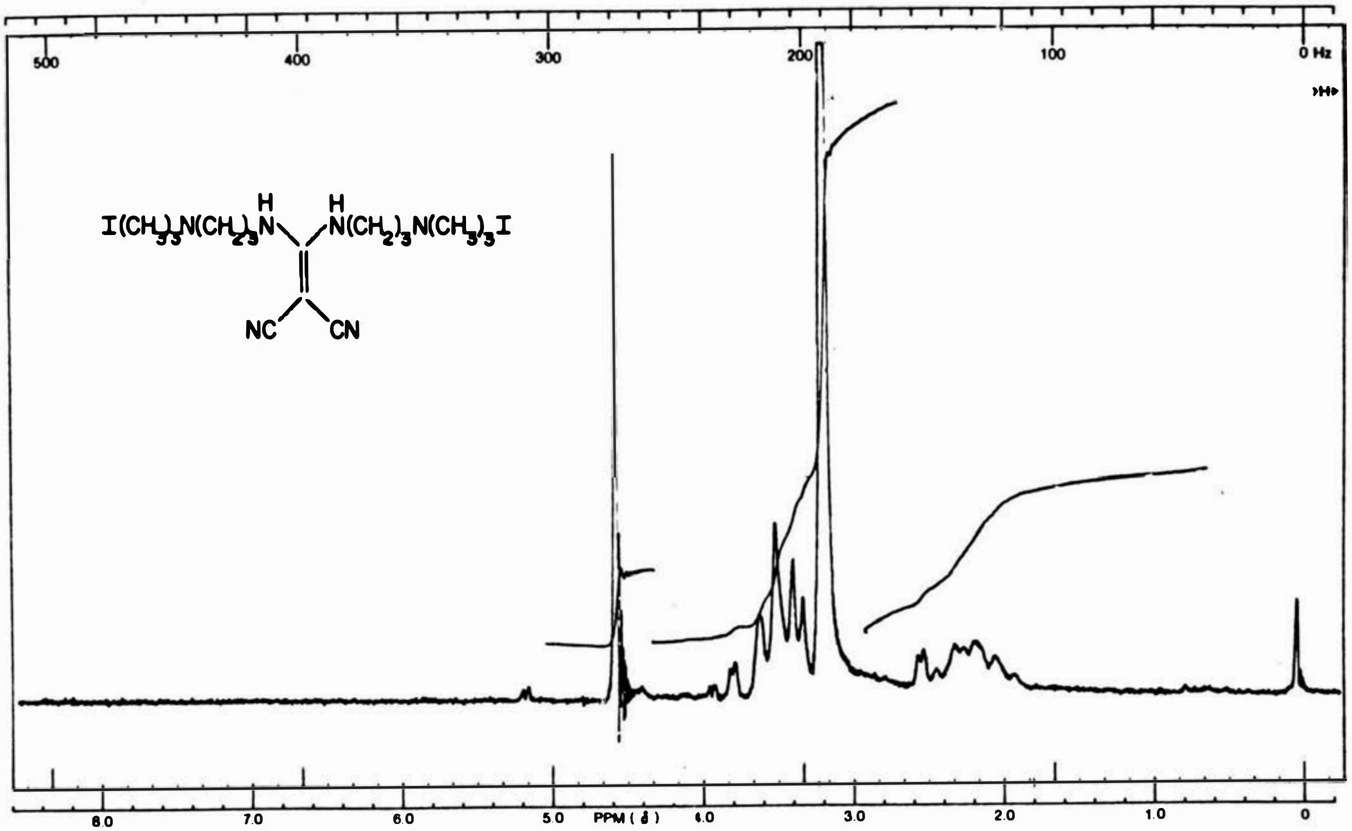
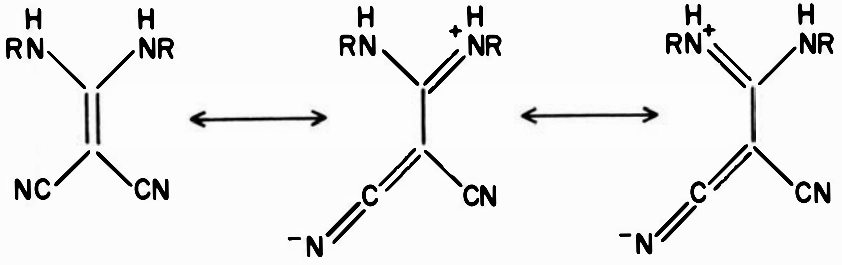


Figure 12: NMR Spectrum of 1,1-Bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene Diiodide (14b) in Deuterium Oxide.

The NMR spectrum of 1-(N,N-dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene (12b) (Figure 13) exhibited a multiplet at δ 1.91 for the methylene groups which were bonded to two other methylene groups. The $-N(CH_3)_2$ peaks appeared as a singlet at δ 2.70. The downfield shift from the expected position of δ 2.16, which was obtained for the methyl groups in compound 13b, has been attributed to nitrogen-hydrogen-nitrogen ($>$N —— H· · ·N$<$) intramolecular hydrogen bonding, which is discussed in another section. The methylene group bonded to the tertiary nitrogen appeared as a triplet at δ 3.28. The absorption of the methylene adjacent to the secondary amine also came as a triplet at δ 3.77. The proton of the secondary amine was a broad singlet at δ 8.33, indicating considerable deshielding. The spectra of 1-(N,N-dimethyl-1,2-ethanediamino)-1,2,2-tricyanoethylene (12a) and 1-(N,N-dimethyl-1,4-butanediamino)-1,2,2-tricyanoethylene (12c) were similar to that of 12b (Table 8).

The ir spectrum of 1,1-bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a) showed the absorption characteristic of a conjugated nitrile group (2165 and 2195 cm^{-1}) (Figure 14). A medium absorption of 1610 cm^{-1} and a strong absorption at 1570 cm^{-1} were attributed to the conjugated C-C double bond and the C-N double bond which arise from resonance forms. In most of the other ir spectra, these same peaks



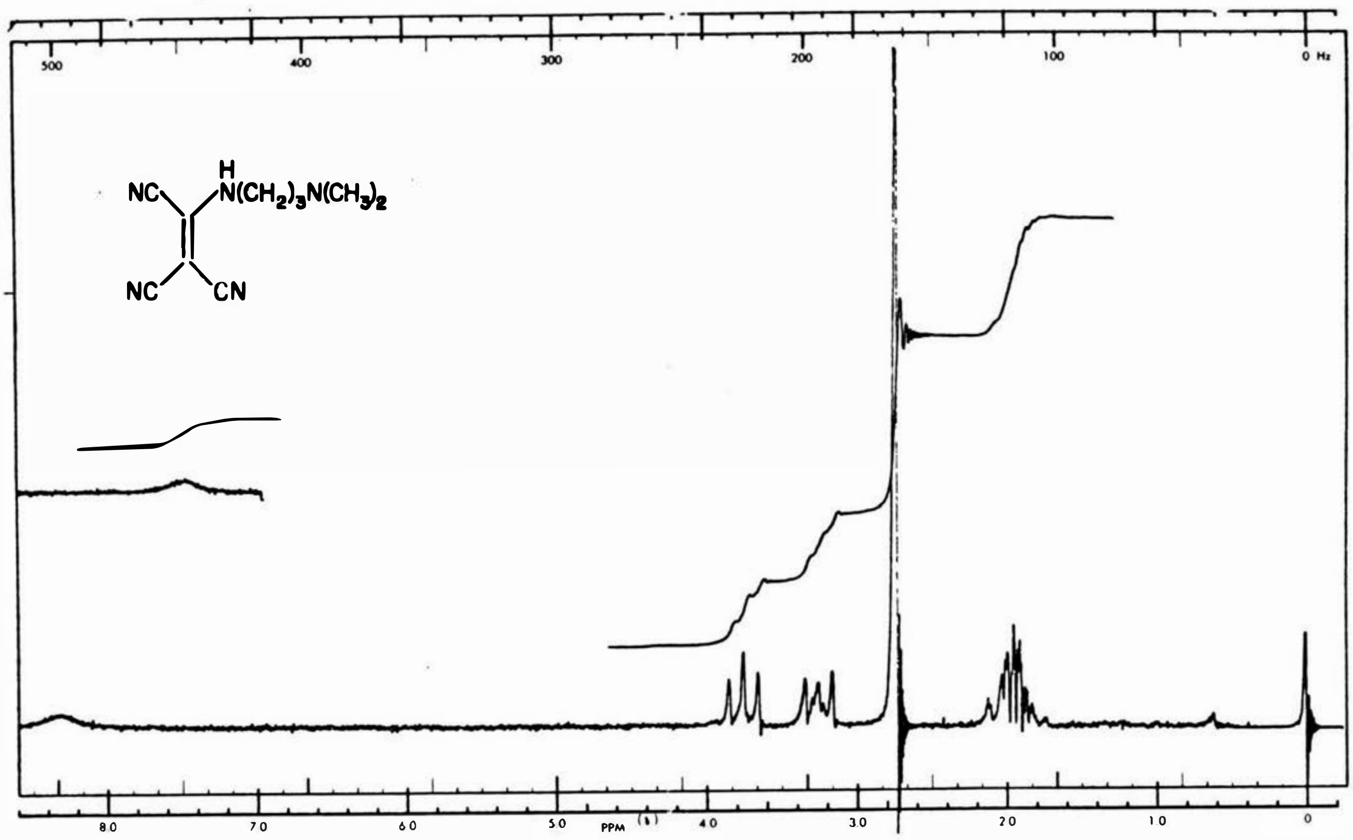


Figure 13: NMR Spectrum of 1-(N,N-Dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene in Deuterated Acetonitrile.

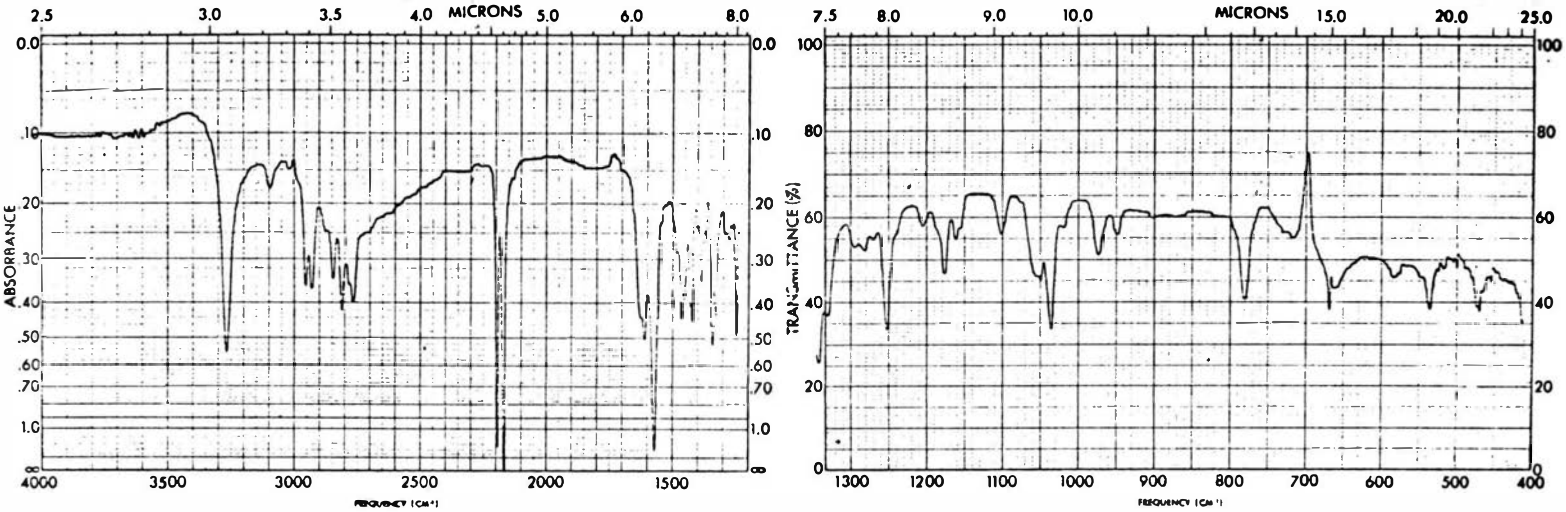


Figure 14: Infrared Spectrum of 1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (12b) as a KBr pellet.

appeared as a single strong broad absorption. The N-H showed a strong absorption at 3270 cm^{-1} (Figure 14) for 13a, but this peak was not as well defined in the spectra of other compounds in this series. There also appeared absorptions between 3000 cm^{-1} and 2750^{-1} which were attributed to the methylene and methyl groups. The other 1,1-bis(N,N-dimethyl-α,ω-alkyldiamino)-2,2-dicyanoethylenes, as well as the 1,1-bis-(ω-trimethylammoniumalkylamino)-2,2-dicyanoethylene and 1-(N,N-dimethyl-α,ω-alkyldiamino)-1,2,2-tricyanoethylene compounds, gave spectra similar to that of 13a (Table 9).

The ir spectra of 1,1-bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene di(tetracyanoquinodimethanide) (15b) and 1,1-bis(2-trimethylammoniumethylamino)-2,2-dicyanoethylene di(tetracyanoquinodimethanide) (15a) were similar to the spectra of the other TCNE derivatives (Table 9). They exhibited strong characteristic absorptions at 2180 and 1580 cm^{-1}.

Synthesis of TCNQ Derivatives and Related Compounds

A procedure similar to that of Acker and Blomstrom was employed to synthesize 7,7-bis(dimethylamino)-8,8-dicyanoethylene[42] (16). Excess dimethylamine was added to a solution of TCNQ in tetrahydrofuran at room temperature. After standing at room temperature for a couple of days, the volume of the solution was reduced on a rotary evaporator and the product isolated.

Quaternization of the amino groups of 16 with hydrochloric acid and methyl iodide was unsuccessful, as was the TCNE analog, 1,1-bis-(N,N-dimethylamino)-2,2-dicyanoethylene (11). It was anticipated that the nonbonded electrons on the two tertiary amines were delocalized by the nitrile groups and, thus, their basic and nucleophilic characteristics were

Table 9

Infrared Spectral Absorptions of 1,1-Bis(N,N-dimethyl-α,ω-alkyldiamino)-2,2-dicyanoethylene, 1,1-Bis(ω-trimethylammoniumalkylamino)-2,2-dicyanoethylene Diiodide and 1-(N,N-Dimethyl-α,ω-alkyldiamino)-1,2,2-tricyanoethylene Compounds

1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a):

3270(s), 3100(w), 2955(m), 2930(m), 2850(m), 2810(m), 2760(m), 2195(s), 2165(s), 1610(m), 1570(s), 1460(m), 1425(m), 1385(m), 1340(m), 1330(m), 1253(m), 1205(w), 1176(m), 1162(w), 1100(w), 1050(m), 1035(m), 973(w), 950(w), 780(m).

1,1-Bis(2-trimethylammoniumethylamino)-2,2-dicyanoethylene diiodide (14a):

3460(m, broad), 3240(m, broad), 3100(m), 3030(m), 2920(m), 2205(s) 2185(s), 1570(s, broad), 1480(s), 1445(m), 1430(w), 1415(s), 1396(w), 1360(m), 1352(m), 1336(m), 1283(w), 1268(w), 1235(w), 1190(w), 1150(w), 1095(w), 1078(w), 1038(w), 1010(w), 980(w), 960(w), 942(w), 900(w), 885(w), 875(w), 750(w), 695(w), 673(w).

1-(N,N-Dimethyl-1,2-ethanediamino)-1,2,2-tricyanoethylene (12a):

3095(s), 2920(m), 2880(m), 2855(m), 2200(s), 2170(s), 1565(s, broad), 1480(m), 1470(m), 1445(m), 1430(w), 1418(w), 1375(s), 1335(s), 1295(m), 1258(m), 1172(m), 1065(m), 1020(w), 990(w), 976(w), 965(m), 920(m), 730(w), 695(m), 676(m), 555(s), 515(m), 500(w).

1,1-Bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b):

3100(s, broad shoulder), 2950(s), 2860(s), 2825(s), 2775(s), 2190(s), 2165(s), 1550(s, broad), 1450(s), 1410(s), 1340(m), 1320(m), 1295(m), 1270(m), 1250(m), 1200(w), 1168(m), 1123(w), 1111(w), 1100(w), 1086(w), 1073(m), 1160(m), 1145(m), 1105(m), 938(m), 905(w), 878(m), 778(m), 730(m), 690(m), 600(w), 550(w).

1,1-Bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene diiodide (14b):

3460(s), 3370(s), 3250(s), 3140(m), 3020(m), 2960(m), 2195(s), 2165(s), 1620(s), 1545(s), 1470(s), 1368(s), 1340(m), 1315(w), 1305(w), 1265(m), 1250(w), 1210(w), 1195(w), 1160(w), 1142(w), 1090(w), 1063(w), 1053(w), 1030(m), 956(s), 918(m), 900(m), 876(m), 776(m), 756(m), 690(m), 585(m), 550(m), 522(m).

Table 9
(Continued)

1-(N,N-Dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene (12b):

3460(w), 3040(w), 2960(w), 2905(m), 2845(m), 2650(m, broad), 2480(m, broad), 2190(s), 2160(s), 1585(s, broad), 1467(s), 1415(m), 1380(m), 1335(s), 1290(m), 1275(m), 1238(m), 1150(w), 1070(m), 1050(m), 1010(m), 985(w), 975(w), 942(m), 912(m), 848(m), 773(m), 726(m), 710(w), 673(m), 548(s), 525(m), 499(m), 318(m).

1-(N,N-Dimethyl-1,4-butanediamino)-1,2,2-tricyanoethylene (12c):

3440 (vw), 3030(w), 3000(w), 2950(m), 2935(m), 2860(m), 2400(m, broad), 2195(s), 2160(s), 1570(s, broad), 1480(m), 1435(m), 1380(m), 1360(m), 1350(m), 1340(s), 1315(w), 1278(w), 1263(m), 1255(m), 1235(m), 1218(m), 1178(w), 1148(w), 1098(w), 1080(m), 1010(m), 975(m), 955(m), 937(m), 903(w), 808(m), 742(m), 702(m), 670(m), 550(s), 522(m), 503(w), 488(w), 470(m), 320(m).

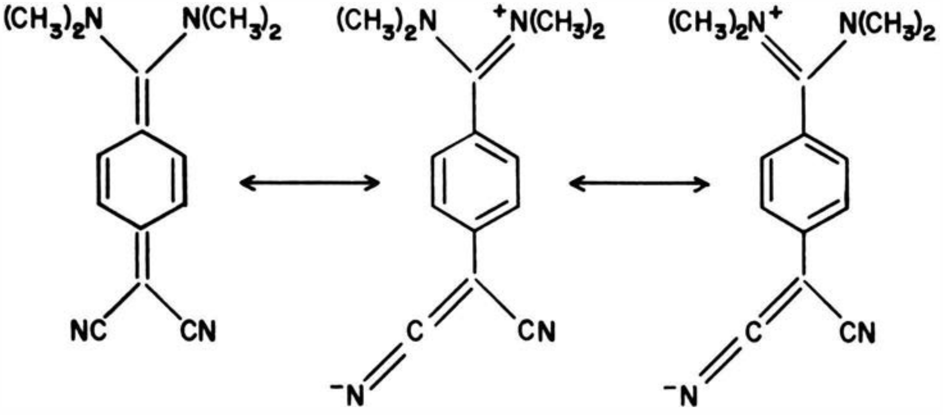
1,1-Bis(2-trimethylammoniumethylamino)-2,2-dicyanoethylene di(tetracyanoquinodimethan) (15a):

3430(w, broad), 2200(s), 2170(m, shoulder), 2150(w, shoulder), 1585(m), 1520(m), 1480(w), 1368(m), 1355(m), 1220(w), 1185(m), 988(w), 822(w).

1,1-Bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene di(tetracyanoquinodimethan) (15b):

3440(s, broad), 2200(s), 2185(s), 2165(s), 1580(s), 1510(s), 1480(w), 1368(s), 1350(s), 1222(w), 1082(s), 1075(m), 988(w), 825(s), 810(w), 720(m), 617(w), 550(w), 520(w), 480(m).

inhibited. The loss of electron density about the tertiary nitrogens was further confirmed by the position of the methyl peak in the NMR spectrum. The $-N(CH_3)_2$ peak was observed at δ 3.10, which was considerably downfield from the expected position of δ 2.25 for an N-methyl group of a tertiary amine.[51] Therefore, the following representative resonance structures, which indicate delocalization of the nonbonded electron pairs of the nitrogens, were considered to be making a large contribution toward the electronic distribution of the compound.



In order to effect quaternization of the tertiary amines, it was again necessary to isolate them from conjugation with the nitrile groups. Therefore, N,N-dimethyl-α,ω-alkyldiamines, such as N,N-dimethyl-1,2-ethanediamine, N,N-dimethyl-1,3-propanediamine and N,N-dimethyl-1,4-butanediamine, were considered for making TCNQ derivatives which could form ionene polymers through the Menschutkin reaction. The procedure used to synthesize the derivatives, 7,7-bis(N,N-dimethyl-α,ω-alkyldiamino)-8,8-dicyanoquinodimethans, was similar to that used by Acker and Blomstrom[42] to synthesize 7,7-bis(dimethylamino)-8,8-dicyanoquinodimethan (16). The 7,7-bis(N,N-dimethyl-1,2-ethanediamino)-8,8-

dicyanoquinodimethan (18a) and 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) were prepared and isolated in good yields as crystalline solids (Figure 15, Table 10). The 7,7-bis(N,N-dimethyl-1,4-butanediamino)-8,8-dicyanoquinodimethan (18c) was obtained as an oil. All attempts to crystallize this latter compound were unsuccessful. Consequently, it was not used in any polymerization studies.

It was noted that when TCNQ and the N,N-dimethyl-α,ω-alkyldiamine were reacted in a 1:1 molar ratio, the monosubstituted 7-(N,N-dimethyl-α,ω-alkyldiamino)-7,8,8-tricyanoquinodimethan derivatives were obtained (Figure 15). This was in accord with results published by Herther and coworkers for other TCNQ-amino derivatives.[41] The 7-(N,N-dimethyl-α,ω-alkyldiamino)-7,8,8-tricyanoquinodimethans were isolated with high yields as dark-colored solids (Table 10). The NMR spectra of these compounds showed dramatic downfield shifts for the alkyl portions of the molecules. This phenomenon is discussed in a later section.

In order to synthesize model monomeric units of the ensuing ionene polymers of 7,7-bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a) and 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b), these compounds were reacted with methyl iodide. The reaction of 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) with excess methyl iodide in absolute ethanol for 24 hours yielded 7,7-bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide (20b) (Figure 16). When 7,7-bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a) was reacted with methyl iodide in absolute ethanol for 24 hours, the product isolated was determined by NMR to be almost totally starting material. The reaction was repeated in excess methyl iodide for two weeks and the product isolated was a mixture of

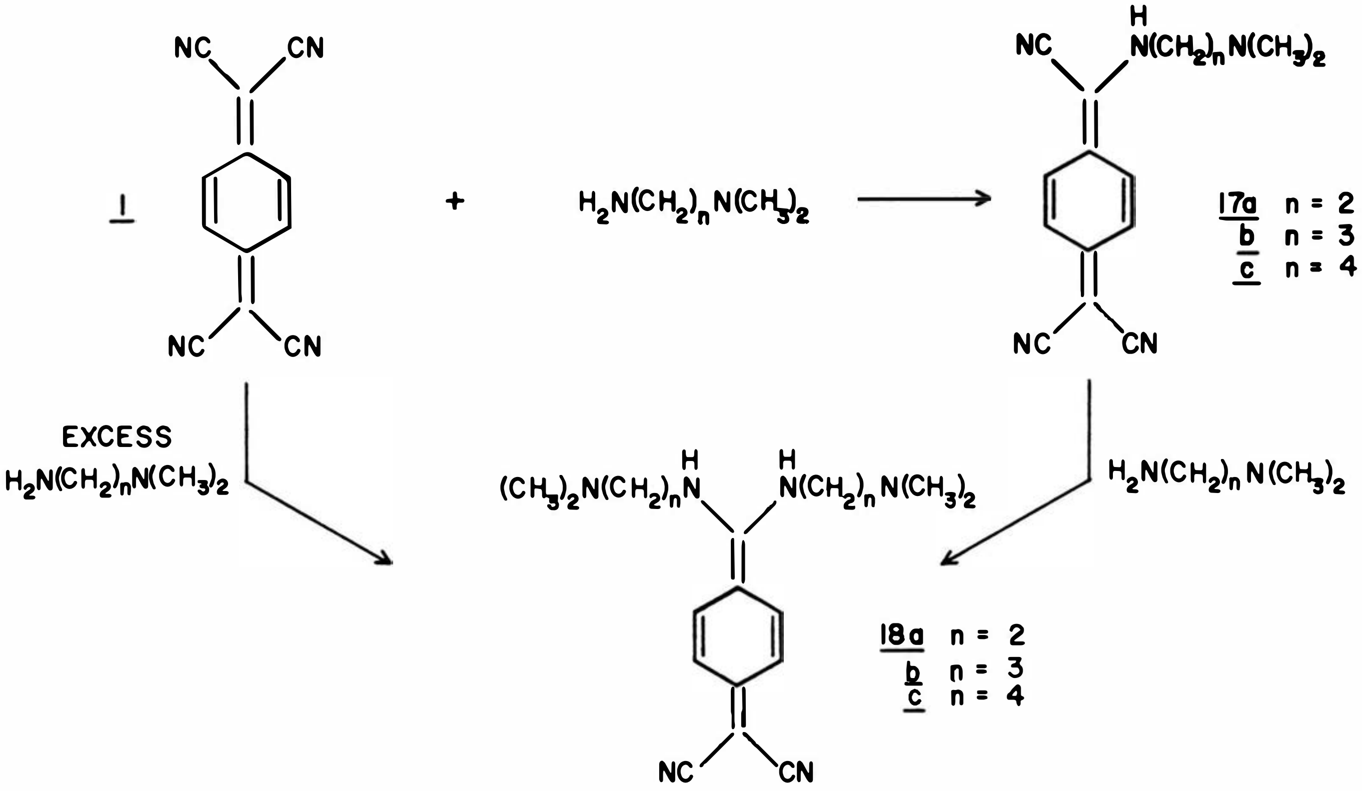


Figure 15: The Reactions of N,N-Dimethyl-α,ω-alkyldiamine with TCNQ.

Table 10

N,N-Dimethyl-α,ω-alkyldiamine Derivatives of TCNQ

Compound	MP ($^{\circ}C$)	% Yield	Elemental Analysis					
			Calculated			Found		
			C	H	N	C	H	N
7-(N,N-Dimethyl-1,2-ethanediamino)-7,8,8-tricyanoquinodimethan (17a)	118 dec.	77.7	67.90	5.70	26.40	64.30	6.29	23.32
7-(N,N-Dimethyl-1,3-propanediamino)-7,8,8-tricyanoquinodimethan (17b)	181-182 dec.	91.2	68.80	6.13	25.07	68.58	5.90	24.95
7-(N,N-Dimethyl-1,4-butanediamino)-7,8,8-tricyanoquinodimethan (17c)	183-185 dec.	95.7	69.60	6.53	23.87	69.20	6.29	23.32
7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a)	253-254 dec.	92.2	66.23	8.03	25.74	66.20	8.15	25.71
7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b)	157-159	66.5	67.76	8.53	23.71	67.58	8.59	23.61
7,7-Bis(N,N-dimethyl-1,4-butanediamino)-8,8-dicyanoquinodimethan (18c)			Isolated as an Oil					

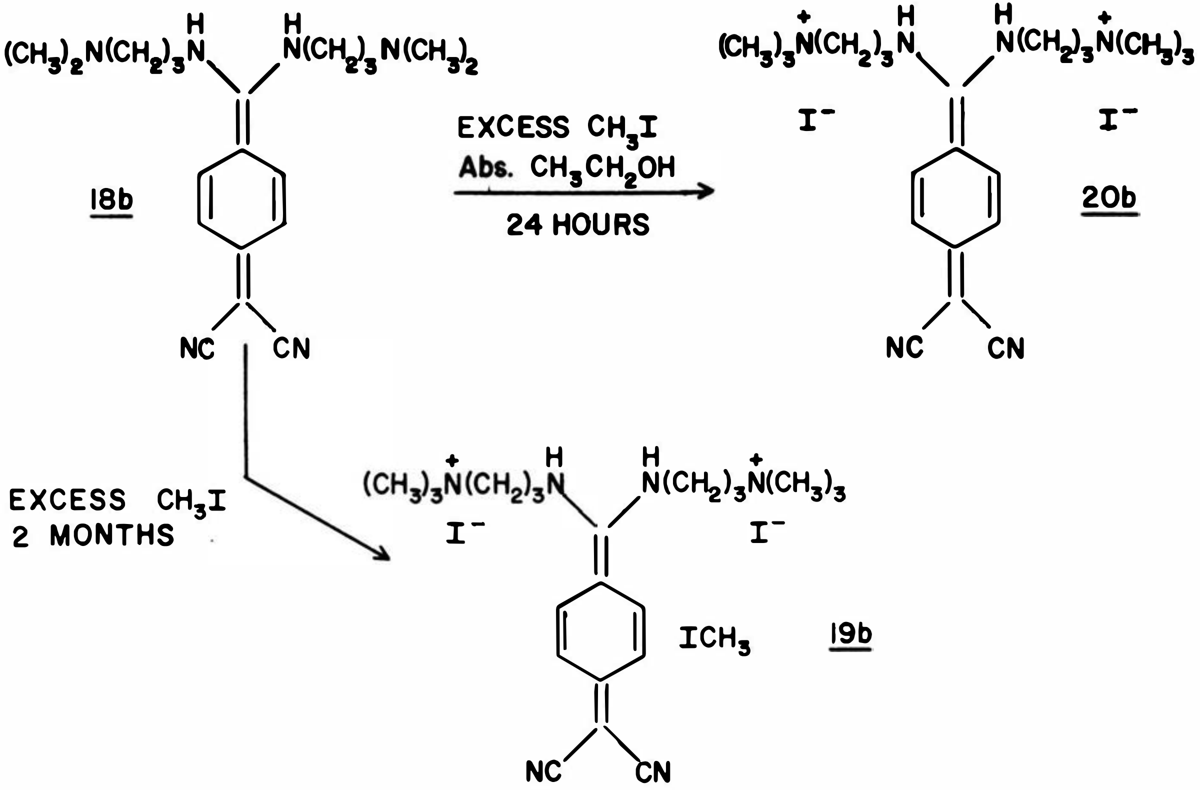
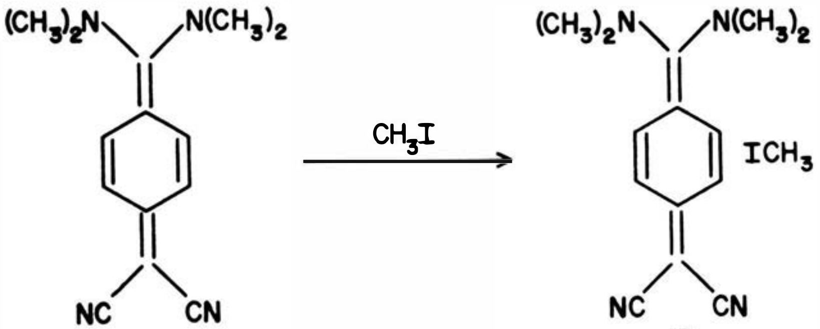


Figure 16: The Reactions of 7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) with Methyl Iodide.

the starting material and the desired product, 7,7-bis(2-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide (20a). The reaction time was extended to approximately one month and the product isolated was 7,7-bis(2-trimethylammoniumethylamino)-8,8-dicyanoquinodimethan diiodide - methyl iodide complex (19a). When 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) was reacted with excess methyl iodide for two months, the 7,7-bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide - methyl iodide complex (19b) was isolated (Figure 16). The reaction of excess methyl iodide with 7,7-bis(dimethylamino)-8,8-dicyanoquinodimethan (16) produced a similar methyl iodide complex. The methyl iodide complexes were characterized using NMR, ir and uv spectroscopy.



16 16a

A model TCNQ$^{\cdot -}$-TCNQ monomer was obtained by treating 7,7-bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide with LiTCNQ. The product, 7,7-bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan di(tetracyanoquinodimethanide) (21), precipitated from the solution as it formed. It was found to be only slightly soluble in water and polar organic solvents.

Spectral Characteristics of the TCNQ Derivatives

The NMR spectrum of 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) has a singlet at δ 2.23 for the methyl groups of the tertiary nitrogens (Figure 17). The methylene groups adjacent to the tertiary nitrogen atoms appeared as a triplet at δ 2.43. A multiplet at δ 1.70 represented the methylene groups which were bonded to two other methylenes. The methylene groups attached to the secondary nitrogen atom appeared as an unresolved absorption at δ 3.41. The broadening of this absorption was attributed to partial averaging of the spin-spin coupling to nitrogen by quadrupole relaxation.[52] The four ring protons appeared as an AB quartet at δ 7.10. The NMR spectra of 7,7-bis-(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a) and 7,7-bis(N,N-dimethyl-1,4-butanediamino)-8,8-dicyanoquinodimethan (18c) were similar to the spectrum of 18b (Table 11).

The NMR spectrum of 7-(N,N-dimethyl-1,3-propanediamino)-7,8,8-tricyanoquinodimethan (17b) exhibited a multiplet at δ 2.10 for the methylene group which was adjacent to the two other methylene groups (Figure 18). A singlet appeared at δ 2.86 which represents the methyl groups. The downfield position of the methyl absorption has been attributed to nitrogen-hydrogen-nitrogen (>N —— H· · ·N<) intramolecular hydrogen bonding which is discussed later. The methylene which was adjacent to the tertiary nitrogen appeared as a triplet at δ 3.28. A triplet at δ 3.87 represents the methylene group bonded to the secondary nitrogen atom. The ring protons appeared as an AB quartet at δ 7.27. The NMR spectra of 7-(N,N-dimethyl-1,2-ethanediamino)-7,8,8-tricyanoquinodimethan (17a) and 7-(N,N-dimethyl-1,4-butanediamino)-7,8,8-tricyanoquinodimethan (17c) were similar to that of 7-(N,N-dimethyl-1,3-propane-

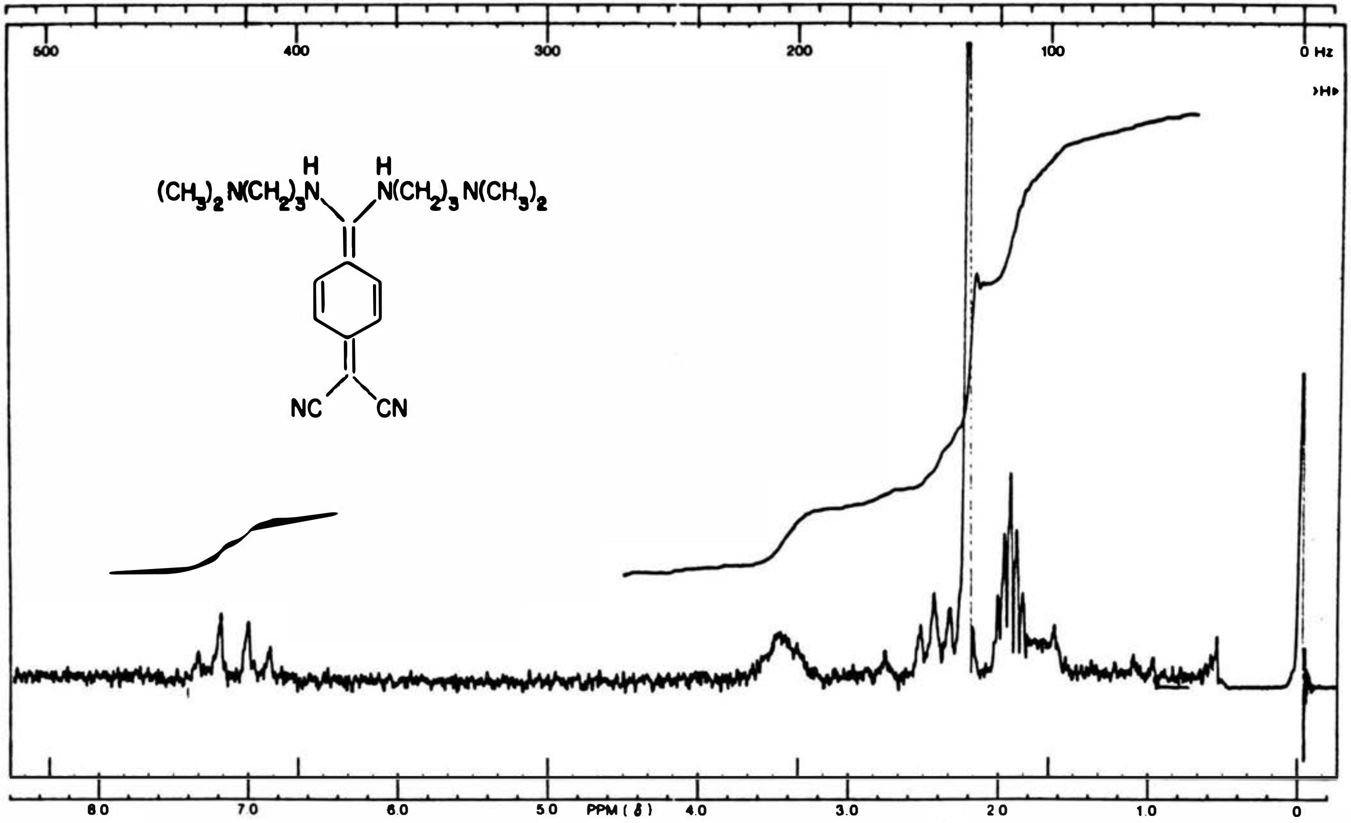


Figure 17: NMR Spectrum of 7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) in Deuterated Acetonitrile.

Table 11

NMR Spectral Absorptions of
7-(N,N-Dimethyl-α,ω-alkyldiamino)-7,8,8-tricyanoquinodimethans,
7,7-Bis(N,N-dimethyl-α,ω-alkyldiamino)-8,8-dicyanoquinodimethans,
7,7-Bis(ω-trimethylammoniumalkylamino)-8,8-dicyanoquinodimethan Diiodide - Methyl Iodide Complexes

Compound	Solvent	Internal Standard	NMR Spectra δ
7-(N,N-Dimethyl-1,2-ethanediamino)-7,8,8-tricyanoquinodimethan (17a)	$(CD_3)_2SO$	TMS	2.90(s,6H), 3.52(t,2H), 4.10(t,2H), 6.90(d,2H), 7.67(d,2H)
7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a)	$(CD_3)_2SO$	TMS	2.10(s,12H), 2.35(t,4H), 3.40(t,4H), 6.86(d,2H), 7.30(d,2H)
7,7-Bis(2-trimethylammoniumethylamino)-8,8-dicyanoquinodimethan diiodide - methyl iodide complex (19a)	D_2O	DSS	2.30(s,3H), 3.23(d,18H), 3.97(m,8H), 8.00(s,4H)
7-(N,N-Dimethyl-1,3-propanediamino)-7,8,8-tricyanoquinodimethan (17b)	$(CD_3)_2SO$	TMS	2.10(m,2H), 2.86(s,6H), 3.28(t,2H), 3.87(t,2H), 6.88(d,2H), 7.65(d,2H)
7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b)	CD_3CN	TMS	1.70(m,4H), 2.23(s,12H), 2.43(t,4H), 3.41(unresolved t,4H), 6.97(d,2H), 7.26(d,2H)

Table 11
(Continued)

Compound	Solvent	Internal Standard	NMR Spectra δ
7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide (20)	D_2O	DSS	2.30(m,2H), 3.20(s,18H), 3.58(m,8H), 6.98(d,2H), 7.45(d,2H)
7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide - methyl iodide complex (19b)	CD_3CN	TMS	2.23(s,3H), 2.30(m,4H), 3.23(d,18H), 3.71(m,8H), 7.97(s,4H)
7-(N,N-Dimethyl-1,4-butanediamino)-7,8,8-tricyanoquinodimethan (17c)	$(CD_3)_2SO$	TMS	1.75(m,4H), 2.80(s,6H), 2.63(t,2H), 3.83(t,2H), 6.90(d,2H), 7.63(d,2H)
7,7-Bis(N,N-dimethyl-1,4-butanediamino)-8,8-dicyanoquinodimethan (18c)	CD_3CN	TMS	1.61(m,8H), 2.25(m,16H), 3.31(t,4H), 6.50(broad s, 2H), 6.97(d,2H), 7.27(d,2H)
7,7-(Bis(dimethylamino)-8,8-dicyanoquinodimethan (16)	$(CD_3)_2SO$	TMS	3.10(s,12H), 6.90(d,2H), 7.13(d,2H)
7,7-Bis(dimethylamino)-8,8-dicyanoquinodimethan - methyl iodide complex (16a)	CD_3CN	TMS	2.23(s,3H), 3.20(s,12H), 7.93(s,4H)

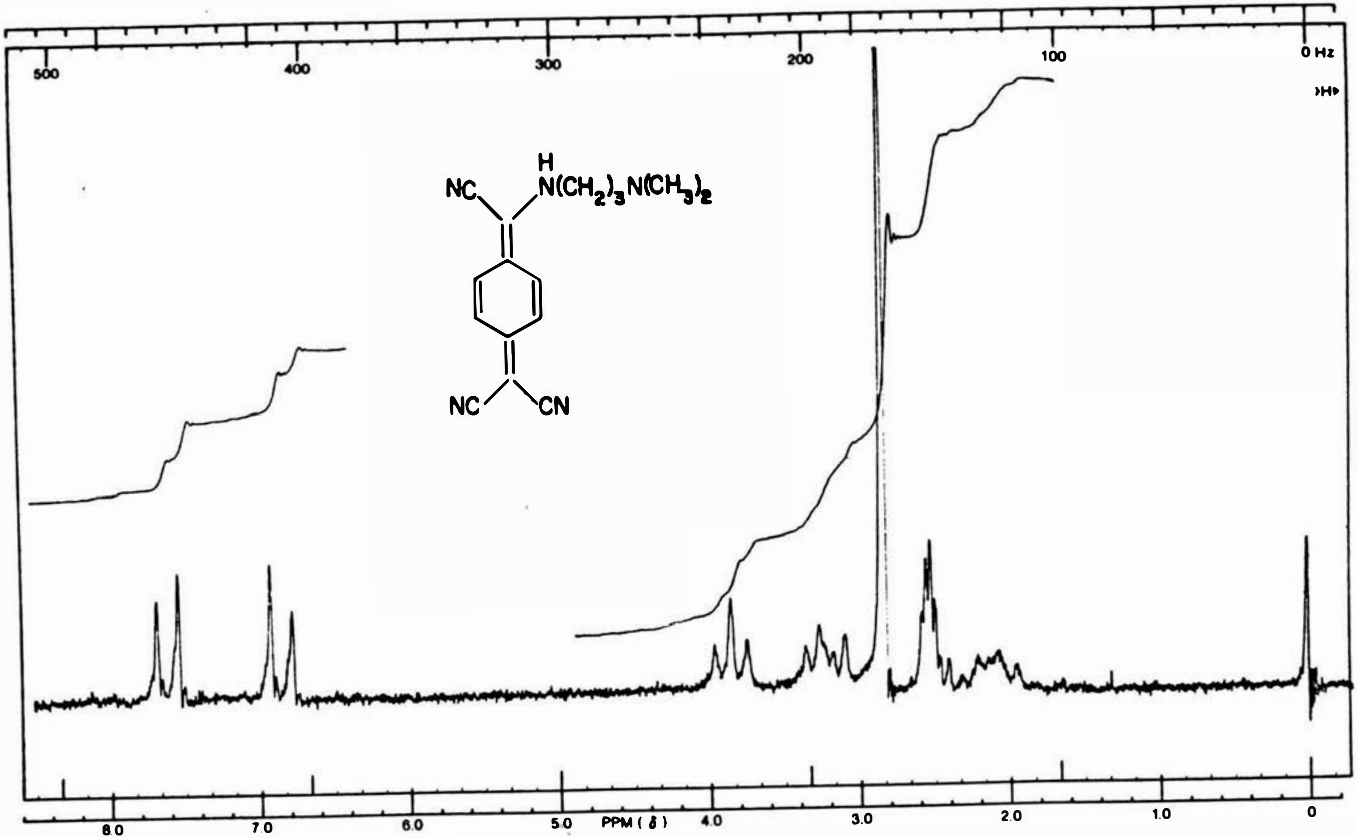


Figure 18: NMR Spectrum of 7-(N,N-dimethyl-1,3-propanediamino)-7,8,8-tricyanoquinodimethan (17b) in Deuterated Dimethyl Sulfoxide.

diamino)-7,8,8-tricyanoquinodimethan (17b) (Table 11).

The quaternization of the tertiary nitrogens of 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) with methyl iodide formed 7,7-bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide (20b). The NMR spectrum showed a large downfield shift for those groups bonded to the quaternary nitrogens. The NMR spectrum of 20b showed a singlet at δ 3.20 for the methyl groups bonded to the quaternary nitrogen atoms (Figure 19, Table 11). The methylenes bonded to the quaternary nitrogen as well as the methylene groups attached to the secondary nitrogen appeared as broad absorptions at δ 3.58. The methylene groups adjacent to two other methylene groups appeared as an unresolved multiplet at δ 2.30. The ring protons appeared as an AB quartet at δ 7.26.

Treatment of 7,7-bis(N,N-dimethyl-α,ω-alkyldiamino)-8,8-dicyanoquinodimethans with excess methyl iodide produced unique methyl iodide complexes. The NMR spectrum of 7,7-bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide - methyl iodide complex (19b) had a singlet at δ 2.23 attributed to the methyl group of the complexed methyl iodide (Figure 20). The methyl groups of the quaternary nitrogens appeared as a doublet at δ 3.23. The methylene groups attached to the quaternary nitrogens appeared as a triplet at δ 3.23 which partially falls under the peaks for the methyl groups. The methylene groups which were adjacent to two methylene groups appeared as a multiplet at δ 2.20. Two significant changes in the spectrum of the ring protons were observed. First, they were shifted approximately 80 Hz downfield from the parent compound (18b), from δ 7.10 to δ 7.97. Further, the absorption peak appeared as a singlet instead of an AB quartet. The other two methyl

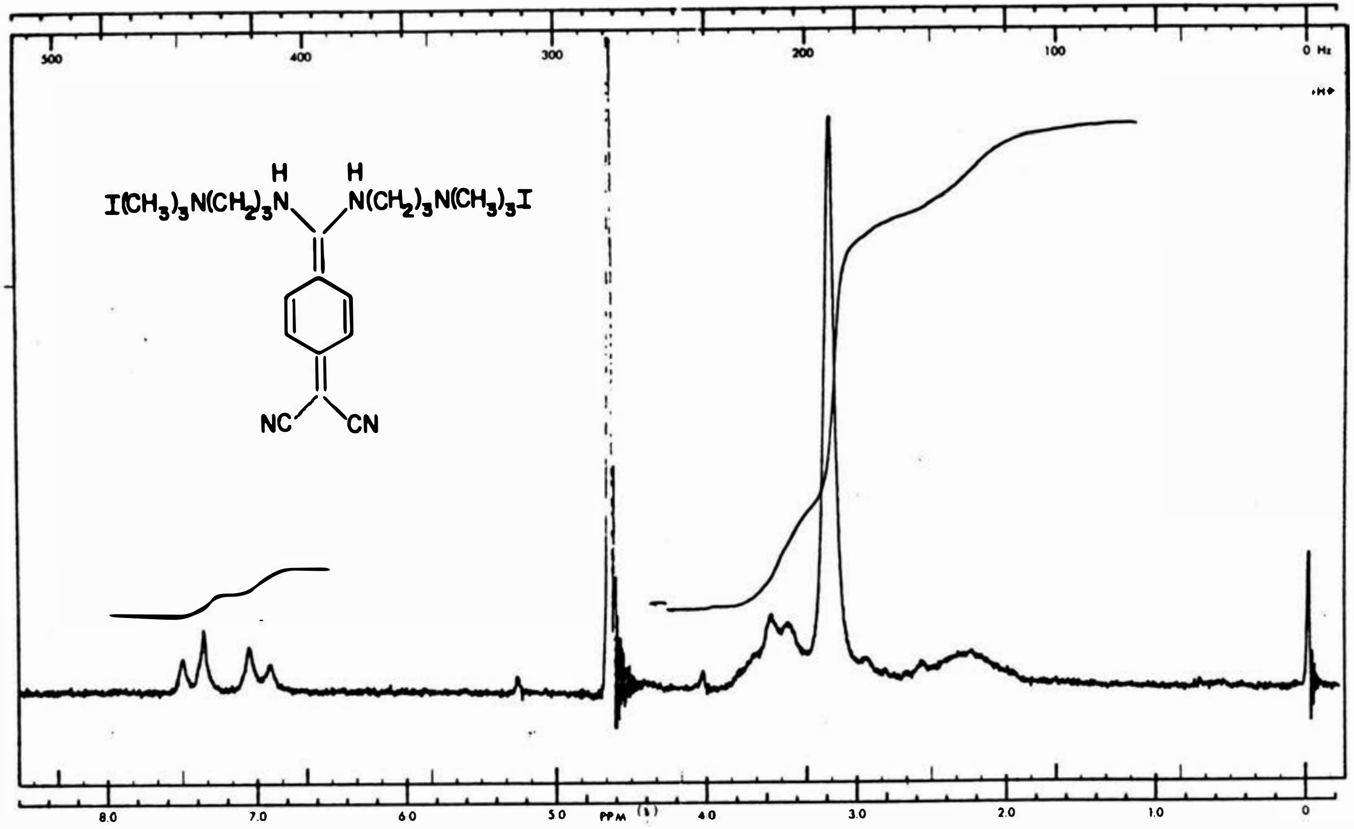


Figure 19: NMR Spectrum of 7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan Diiodide (20b) in Deuterium Oxide.

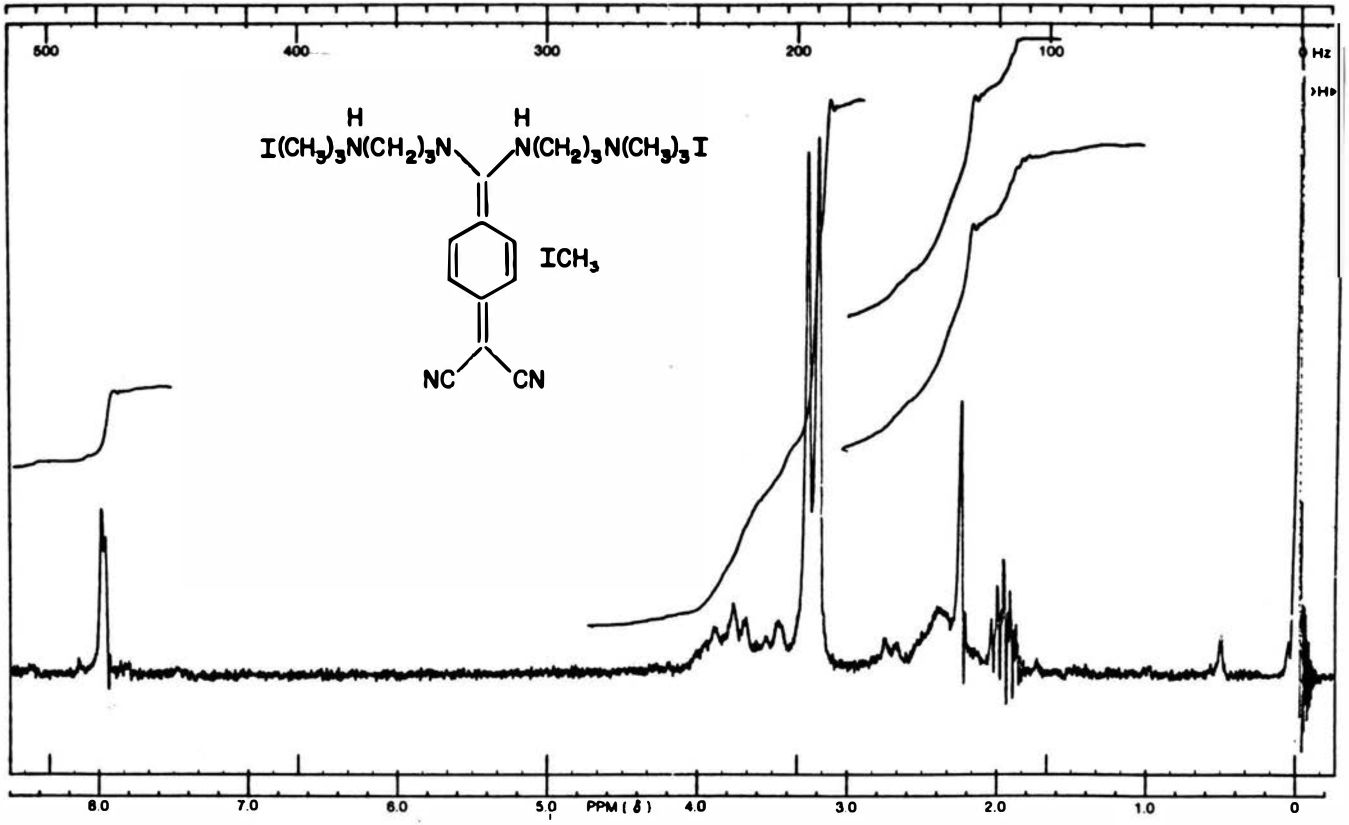


Figure 20: NMR Spectrum of 7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan Diiodide - Methyl Iodide Complex (<u>19b</u>) in Deuterated Acetonitrile.

iodide complexes, 7,7-bis(dimethylamino)-8,8-dicyanoquinodimethan - methyl iodide complex (16a) and 7,7-bis(2-trimethylammoniumethylamino)-8,8-dicyanoquinodimethan - methyl iodide complex (19a), exhibited spectra similar to that of the methyl iodide complex (19b) discussed above (Table 11).

The ir spectra of the 7-(N,N-dimethyl-α,ω-alkyldiamino)-7,8,8-tricyanoquinodimethans, 7,7-bis(N,N-dimethyl-α,ω-alkyldiamino)-8,8-dicyanoquinodimethans, and the 7,7-bis(ω-trimethylammoniumalkylamino)-8,8-dicyanoquinodimethan diiodides are all similar (Table 12). For example, the ir spectrum of 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) exhibited peaks at 2175 cm^{-1} and 2140 cm^{-1}, characteristic of conjugated nitriles (Figure 21). The absorptions at 1630 cm^{-1} (shoulder), 1600 cm^{-1} and 1575 cm^{-1} (shoulder) were attributed to the conjugated C-C double bonds and the C-N double bond which arises from resonance forms. Absorptions between 3200 and 3000 cm^{-1} were attributed to the four aromatic protons of the ring. The peaks between 3000 cm^{-1} and 2750 cm^{-1} represent the methylene and methyl groups. The N-H showed a strong absorption at 3225 cm^{-1}, but this

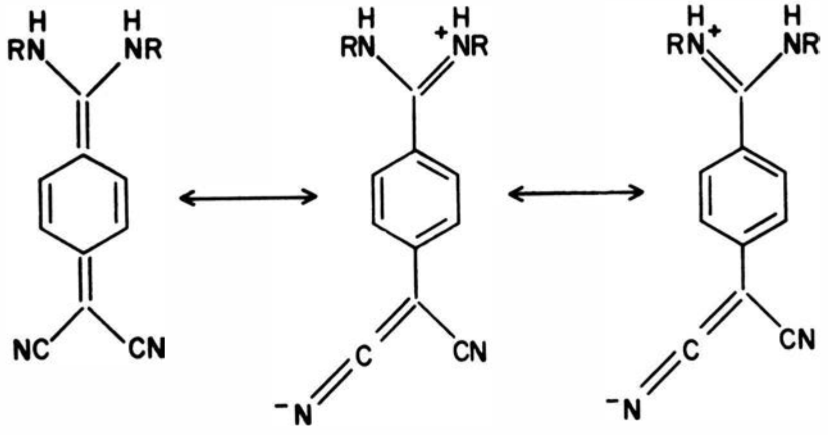


Table 12

Infrared Spectral Absorptions of 7-(N,N-Dimethyl-α,ω-alkyldiamino)-7,8,8-tricyanoquinodimethans, 7,7-Bis(N,N-dimethyl-α,ω-alkyldiamino)-8,8-dicyanoquinodimethans and Related Compounds

7-(N,N-Dimethyl-1,2-ethanediamino)-7,8,8-tricyanoquinodimethan (<u>17a</u>):

3060(w), 3030(w), 2920(w), 2850(w), 2180(s), 2130(s), 1600(s), 1580(s), 1510(m), 1330(m), 1285(m), 1185(s), 835(w), 695(m).

7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (<u>18a</u>):

3225(s), 3110(m), 3060(m), 2970(m), 2940(s), 2860(m), 2825(m), 2765(s), 2175(s), 2140(s), 1630(s), 1590(s), 1560(s), 1500(s), 1450(m), 1415(m), 1360(s), 1270(s), 1245(s), 1225(m), 1195(s), 1178(s), 1150(m), 1135(s), 833(s).

7,7-Bis(2-trimethylammoniumethylamino)-8,8-dicyanoquinodimethan diiodide - methyl iodide complex (<u>19a</u>):

3430(s, broad), 3020(s), 2920(s), 2175(w), 2130(w), 1640(s, broad), 1480(s), 1455(m), 1420(w), 1330(w), 1280(w), 1215(w), 1178(w), 1100(w), 1020(w), 970(w), 945(w), 922(w), 840(w), 750(w), 695(m).

7-(N,N-Dimethyl-1,3-propanediamino)-7,8,8-tricyanoquinodimethan (<u>17b</u>):

3035(w), 2170(s), 2130(s), 1605(m), 1580(s), 1507(m), 1330(m), 1312(m), 1308(m), 1290(m), 1185(m), 1179(m), 840(m).

7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (<u>18b</u>):

3235(s), 3120(m), 3050(m), 2950(s), 2860(m), 2820(s), 2790(s), 2775(s), 2180(s), 2140(s), 1640(s, shoulder), 1600(s), 1510(s), 1460(m), 1325(s), 1290(m), 1260(m), 1228(m), 1195(m), 1170(m), 1113(w), 1100(w), 1080(w), 1026(w), 1005(w), 995(w), 970(w), 935(w), 900(w), 880(w), 840(s), 755(w), 742(w).

7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide (<u>20</u>):

3445(s, broad), 3190(s, broad), 3100(m), 3040(m), 2960(m), 2175(s), 2130(s), 1625(s), 1600(s), 1565(s), 1505(s), 1477(s), 1375(m), 1355(w), 1320(s), 1265(w), 1230(w), 1208(w), 1193(m), 1175(m), 1150(w), 1060(w), 958(w), 940(w), 915(w), 880(w), 835(m), 772(w).

Table 12
(Continued)

7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide - methyl iodide complex (19b):

3442(s, broad), 3015(m), 2888(w), 2823(w), 1643(s), 1510(w), 1477(m), 1411(w), 1363(w), 1265(w), 1210(w), 1175(w), 1098(w), 1062(w), 1015(w), 956(w), 915(w), 892(w), 874(w), 839(w), 744(w), 503(w).

7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan di(tetracyanoquinodimethanide) (21):

3440(m, broad), 3260(m, broad), 3060(w), 3040(w), 2960(w), 2205(s), 2185(s), 2170(shoulder), 2135(s), 1630(s), 1600(s), 1580(s), 1510(s), 1490(m, shoulder), 1480(m), 1368(s), 1335(s), 1265(w), 1222(w), 1180(s), 1175(m, shoulder), 988(m), 824(s), 720(m).

7-(N,N-Dimethyl-1,4-butanediamino)-7,8,8-tricyanoquinodimethan (18c):

3440(w, broad), 3045(m), 2950(m), 2740(w, broad), 2178(s), 2140(s), 1602(s), 1580(s), 1545(m), 1510(s), 1483(m), 1470(m), 1447(w), 1430(m), 1380(m), 1325(s), 1305(s), 1280(s), 1253(m), 1230(w), 1190(s), 1087(w), 1055(w), 1004(w), 948(w), 843(m), 825(w), 731(w), 667(w), 570(w), 500(w).

7,7-(Dimethylamino)-8,8-dicyanoquinodimethan (16):

3350(s, broad), 2965(w), 2945(m), 2175(s), 2145(s), 1590(s), 1530(m), 1490(s), 1460(m), 1445(m), 1420(s), 1405(s), 1390(s), 1325(s), 1290(s), 1220(m), 1207(m), 1178(s), 1135(m), 1100(w), 1080(m), 1162(m), 1155(m), 990(m), 917(m), 890(m), 840(m), 828(m).

7,7-(Dimethylamino)-8,8-dicyanoquinodimethan - methyl iodide complex (16a):

3450(m), 3380(w), 3040(w), 2980(w), 2960(w), 2260(w), 2245(w), 1620(s), 1530(m), 1500(m), 1470(m), 1400(s), 1290(m), 1210(m), 1178(m), 1155(w), 1122(w), 1100(m), 1068(w), 1058(w), 1016(m), 986(w), 972(w), 890(m), 850(m), 833(m).

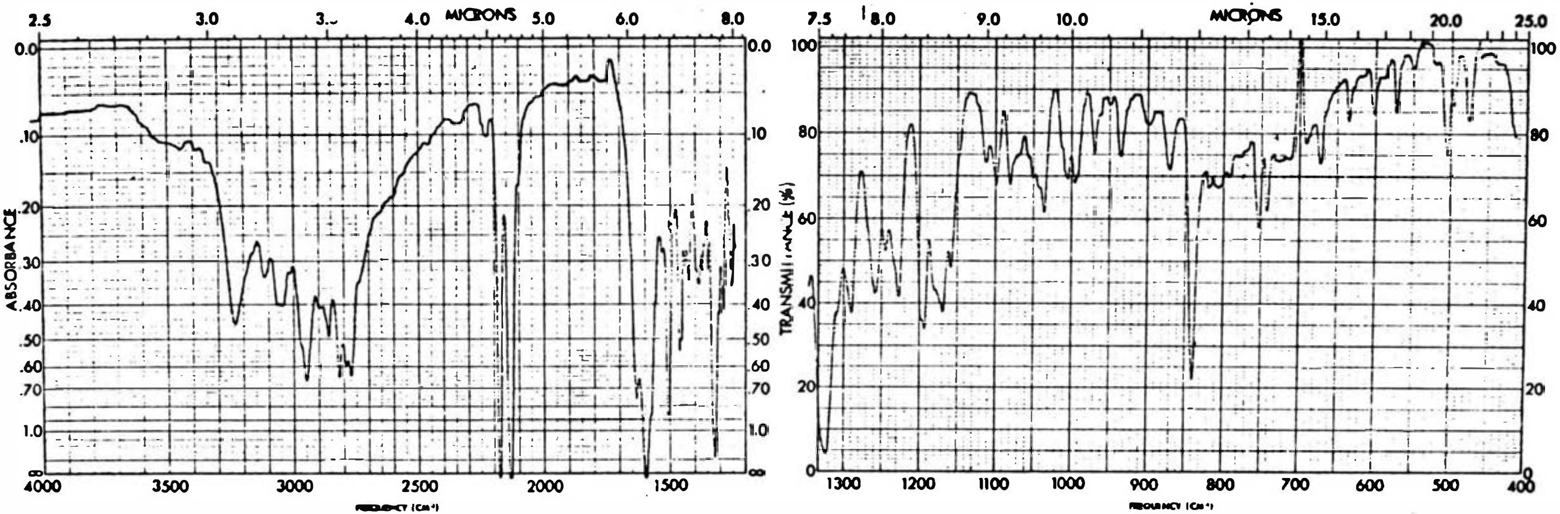


Figure 21: Infrared Spectrum of 7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) as a KBr Pellet.

peak was not as well defined in spectra of the other compounds in this series.

The methyl iodide complexes (16a, 19a and 19b) exhibited ir spectra which were similar to the spectrum of the quaternized precursor, 18b, with the exception of the nitrile absorptions (Table 12). Although the nitrile absorptions appeared as a doublet between 2200 and 2100 cm^{-1}, the intensity was very weak in comparison to the nitrile absorptions of 18b. The spectrum of 7,7-bis(2-trimethylammoniumethylamino)-8,8-dicyanoquinodimethan diiodide - methyl iodide complex (19a) showed a weak nitrile absorption as a doublet (2175 cm^{-1} and 2130 cm^{-1}) (Figure 22).

The ir spectrum for 7,7-bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan di(tetracyanoquinodimethanide) (21) was like the ir spectrum of 18b, exhibiting strong absorptions for the nitrile groups between 2200 and 2100 cm^{-1} (Table 12). Strong absorptions between 1650 and 1550 cm^{-1} reflect a high degree of π-π conjugation in this compound.

The uv spectra of the methyl iodide complexes (16a, 19a and 19b) differed substantially from the uv spectra of their precursors. The comparison of the spectra of 7,7-bis(N,N-dimethyl-1,3-propane)-8,8-dicyanoquinodimethan (18b), 7,7-bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide (20b) and 7,7-bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide - methyl iodide complex (19b) showed that 18b and 20b have absorptions that appeared at 366 nm (ε = 24,470) and 374 nm (ε = 18,990), respectively. This peak was absent in the uv spectrum of 19b. Further, in the spectrum of 18b, a shoulder appeared at 210 nm (ε = 22,820) which was not observed in the spectra for 20b and 19b (Figure 23).

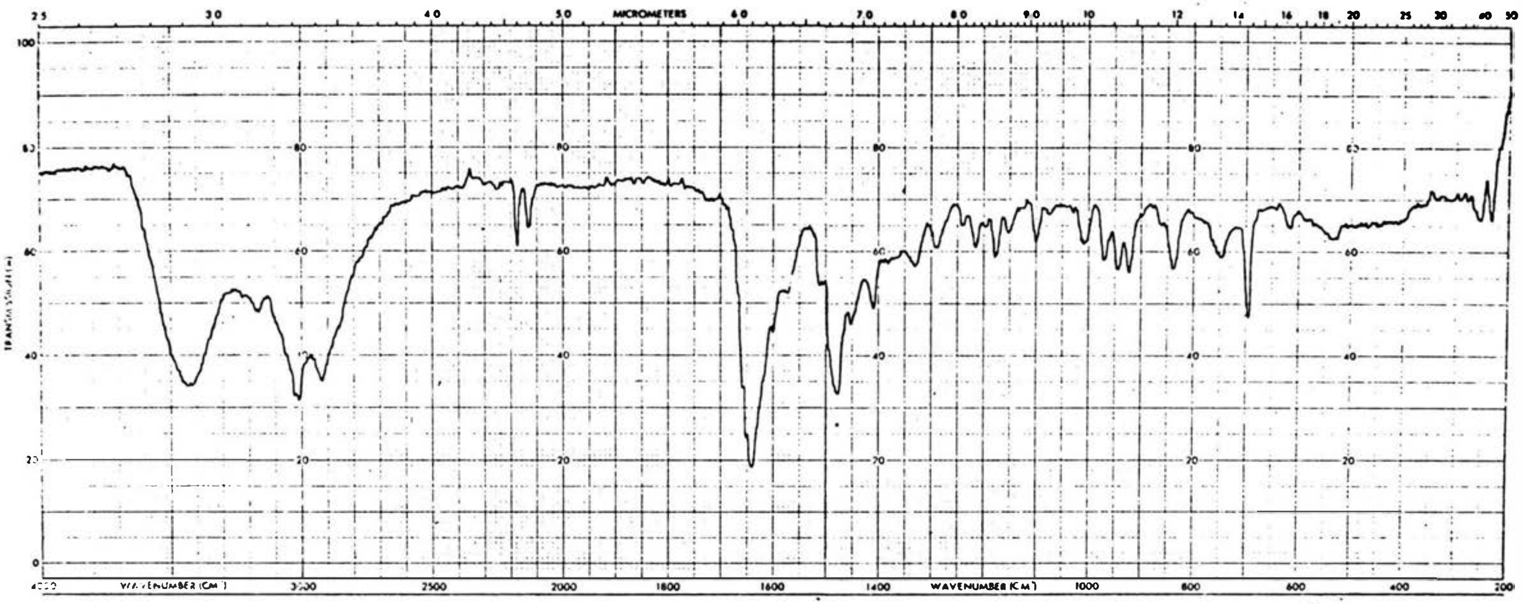


Figure 22: Infrared Spectrum of 7,7-Bis(2-trimethylammoniumethylamino-8,8-dicyanoquinodimethan Diiodide - Methyl Iodide Complex (19a) as a KBr Pellet.

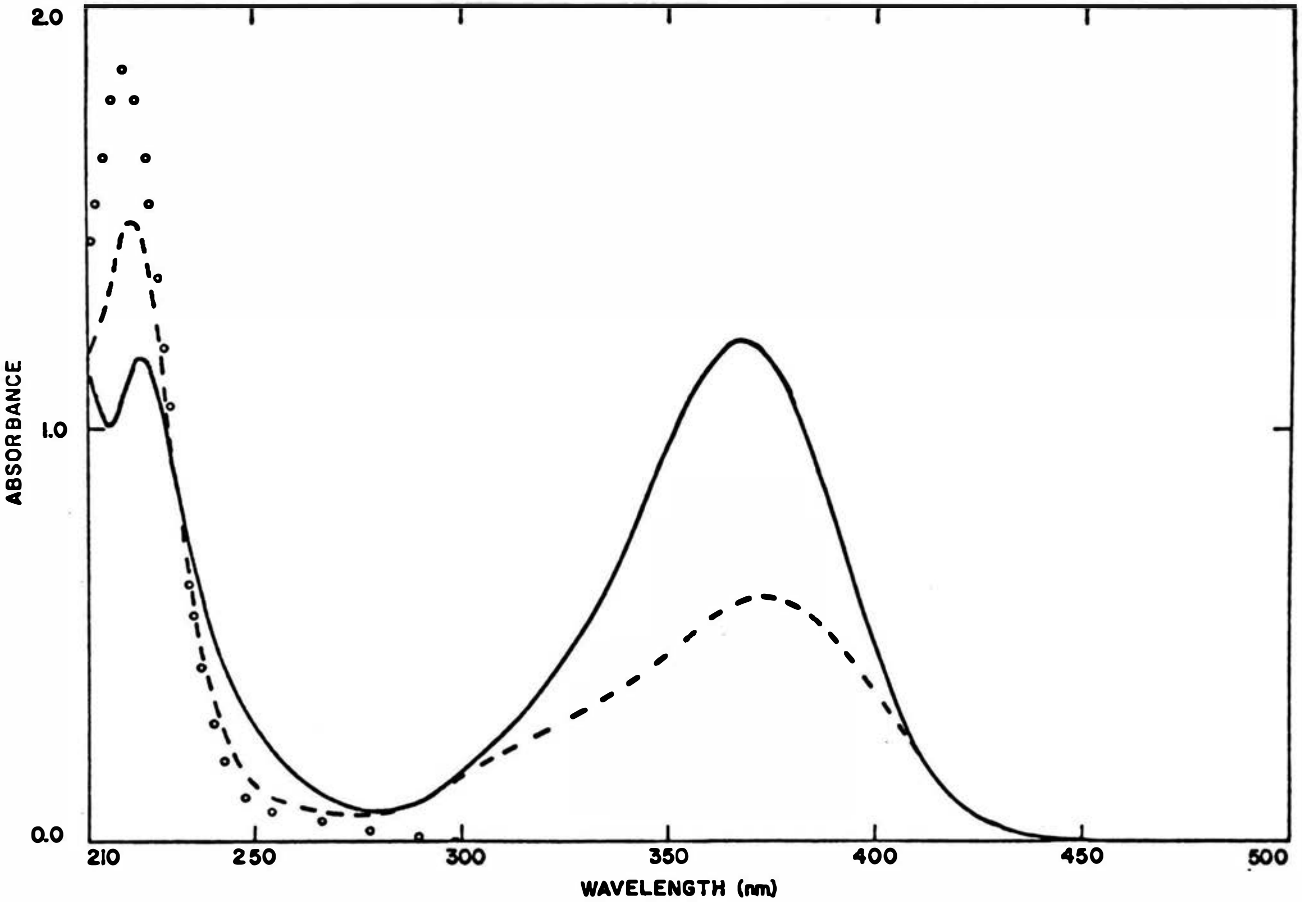


Figure 23: Ultraviolet Spectra of 7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b), 7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan Diiodide (20b) and 7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan Diiodide - Methyl Iodide Complex (19b) in Methanol.

Intramolecular Nitrogen-Hydrogen-Nitrogen Hydrogen Bonding of the 1-(N,N-Dimethyl-α,ω-alkyldiamino)-1,2,2-tricyanoethylene and 7-(N,N-Dimethyl-α,ω-alkyldiamino)-7,8,8-tricyanoquinodimethan Compounds

The $-N(CH_3)_2$ peak in the NMR spectrum of 1-(N,N-dimethyl-α,ω-alkyldiamino)-1,2,2-tricyanoethylene was observed approximately δ 0.50 downfield from the normal position of δ 2.25 reported for a methyl group attached to a tertiary nitrogen atom.[51] For example, the $-N(CH_3)_2$ peak for 1-(N,N-dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene (12b) was observed at δ 2.70, which is δ 0.65 downfield from the position for the $-N(CH_3)_2$ peak (δ 2.15) of the starting material, N,N-dimethyl-1,3-propanediamine. Since the observed downfield chemical shift of 12b is close to the normal position of a quaternized N-methyl group, which is δ 2.95, it appears that the $-N(CH_3)_2$ amine may be involved in a >N —— H• • •N< hydrogen bonding situation which would impart quaternary character to this moiety and cause this unique shift. Similar NMR shifts have been reported by Hine and Li for alkyl tertiary diamines which exhibited intramolecular nitrogen-hydrogen-nitrogen hydrogen bonding involving a hydrogen from a quaternary nitrogen with a tertiary nitrogen.[53]

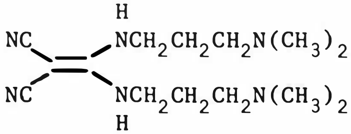
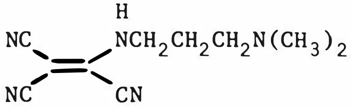
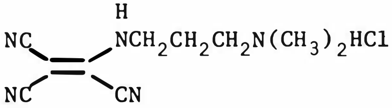
The $-N(CH_3)_2$ group of 1-(N,N-dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene (12b) was quaternized with hydrochloric acid to form 1-(N,N-dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene-N-hydrochloride (22b). The NMR absorption of the quaternized $-N(CH_3)_2$ protons appeared further downfield at δ 2.85 which is 15 Hz downfield from the original $-N(CH_3)_2$ position for compound 12b. This additional downfield shift for the N-methyl groups of the hydrochloride salt (22b) indicates that the tertiary amine of 12b may not have been completely in the quaternized form. Further, it was observed that the methylene groups bonded to the secondary nitrogen and the tertiary nitrogen of 12b appeared at δ 3.77 and δ 3.28, respectively, which are both downfield from the positions of the corresponding methylene groups of the hydrochloride salt (22b) (Table 13). These downfield shifts of the methylene groups of 12b were attributed to diamagnetic anisotropy effects due to the multiple bonds of the remainder of the molecule, indicating that the geometry of compound 12b must differ substantially from that of 22b.

The nitrogen-hydrogen-nitrogen hydrogen bonding was further corroborated by the ir spectrum of 1-(N,N-dimethyl-1,2-ethanediamino)-1,2,2-tricyanoethylene (12a). The N-H stretching was shifted to a longer wavelength (3090 cm^{-1}) for 12a in comparison the absorption at 3270 cm^{-1} for the N-H stretching of 1,1-bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a) indicating strong hydrogen bonding for 12a. The N-H stretching frequencies for 12b and 12c were not as conclusive because the N-H stretch for these compounds was apparently absorbed at the same frequency as the C-H stretch. However, the ir spectra of 12b and 12c exhibited absorptions in the 2700-2250 cm^{-1} region, indicating $R_3\overset{+}{N}H$ character.[54]

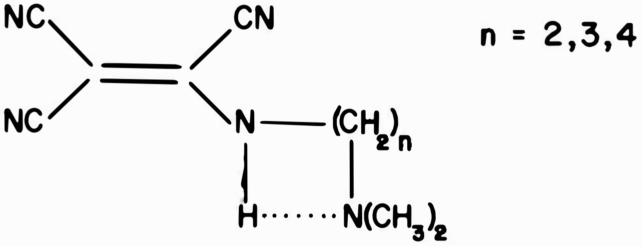
The chemical ionization mass spectrum of compound 12b indicated that it has a mass of 203 (theoretical mol wt 203.2). The molecular weight determination by a thermoelectric measurement in acetonitrile indicated a molecular weight of 199. This data suggest that the compound apparently exists in a monomeric form which would necessitate an intramolecular interaction. Further, if intramolecular hydrogen bonding were to exist, the molecule would have to assume a cyclic conformation approximately 8.5 Å in length. On the other hand, if compound 12b were intermolecularly hydrogen bonded, it would be expected to exist as a linear molecule approximately 12 Å in length. Preliminary X-ray data was obtained which was in agreement with the cyclic conformation

Table 13

NMR Chemical Shifts of 1,1-Bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene, 1-(N,N-Dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene and 1-(N,N-Dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene-N-hydrochloride

Compound	Chemical Shifts δ NH	CH_2	CH_2	CH_2	$N(CH_3)_2$
	7.87	3.35	1.65	2.40	2.16
	8.33	3.77	1.92	3.28	2.70
	8.00	3.67	2.20	3.13	2.85

and an intramolecular arrangement.



The observed position of the NMR absorption for the -N$(CH_3)_2$ peak of the disubstituted derivative, 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b), was δ 2.16 (Table 13). This position was about the same as that of the -N$(CH_3)_2$ group (δ 2.15) of the starting material, N,N-dimethyl-1,3-propanediamine, and indicated that the amine groups of 13b were not exhibiting quaternary character as observed with the monosubstituted TCNE derivative (12b). Compound 13b has two nitrile groups which are delocalizing the nonbonded electron pairs of two nitrogen atoms. The delocalization of the nonbonded electrons of 13b would not, therefore, be expected to be as extensive as in the case of compound 12b since 12b has only one nonbonded pair of electrons delocalized by three electron-withdrawing nitrile groups. The greater delocalization of the nonbonded electrons of compound 12b would result in the decrease of the electron density of the N-H bond, thus making this amine hydrogen more susceptible to a hydrogen bonding interaction than the corresponding amine hydrogens of compound 13b.

The TCNQ analogs, 7-(N,N-dimethyl-1,2-ethanediamino)-7,8,8-tricyanoquinodimethan (17a), 7-(N,N-dimethyl-1,3-propanediamino)-7,8,8-tricyanoquinodimethan (17b) and 7-(N,N-dimethyl-1,4-butanediamino)-7,8,8-tricyanoquinodimethan (17c), also exhibited a downfield chemical shift of approximately δ 0.50 from that expected for a tertiary N-methyl group. For example, the NMR spectrum of compound 17b exhibited the $-N(CH_3)_2$ peak at δ 2.86, which is δ 0.61 downfield from the position of the $-N(CH_3)_2$ peak of the starting material, N,N-dimethyl-1,3-propanediamine. Consequently, it was concluded by the same argument that these compounds were intramolecularly nitrogen-hydrogen-nitrogen hydrogen bonded as well. The ir spectra, however, were not as corroborative as the ir spectra of the TCNE analogs.

Synthesis and Characterization of the TCNE and TCNQ Polymers

The bisamino TCNE derivatives, 1,1-bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a) and 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b), and the bisamino TCNQ derivatives, 7,7-bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a) and 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b), were copolymerized with α,ω-alkyldibromides to produce ionene polymers (Figure 24). The polymerization solutions were prepared in N,N-dimethylformamide (DMF) so that the monomers were in a 1:1 molar ratio and constituted 50 percent of the solution by weight (Tables 14, 15, 16 and 17). The polymerizations of 13a, 13b and 18b were carried out at room temperature for seven days. Due to the insolubility of 18a at room temperature, it was necessary to polymerize it for seven days at an elevated temperature (50°C). The polymers were isolated and dried at 110°C

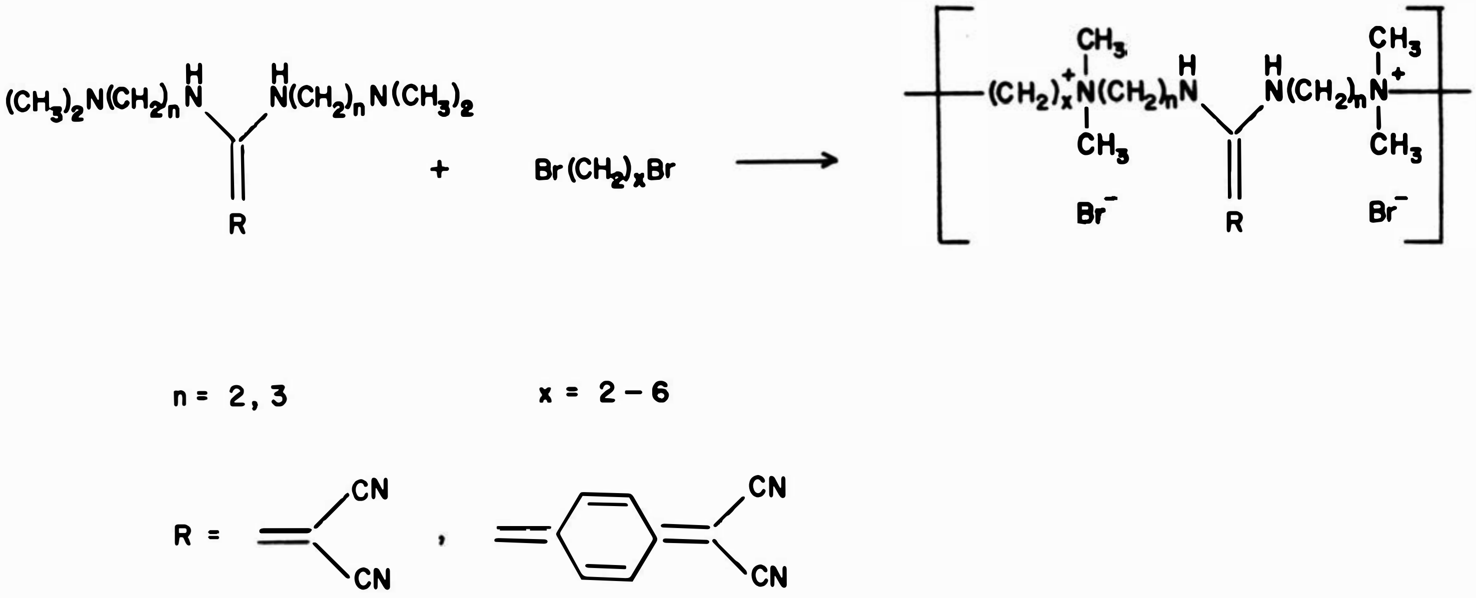


Figure 24: Copolymerization of Bisamino TCNE and TCNQ Derivatives with α,ω-Alkyldibromides.

Table 14

Polymerization of 1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a) at Room Temperature for Seven Days

Dibromide	DiBr mmol	TCNQ Derivative mmol	DMF g	% Yield	Elemental Analysis Calculated C	H	N	Br	Found C	H	N	Br
$Br(CH_2)_2Br$	15.0	15.0	6.5406	62.59	38.37	5.98	19.18	36.47	36.78	5.96	18.27	ND[a]
$Br(CH_2)_3Br$	20.0	20.0	9.0394	93.62	39.84	6.24	18.58	35.34	38.63	6.28	17.98	ND[a]
$Br(CH_2)_4Br$	20.0	20.0	9.2548	94.86	41.22	6.48	18.02	34.28	40.21	6.87	17.74	ND[a]
$Br(CH_2)_5Br$	15.0	15.0	7.2345	98.73	42.51	6.71	17.50	33.27	40.53	6.70	16.55	ND[a]
$Br(CH_2)_6Br$	15.0	15.0	7.4134	97.37	43.74	6.93	17.00	32.33	42.49	6.91	16.49	ND[a]

[a] ND = Not Determined.

Table 15

Polymerization of 1,1-Bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (<u>13b</u>) at Room Temperature for Seven Days

Dibromide	DiBr mmol	TCNQ Derivative mmol	DMF g	% Yield	Elemental Analysis Calculated C	H	N	Br	Found C	H	N	Br
$Br(CH_2)_2Br$	12.5	12.5	5.8182	72.16	41.72	6.43	17.87	33.98	34.88	5.57	14.43	ND[a]
$Br(CH_2)_3Br$	10.0	10.0	4.8030	97.02	42.51	6.72	17.50	33.27	40.47	6.66	16.06	ND[a]
$Br(CH_2)_4Br$	12.5	12.5	6.1828	89.88	43.74	6.93	17.00	32.33	42.43	6.96	16.35	ND[a]
$Br(CH_2)_5Br$	12.5	12.5	6.3231	98.84	44.89	7.14	16.53	31.44	43.11	7.15	15.81	ND[a]
$Br(CH_2)_6Br$	12.5	12.5	6.5355	97.37	45.99	7.33	16.09	30.59	43.98	7.22	15.31	ND[a]

[a] ND = Not Determined.

Table 16

Polymerization of 7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (<u>18a</u>) at 50°C for Seven Days

Dibromide	DiBr mmol	TCNQ Derivative mmol	DMF g	% Yield	Elemental Analysis Calculated C	H	N	Br	Found C	H	N	Br
$Br(CH_2)_2Br$	10.0	10.0	5.1552	60.19	46.71	5.88	16.34	31.07	54.02	6.85	20.21	ND[a]
$Br(CH_2)_3Br$	10.0	10.0	5.2802	91.44	47.74	6.10	15.91	30.25	44.68	6.13	14.69	ND[a]
$Br(CH_2)_4Br$	10.0	10.0	5.5223	91.13	48.72	6.32	15.49	29.47	46.63	6.29	14.73	ND[a]
$Br(CH_2)_5Br$	10.0	10.0	5.5346	91.38	49.65	6.52	15.11	28.72	47.70	6.57	14.06	ND[a]
$Br(CH_2)_6Br$	10.0	10.0	5.7038	94.04	50.54	6.71	14.73	28.02	48.48	6.62	14.06	ND[a]

[a] ND = Not Determined.

Table 17

Polymerization of 7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) at Room Temperature for Seven Days

Dibromide	DiBr mmol	TCNQ Derivative mmol	DMF g	% Yield	Elemental Analysis							
					Calculated				Found			
					C	H	N	Br	C	H	N	Br
$Br(CH_2)_2Br$	15.0	15.0	8.1349	72.93	48.72	6.32	15.49	29.47	45.76	6.19	13.92	ND[a]
$Br(CH_2)_3Br$	15.0	15.0	8.3459	94.20	49.65	6.52	15.11	28.72	47.20	6.52	14.05	ND[a]
$Br(CH_2)_4Br$	15.0	15.0	8.5161	94.53	50.54	6.71	14.73	28.02	46.25	6.49	13.26	ND[a]
$Br(CH_2)_5Br$	15.0	15.0	8.7220	96.25	51.38	6.90	14.38	27.34	47.00	6.69	13.00	ND[a]
$Br(CH_2)_6Br$	15.0	15.0	8.9587	95.43	52.18	7.08	14.04	26.70	48.80	6.86	12.97	ND[a]

[a] ND = Not Determined.

for several days. All the ionene polymers prepared were

The ir spectra of the polymers were similar and their absorptions are reported in Table 18. For example, the ir spectrum of 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan-1,4-dibromobutane copolymer (TCNQ 3-4) exhibited the characteristic doublet for the nitrile groups between 2200 and 2100 cm^{-1} (Figure 25). Absorptions appeared near 1600 cm^{-1} which were attributed to the conjugated C-C double bonds. The broad absorption at 3400 cm^{-1} was attributed to moisture absorbed by the polymer due to its hygroscopic nature. The ir spectrum of 1,1-bis-(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene-1,5-dibromopentane copolymer (TCNE 3-5) also exhibited the nitrile absorptions between 2200 and 2100 cm^{-1}. The broad water absorption appeared at 3400 cm^{-1} as well as the absorption at 1570 cm^{-1} for the C-C double bonds (Figure 26).

The NMR spectra of the polymers were similar and exhibited broad absorptions. In general, the quaternary N-methyl groups appeared as a singlet between δ 3.00 and δ 3.20. The methylene groups adjacent to other methyl groups showed up as a broad unresolved absorption between δ 1.5 and δ 2.5. The methylene groups bonded to the secondary and quaternary nitrogen atoms were observed between δ 3.2 and δ 4.0. The polymer synthesized from TCNQ derivatives showed the characteristic AB quartet at approximately δ 7.3. The TCNQ polymers also exhibited another peak downfield from the quartet at about δ 7.9 which was interpreted as representing the N-H protons. The NMR spectra of TCNE 3-4 and TCNQ 3-5 represent typical polymer spectra (Figures 27 and 28).

Viscosity measurements of dilute polymer solutions are commonly used to characterize polymers. The intrinsic viscosity $[\eta]$ of a polymer increases with molecular weight and, thus, affords a measure of molecular

Table 18

Infrared Absorptions of Ionene Polymers

1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-1,2-dicyanoethylene-1,2-dibromoethane copolymer (TCNE 2-2):

3420(s, broad), 3250(m), 3025(m), 2975(m), 2890(w), 2700(m, broad), 2210(s), 2180(s), 1570(s), 1500(s), 1460(s), 1425(m), 1285(m), 1165(w), 1080(w), 1020(m), 960(m), 922(m).

1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-1,2-dicyanoethylene-1,3-dibromopropane copolymer (TCNE 2-3):

3400(s, broad), 3200(m), 3000(m), 2950(m), 2875(w), 2200(s), 2175(s), 1570(s), 1475(s), 1425(m), 1375(m), 1340(m), 1285(m), 1240(w), 1050(w, broad), 920(w, broad).

1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-1,2-dicyanoethylene-1,4-dibromobutane copolymer (TCNE 2-4):

3400(s, broad), 3225(s), 3000(m), 2950(m), 2875(w), 2200(s), 2175(s), 1570(s), 1475(m), 1375(m), 1340(m), 1275(w), 908(w).

1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-1,2-dicyanoethylene-1,5-dibromopentane copolymer (TCNE 2-5):

3400(s, broad), 3225(s), 3025(m), 3950(m), 2925(m), 2850(m), 2200(s), 2175(s), 1570(s), 1475(s), 1380(m), 1345(m), 1275(w), 695(m).

1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-1,2-dicyanoethylene-1,6-dibromohexane copolymer (TCNE 2-6):

3400(s, broad), 3200(s), 3100(m), 3000(m), 2945(m), 2860(m), 2200(s), 2175(s), 1570(s), 1475(m), 1380(m), 1345(m), 1280(m).

1,1-Bis(N,N-dimethyl-1,3-propanediamino)-1,2-dicyanoethylene-1,2-dibromoethane copolymer (TCNE 3-2):

3400(s, broad), 3225(s), 3125(m), 3010(m), 2960(m), 2825(w), 2725(w), 2200(s), 2175(s), 1575(s), 1475(m), 1350(m), 1250(m).

1,1-Bis(N,N-dimethyl-1,3-propanediamino)-1,2-dicyanoethylene-1,3-dibromopropane copolymer (TCNE 3-3):

3400(s, broad), 3225(s), 3030(m), 3000(m), 2960(m), 2875(w), 2200(s), 2175(s), 1575(s), 1475(m), 1360(m), 1250(m).

Table 18
(Continued)

1,1-Bis(N,N-dimethyl-1,3-propanediamino)-1,2-dicyanoethylene-1,4-dibromobutane copolymer (TCNE 3-4):

3400(s, broad), 3225(s), 3125(m), 3015(m), 2950(m), 2200(s), 2175(s), 1575(s), 1475(s), 1300(m), 1360(m), 1250(m).

1,1-Bis(N,N-dimethyl-1,3-propanediamino)-1,2-dicyanoethylene-1,5-dibromopentane copolymer (TCNE 3-5):

3400(s, broad), 3225(s), 3125(m), 3025(m), 3000(m), 2950(m), 2875(m), 2200(s), 2175(s), 1575(s), 1475(s), 1380(m), 1350(m), 1245(m).

1,1-Bis(N,N-dimethyl-1,3-propanediamino)-1,2-dicyanoethylene-1,6-dibromohexane copolymer (TCNE 3-6):

3425(s, broad), 3225(s), 3050(m), 3010(m), 2960(m), 2875(m), 2210(s), 2180(s), 1580(s), 1475(s), 1440(m), 1400(m), 1360(m), 1250(m).

7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan-1,2-dibromoethane copolymer (TCNQ 2-2):

3400(s, broad), 3225(s), 3060(m), 3030(m), 3000(m), 2960(m), 2940(m), 2850(m), 2825(m), 2775(m), 2170(s), 2130(s), 1625(s), 1580(s), 1490(s), 1455(s), 1425(m), 1360(m), 1325(s), 1275(m), 1250(m), 1230(m), 1197(m), 1180(m), 1095(w), 1038(m), 1010(w), 835(m), 500(m).

7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan-1,3-dibromopropane copolymer (TCNQ 2-3):

3400(s, broad), 3040(m), 3000(m), 2955(m), 2875(m), 2175(s), 2130(s), 1625(s), 1590(s), 1495(s), 1475(s), 1360(w), 1320(s), 1190(m), 840(m).

7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan-1,4-dibromobutane copolymer (TCNQ 2-4):

3400(s, broad), 3040(m), 3000(m), 2950(m), 2880(m), 2825(m), 2675 (m, broad), 2175(s), 2130(s), 1625(s), 1590(s), 1495(s), 1470(m), 1360(m), 1315(s), 1275(m), 1225(w), 1185(m, broad), 840(m).

Table 18
(Continued)

7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan-1,5-dibromopentane copolymer (TCNQ 2-5):

3400(s, broad), 3025(m), 3000(m), 2950(m), 2875(m), 2830(m), 2680(m, broad), 2175(s), 2130(s), 1625(s), 1590(s), 1500(s), 1475(s), 1370(m), 1325(s), 1275(m), 1225(w), 1190(m), 1170(m), 837(m).

7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan-1,6-dibromohexane copolymer (TCNQ 2-6):

3400(s, broad), 3060(m), 3030(m), 3000(m), 2940(m), 2875(m), 2675(m, broad), 2165(s), 2125(s), 1590(s), 1490(s), 1470(m), 1360(m), 1320(s), 1275(m), 1225(w), 1185(m), 840(m).

7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan-1,2-dibromoethane copolymer (TCNQ 3-2):

3420(s, broad), 3035(m), 3000(m), 2960(m), 2875(m), 2070(s), 2030(s), 1630(s), 1590(s), 1500(m), 1475(m), 1320(m).

7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan-1,3-dibromopropane copolymer (TCNQ 3-3):

3400(s, broad), 3030(m), 3010(m), 2950(m), 2875(m), 2170(s), 2120(s), 1625(s), 1590(s), 1500(s), 1475(m), 1370(m), 1315(s), 1250(w), 1225(w), 1190(m), 1170(m), 838(m).

7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan-1,4-dibromobutane copolymer (TCNQ 3-4):

3400(s, broad), 3035(w), 3000(w), 2950(w), 2175(s), 2130(s), 1625(s), 1590(s), 1500(m), 1425(m), 1375(w), 1320(s), 1190(m), 1170(m), 835(m).

7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan-1,5-dibromopentane copolymer (TCNQ 3-5):

3400(s, broad), 3270(s, broad), 3020(s), 2940(s), 2875(s), 2170(s), 2125(s), 1625(s), 1590(s), 1500(s), 1475(s), 1375(m), 1320(s), 1250(m), 1225(m), 1187(s), 1170(m), 835(m).

Table 18

(Continued)

7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan-1,6-dibromohexane copolymer (TCNQ 3-6):

3400(s, broad), 3200(m, broad), 3040(m), 3000(m), 2940(m), 2870(m), 2170(s), 2120(s), 1625(s), 1590(s), 1500(m), 1475(m), 1375(w), 1320(s), 1250(w), 1225(w), 1190(m), 1170(m), 838(m).

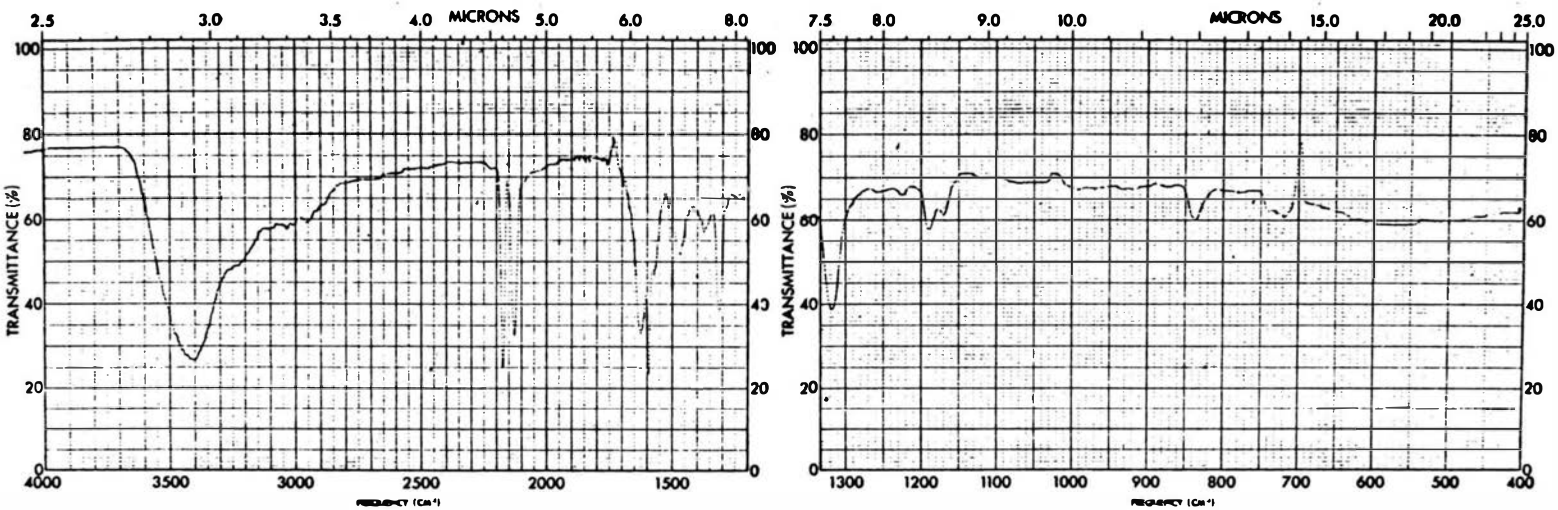


Figure 25: Infrared Spectrum of TCNQ 3-4 as a KBr Pellet.

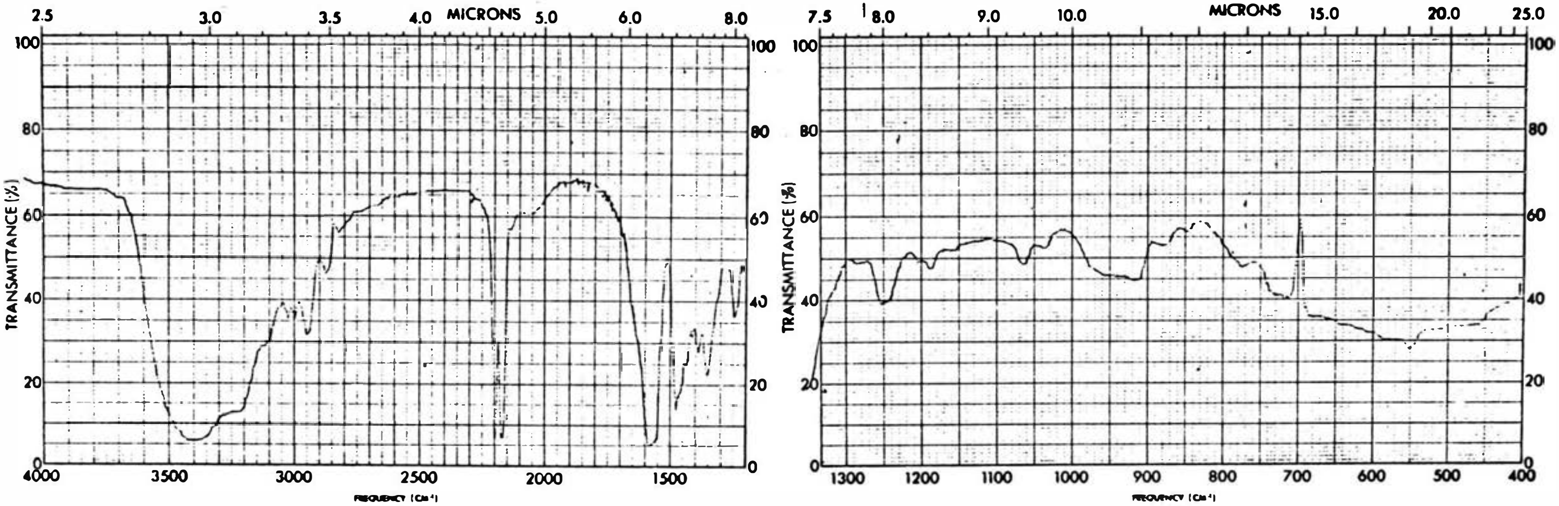


Figure 26: Infrared Spectrum of TCNE 3-5 as a KBr Pellet.

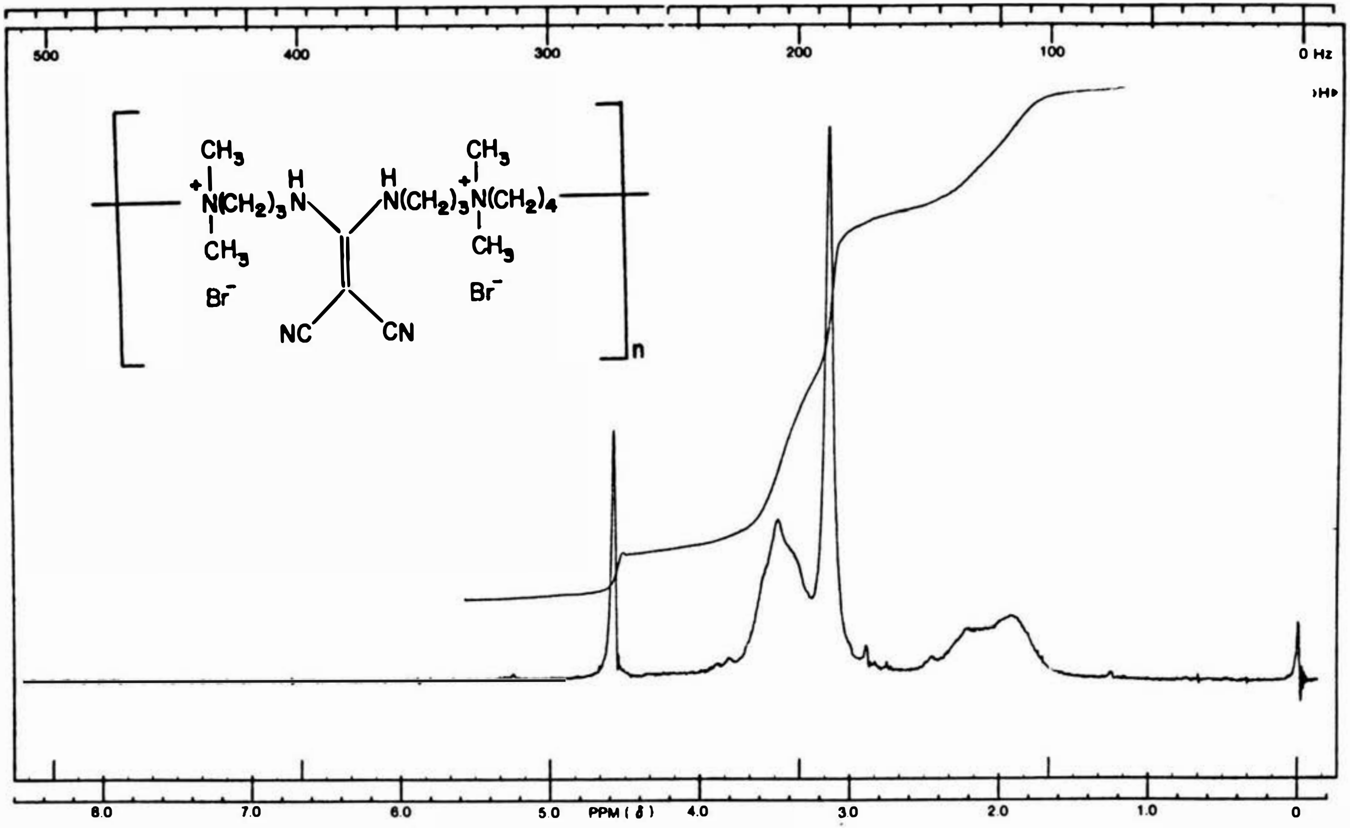


Figure 27: NMR Spectrum of TCNE 3-4 in Deuterium Oxide.

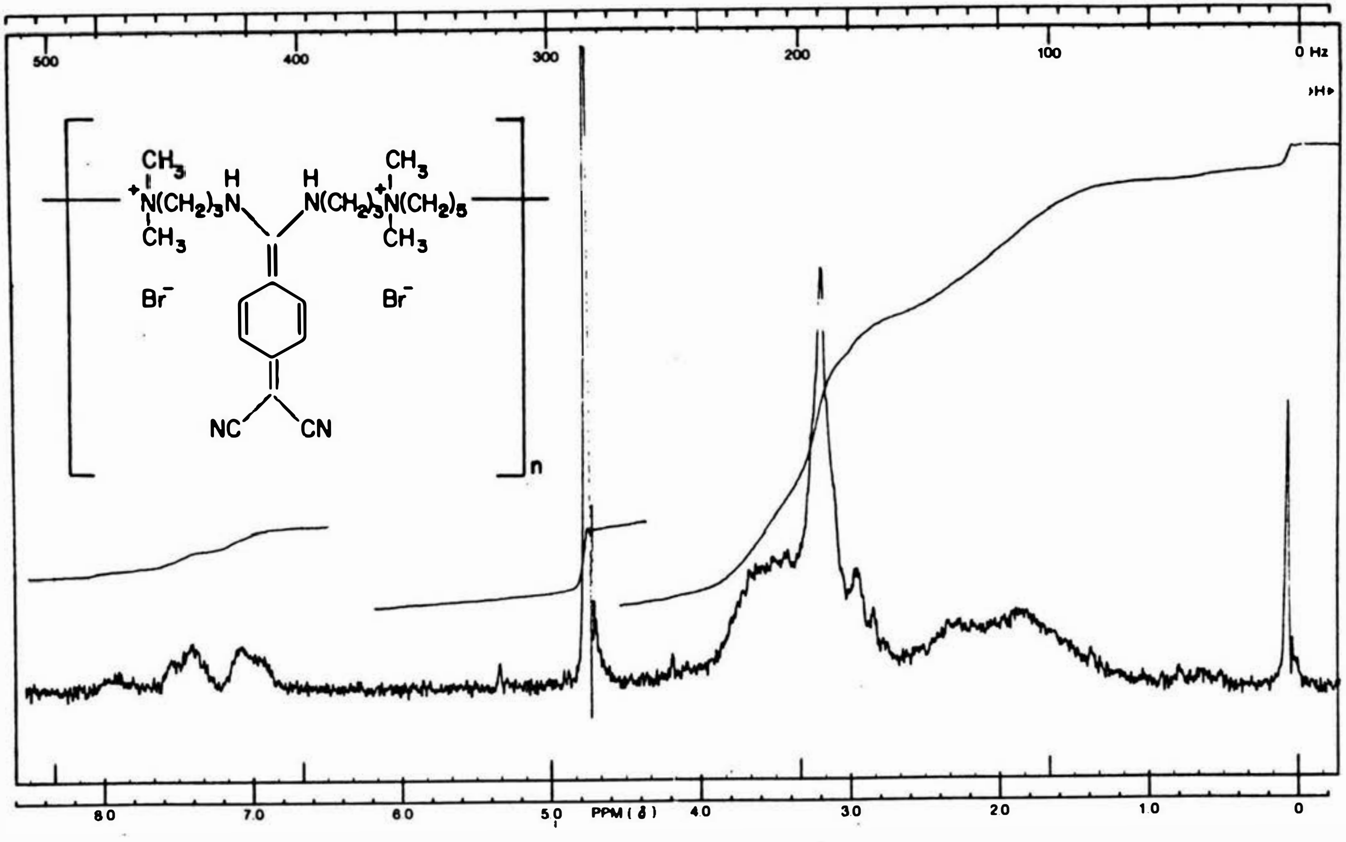


Figure 28: NMR Spectrum of TCNQ 3-5 in Deuterium Oxide.

weight. Viscosity measures can be used to indicate the relative molecular weights of a series of linear polymer homologs. However, an absolute value for the molecular weight of a polymer cannot be derived from solution viscosity measurements.

Polyelectrolytes usually undergo abnormal expansion in dilute solutions, which complicates the viscosity data. The expansion of the polyelectrolyte may be minimized, thus simplifying the viscosity data, by the addition of a low molecular weight salt.[34,35,55,56] There are two explanations for the viscosity of an ionized polyelectrolyte to decrease with the addition of a salt. First, in very dilute, salt-free solutions, as the polyelectrolyte ionizes, the counterions diffuse into the solution leaving positive sites on the polymer backbone. In the case of the polycationic ionenes, these counterions are anions. As the anions move farther from the positive sites, the electrostatic repulsion between the positive charges increases and the polymer expands to a greater than normal volume to achieve maximum charge separation. The increase in the molecular volume of the polymer causes the viscosity to increase. The addition of a salt to the solution reduces the ionization of the polycation and increases the shielding effect of the anions (counterions) on the charged groups. The mutual repulsion between adjacent charged sites on the macromolecule is reduced allowing contraction of the polymer chain and a decrease in viscosity. Electrostatic forces play the dominant role in polymer expansion only in extremely dilute solutions.

At high concentrations of polymer, the ionic atmosphere surrounding the polymer becomes so thin that the majority of the counterions remain within the molecular coil. When the concentration of the counterions inside the coil becomes greater than that in solution, solvent molecules enter the coil causing the macromolecule to expand. Thus, osmotic forces are responsible for polymer expansion at high polymer concentrations. The addition of a salt to the solution increases the ionic strength, causing the solvent molecules to migrate out of the polymer coil and allowing it to contract.

At intermediate polymer concentrations, both osmotic and electrostatic forces contribute to the polymer expansion.[56] The expansion of the polymer must be minimized in order to obtain coherent viscosity data. Viscosity data of polyelectrolytes are, therefore, obtained from solutions in which the polyelectrolytes do not ionize or form solutions in which the salt concentration is sufficiently high to prevent polymer expansion. The latter approach was employed in the study of the TCNE and TCNQ polymers.

The effect of the concentration of KBr on the reduced viscosity of the TCNE 3-3, TCNE 2-6 and TCNQ 3-6 polymers is illustrated in Figures 29, 30 and 31, respectively. The reduced viscosity of the polymer is plotted versus the concentration of KBr. The sharp drop in the reduced viscosity of TCNE 3-3 as compared to TCNE 2-6 or TCNQ 3-6 is an indication that the former has a higher molecular weight. At 0.20 M KBr or greater concentration, the reduced viscosities of TCNE 3-3 and TCNE 2-6 underwent relatively little change indicating a decrease in significant polymer contraction. For the TCNQ 3-6 polymer, it was determined that a salt concentration above 0.10 M produced no significant change in the reduced viscosity. The solubility of TCNE 3-3 and TCNQ 3-6 in aqueous KBr solutions decreased sharply when the salt concentration was greater than 0.25 M and 0.17 M, respectively, thus making it impossible to obtain viscosity data at higher salt concentrations.

The viscosity study of TCNE 3-3 in N,N-dimethylformamide (DMF) was

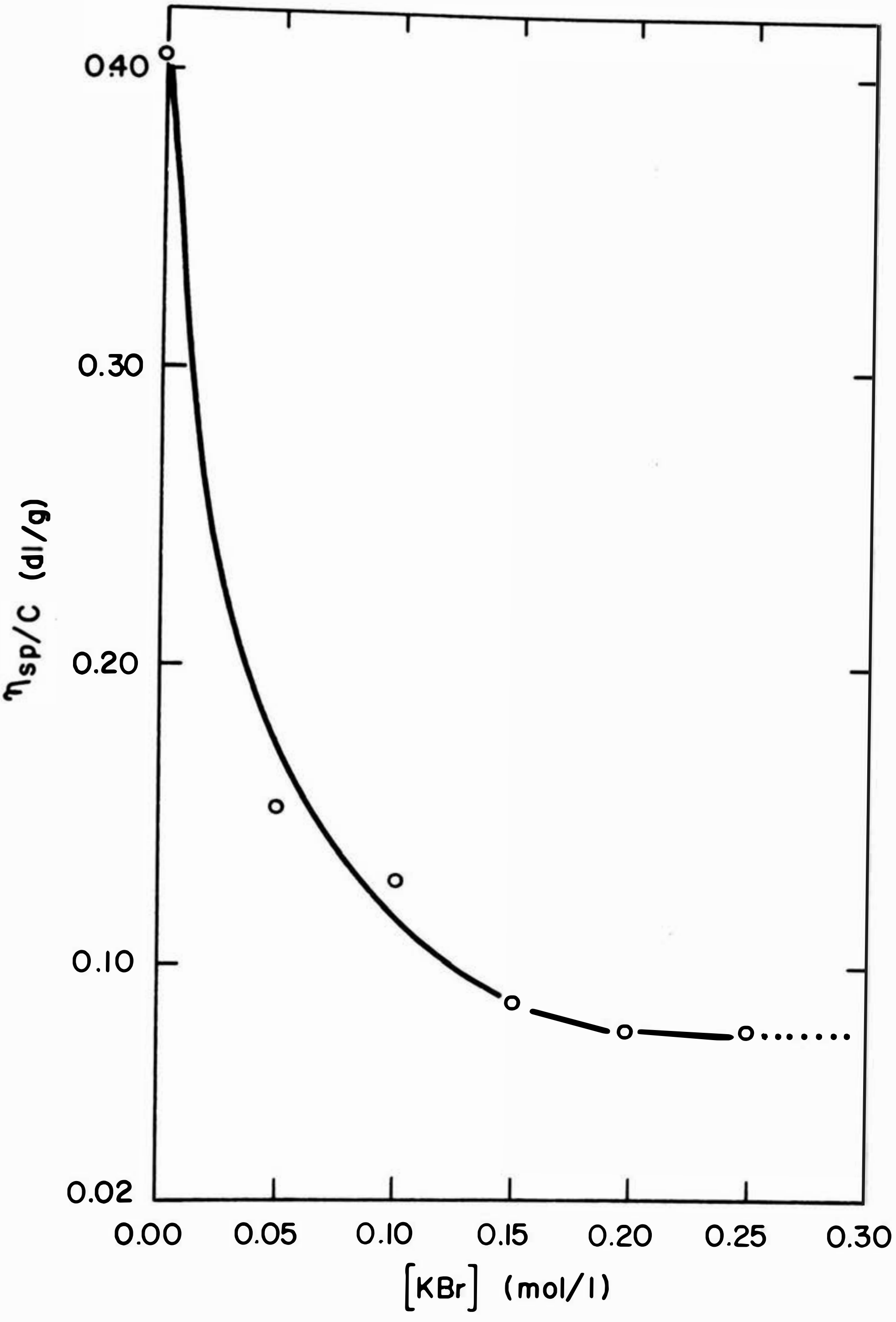


Figure 29: Reduced Viscosity of TCNE 3-3 in Water as a Function of KBr Concentration.

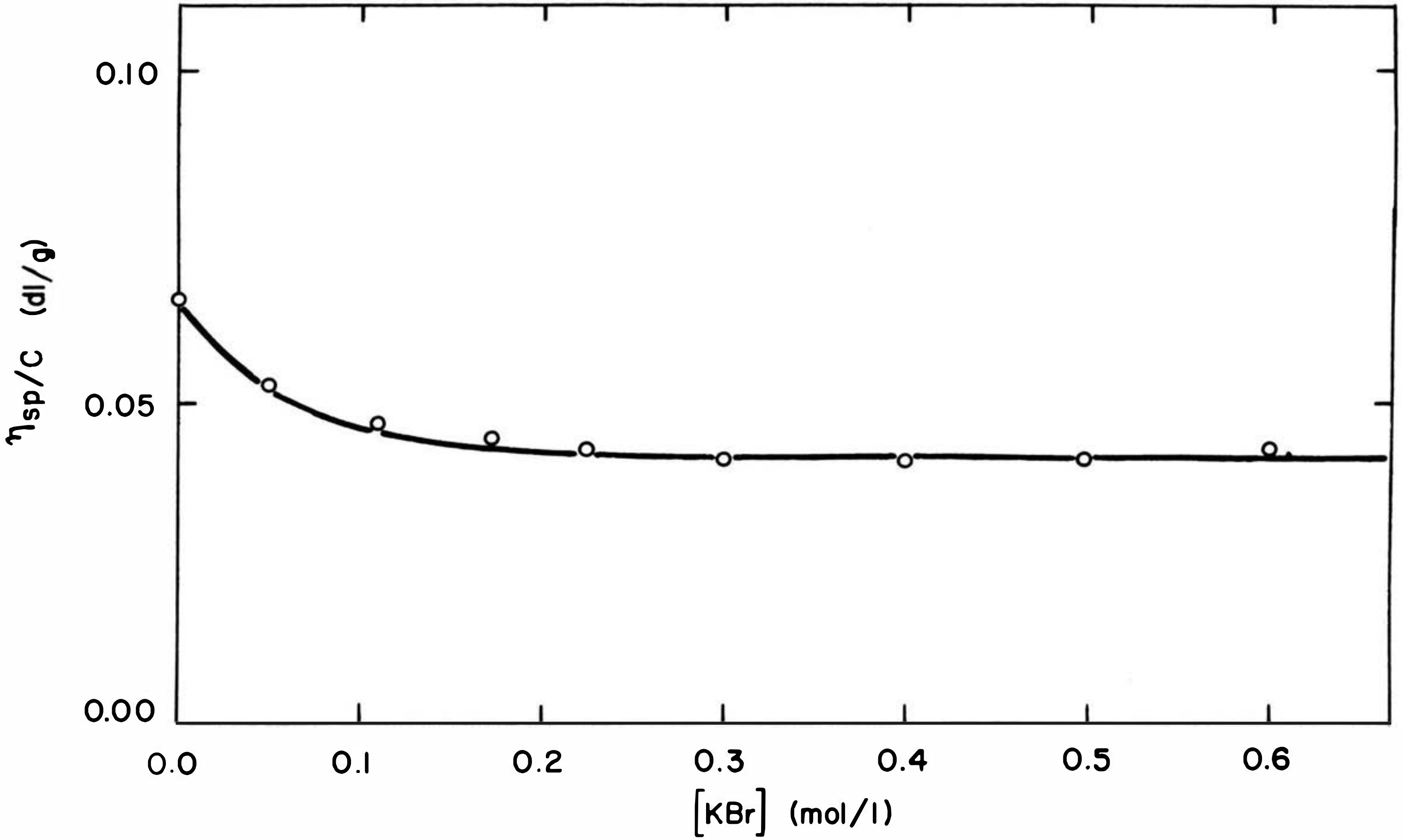


Figure 30: Reduced Viscosity of TCNE 2-6 as a Function of KBr Concentration.

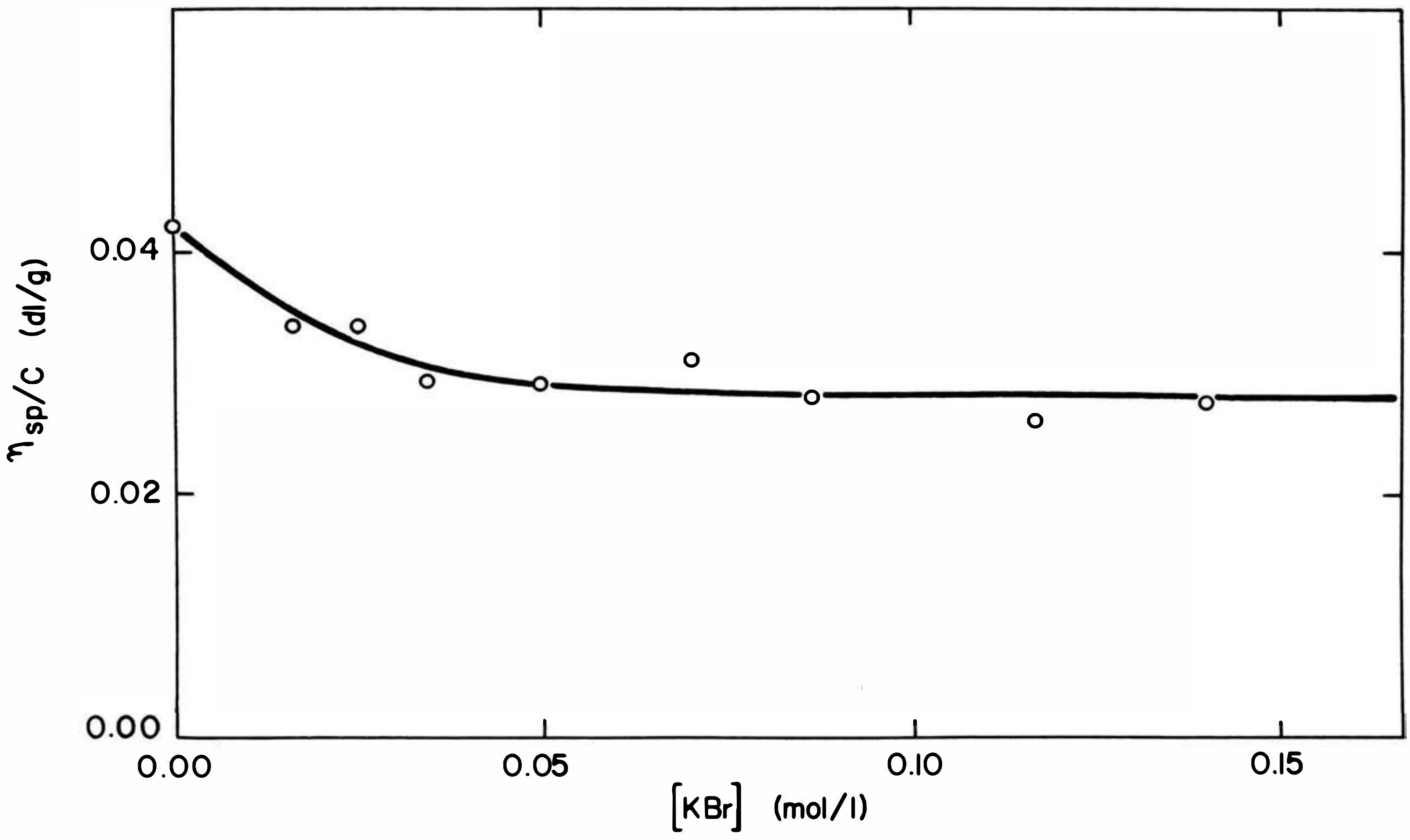


Figure 31: Reduced Viscosity of TCNQ 3-6 as a Function of KBr Concentration.

attempted in order to obtain a solvent system which would permit the solubility of the polymers at higher salt concentrations, thereby allowing a more complete generation of the horizontal portion of the plot of relative viscosity versus salt concentration. Two salts, lithium bromide and ammonium bromide, were used because of their high solubility in DMF and the fact that the anion, Br^-, is the same as the counterion of the polymers. The graph of the relative viscosity of TCNE 3-3 versus lithium bromide concentration is illustrated in Figure 32. A similar plot was obtained when ammonium bromide was the salt. The sharp increase in the relative viscosity as the lithium bromide concentration increased from 0.2 M to 0.9 M is not understood at this time. It may be related to the fact that the elution times of the LiBr-DMF solution increased from 102 seconds for 0.05 M LiBr to 201 seconds for 0.90 M LiBr. Due to this peculiar behavior in these DMF salt solutions, further studies of these polymers in such solutions were not pursued.

The intrinsic viscosities $[\eta]$ of the TCNE and TCNQ ionene polymers were determined in aqueous KBr solutions (Table 19). Representative graphs from which intrinsic viscosities were determined appear in Figure 33. The TCNE 3-5 polymer had the highest intrinsic viscosity, indicating that it was of higher molecular weight than the other polymers. The intrinsic viscosities indicated that generally lower molecular weight polymers were obtained when 7,7-bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (<u>18a</u>) or 1,2-dibromoethane was used as one of the monomers in a polymerization. It was assumed that the former resulted in lower molecular weight material because of its insolubility in the solvent media which necessitated that the polymerizations be conducted at an elevated temperature. It has previously been reported that the increase

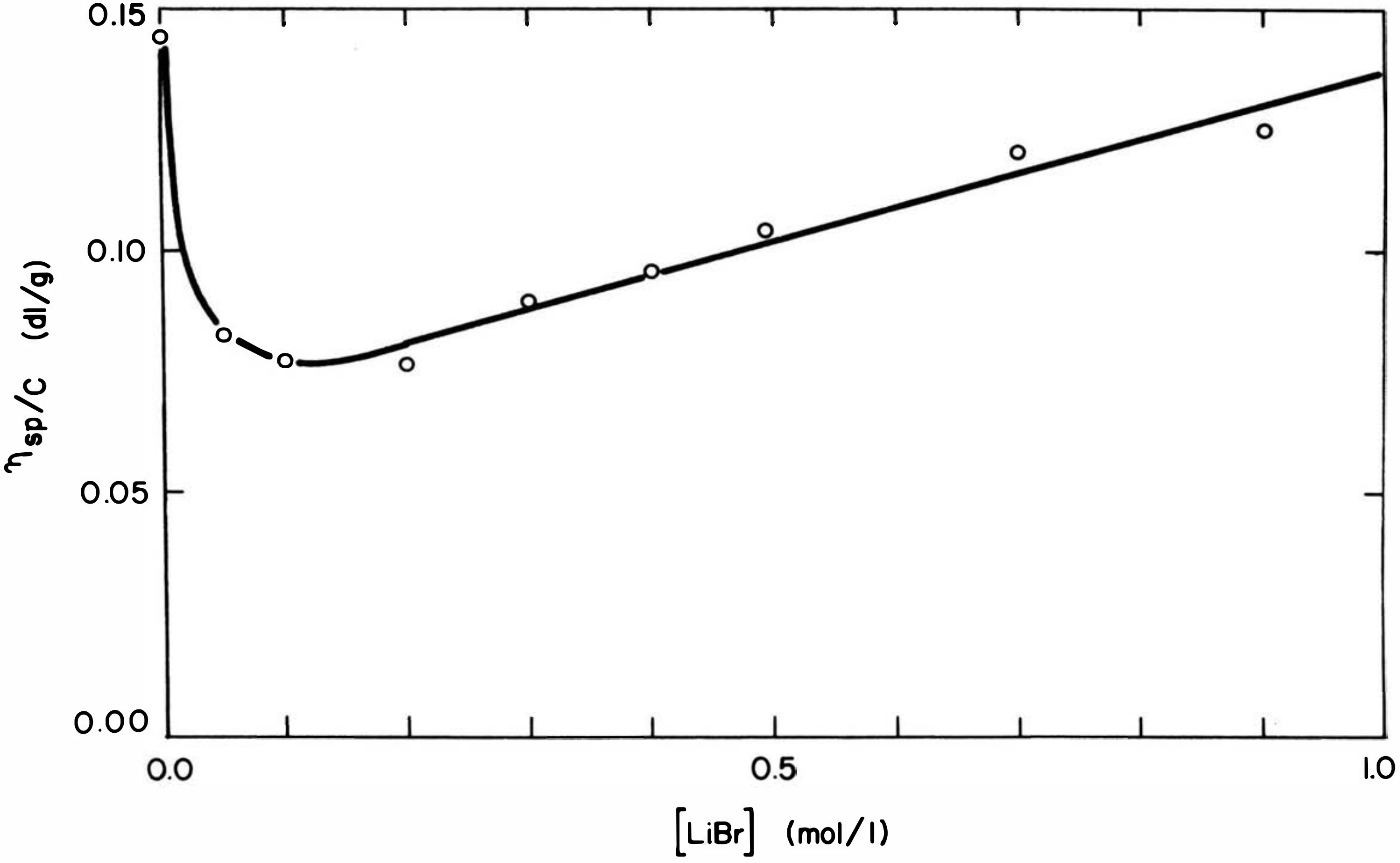


Figure 32: Reduced Viscosity of TCNE 3-3 in DMF as a Function of LiBr.

Table 19

Intrinsic Viscosities of TCNQ and TCNE Ionene Polymers

Polymer	M KBr	[η] dl/g
TCNE 2-2	0.25	0.0092
TCNE 2-3	0.25	0.0267
TCNE 2-4	0.25	0.0534
TCNE 2-5	0.25	0.0653
TCNE 2-6	0.25	0.0394
TCNE 3-2	0.25	-0.0010
TCNE 3-3	0.25	0.0679
TCNE 3-4	0.25	0.0341
TCNE 3-5	0.25	0.1320
TCNE 3-6	0.25	0.0814
TCNQ 2-2	Insoluble in Aqueous KBr	
TCNQ 2-3	0.15	0.0066
TCNQ 2-4	0.15	0.0029
TCNQ 2-5	0.15	0.0169
TCNQ 2-6	0.15	0.0094
TCNQ 3-2	0.15	0.0131
TCNQ 3-3	0.07	0.0147
TCNQ 3-4	0.15	0.0063
TCNQ 3-5	0.15	0.0200
TCNQ 3-6	0.15	0.0175

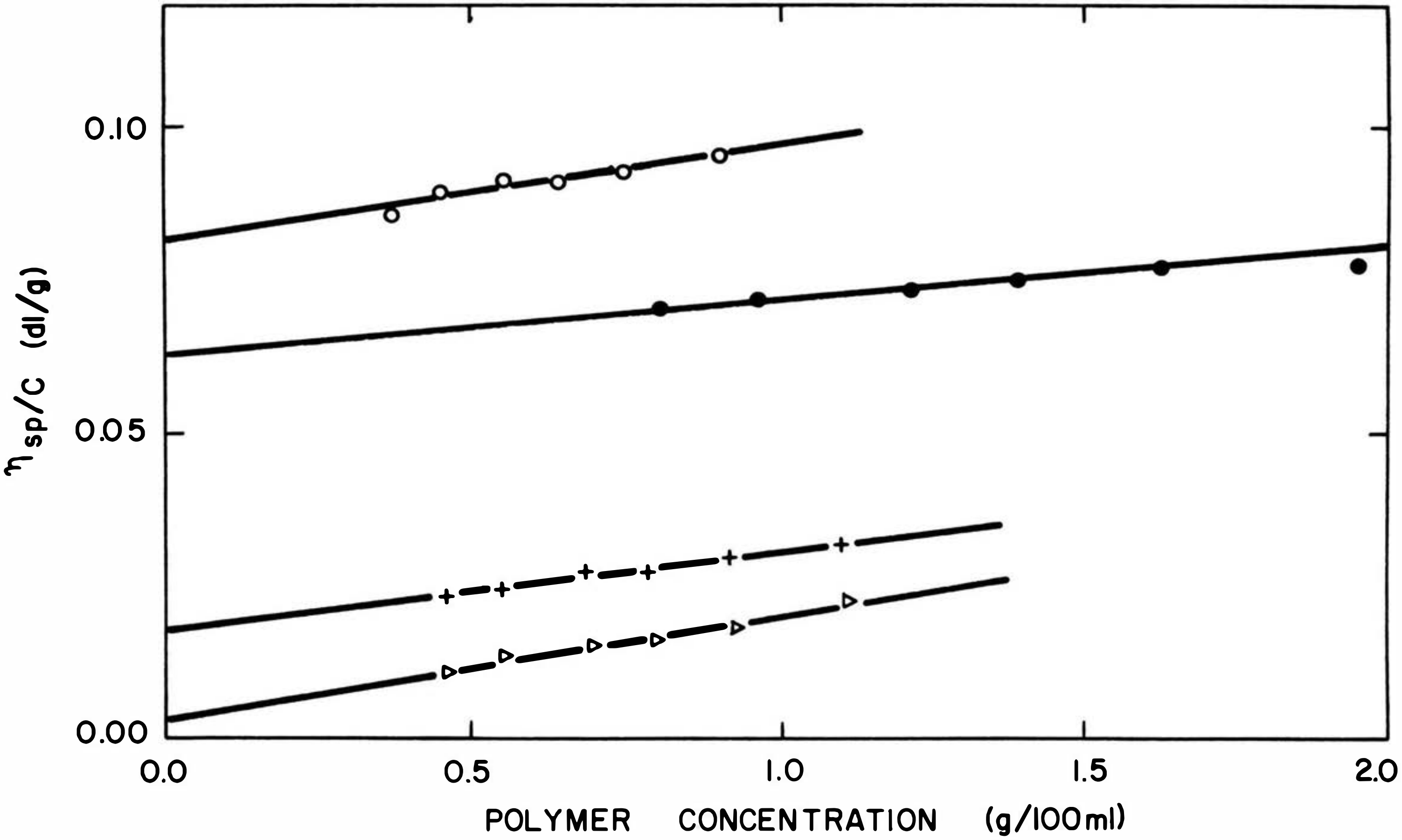


Figure 33: The Reduced Viscosities of TCNE 3-6 (○), TCNE 2-5 (●), TCNQ 3-6 (+) and TCNQ 2-4 (▷) as a Function of Polymer Concentration in an Aqueous KBr Solution.

in polymerization temperature apparently produces a lower molecular weight ionene polymer.[32] The fact that the use of 1,2-dibromoethane results in low molecular weight ionene polymers has previously been reported.[35]

Conductivities

The 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene and 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan polymers were treated with LiTCNQ in order to produce conducting materials. The following polymers were reacted in a 1:2 molar ratio of repeating polymer unit to LiTCNQ (Tables 20 and 21): TCNE 3-3, TCNE 3-4, TCNE 3-5, TCNE 3-6, TCNQ 3-3, TCNQ 3-4, TCNQ 3-5 and TCNQ 3-6. In each case, a hot solution of LiTCNQ was added to a hot polymer solution in DMF-methanol and the product precipitated as a dark-blue solid. In addition, the TCNE 3-5 and TCNQ 3-6 polymers were treated with LiTCNQ and $TCNQ^o$ in a ratio of repeating polymer unit to LiTCNQ to TCNQ of 1:2:1 and 1:2:2. The doping of these latter two polymers was accomplished in order to determine the effect of $TCNQ^o$ on the conductivity of the polymers.

The resistivities of the model compounds, 1,1-bis(2-trimethylammoniumethylamino)-2,2-dicyanoethylene di(tetracyanoquinodimethanide) (15a) and 1,1-bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene di(tetracyanoquinodimethanide) (15b), were measured. The resistivities ρ of these compounds were 5.5×10^6 and 6.6×10^5 ohm cm, respectively. Thus, their conductivities ($1/\rho$) were 1.8×10^{-7} and 1.5×10^{-6} ohm^{-1} cm^{-1}, respectively. The ionene model compounds prepared by Rembaum et al,[27] which had six, eight and ten methylene groups separating the tertiary amines, when treated with LiTCNQ, had resistivities of 5.0×10^{10}, 3.7×10^7 and 3.6×10^7 ohm cm,

Table 20

TCNE Polymers Doped with $\mathrm{TCNQ}^{\bar{\cdot}}$

Polymer	mmol[a] Polymer	mmol LiTCNQ	% Yield	Elemental Analysis Calculated C	H	N	Found C	H	N
TCNE 3-3	2.08	4.16	44.8	67.56	5.53	26.91	62.28	5.58	24.43
TCNE 3-4	2.02	4.05	65.5	67.91	5.70	26.39	62.83	5.67	24.10
TCNE 3-5	1.96	3.93	63.4	68.23	5.86	25.91	63.22	6.24	23.82
TCNE 3-6	1.91	3.83	48.7	68.55	6.01	25.44	63.69	6.01	23.18

[a] Based on repeating unit.

Table 21

TCNQ Polymers Doped with TCNQ$^{\dot{-}}$

Polymer	mmol[a] Polymer	mmol LiTCNQ	% Yield	Elemental Analysis Calculated C			Found C		
				C	H	N	C	H	N
TCNQ 3-3	1.80	3.59	45.3	70.13	5.51	24.36	62.64	5.65	20.63
TCNQ 3-4	1.75	3.51	23.8	70.40	5.66	23.94	62.34	5.72	19.88
TCNQ 3-5	1.71	3.42	40.3	70.65	5.81	23.54	62.81	5.95	19.82
TCNQ 3-6	1.67	3.34	47.0	70.90	5.95	23.15	63.23	6.21	18.70

[a] Based on repeating unit.

respectively. These ionene model compounds had approximately the same distances between the tertiary amine groups as compounds 15a and 15b, yet both 15a and 15b had lower resistivities. Thus, it appears that the electron-accepting TCNE moiety of compounds 15a and 15b effectively increased the conductivities of these two compounds. However, the resistivities of the ionene model compounds with six, eight and ten methylene groups separating the tertiary amines and which had been treated with both LiTCNQ and $TCNQ^o$ were 1.0×10^2, 7.0 and 4.1×10^5 ohm cm, respectively. These values are substantially lower than the resistivities of compounds 15a and 15b, indicating that the ability of the TCNE moiety to lower electrical resistance is not as great as that of neutral TCNQ.

The resistivity of the model compound, 7,7-bis(3-trimethylammonium-propylamino)-8,8-dicyanoquinodimethan di(tetracyanoquinodimethanide) (21), was determined to be 1.2×10^7 ohm cm. The ionene model compounds prepared by Rembaum et al,[27] which had eight and ten methylene groups separating the tertiary nitrogens and therefore had approximately the same distances between the tertiary amine groups as compound 21, had resistivities of 3.7×10^7 and 3.6×10^7 ohm cm, respectively. Since the resistivity of compound 21 was not significantly lower than the resistivities of the ionene model compounds, it appears that the TCNQ moiety had little effect upon the conduction process.

The resistivities of the LiTCNQ-treated TCNE and TCNQ polymers are reported in Table 22. The TCNE polymers had lower resistivities than the TCNQ polymers, indicating that the TCNE moiety had a greater effect on the conduction process than did the TCNQ moiety. In general, these polymers had higher resistivities than the corresponding TCNE model

Table 22

Resistivities and Conductivities of the Polymers Treated with LiTCNQ

Polymer	Resistivity ρ ohm cm	Conductivity σ ohm^{-1} cm^{-1}
TCNE 3-3	9.79×10^{6}	1.02×10^{-7}
TCNE 3-4	4.07×10^{6}	2.46×10^{-7}
TCNE 3-5	1.11×10^{6}	9.01×10^{-7}
TCNE 3-6	2.16×10^{7}	4.63×10^{-8}
TCNQ 3-3	8.16×10^{7}	1.23×10^{-8}
TCNQ 3-4	2.94×10^{8}	3.40×10^{-9}
TCNQ 3-5	9.13×10^{6}	1.10×10^{-7}
TCNQ 3-6	1.30×10^{9}	7.69×10^{-10}

compound 15b or the TCNQ model compound 21. The higher resistivities of the polymers could be an indication that poorer stacking of the TCNQ moieties occurred in the polymers than in the corresponding model compounds. Another explanation for the poorer conductivities of the polymers could be that, during treatment with LiTCNQ, exchange of the $TCNQ^{\overline{\cdot}}$ for Br^- of the polymer might not have been completed before the polymer precipitated from the solution. Analysis of the TCNE 3-5 and TCNQ 3-6 polymers for bromide seemed to confirm this possibility since these polymers contained 4.64 and 5.18 percent bromide, respectively. Incomplete exchange could have resulted in a poor arrangement of the TCNQ moieties, thereby increasing the resistivity.

The TCNE 3-5 and TCNQ 3-6 polymers were treated with LiTCNQ and $TCNQ^o$ (Table 23). The resistivity of the TCNQ 3-6 polymer was lowered five orders of magnitude with the addition of one $TCNQ^o$ for every repeating unit, while the resistivity of the TCNE 3-5 polymer was lowered two orders of magnitude. Addition of a second $TCNQ^o$ moiety for every repeating unit further lowered the resistivities of these polymers. Therefore, the $TCNQ^o$ moiety appears to have enhanced the conductivities of these polymers, as has been observed with other ionene polymers.[27]

An increase in the conductivity of the polymers when the ratio of repeating unit to $TCNQ^{\overline{\cdot}}$ to $TCNQ^o$ was 1:2:1 was expected because the polymer design permitted the insertion of $TCNQ^o$ between adjacent $TCNQ^{\overline{\cdot}}$ (Figure 34). The separation of the $TCNQ^{\overline{\cdot}}$ by $TCNQ^o$ would diminish Coulombic forces which would have been created during electrical conduction in the polymer by the formation of the TCNQ dianion in the absence of $TCNQ^o$ (Figure 7). The addition of a second $TCNQ^o$ per repeating unit of the polymer resulted in a further increase in conductivity. It is

Table 23

Resistivities of the Polymers Treated with LiTCNQ and $TCNQ^{o}$

Polymer	One Repeating Unit to Two $TCNQ^{\bar{\cdot}}$ To One $TCNQ^{o}$ Resistivity ρ ohm cm	One Repeating Unit to Two $TCNQ^{\bar{\cdot}}$ To Two $TCNQ^{o}$ Resistivity ρ ohm cm
TCNE 3-5	8.74×10^{4}	1.24×10^{3}
TCNQ 3-6	1.45×10^{4}	6.08×10^{2}

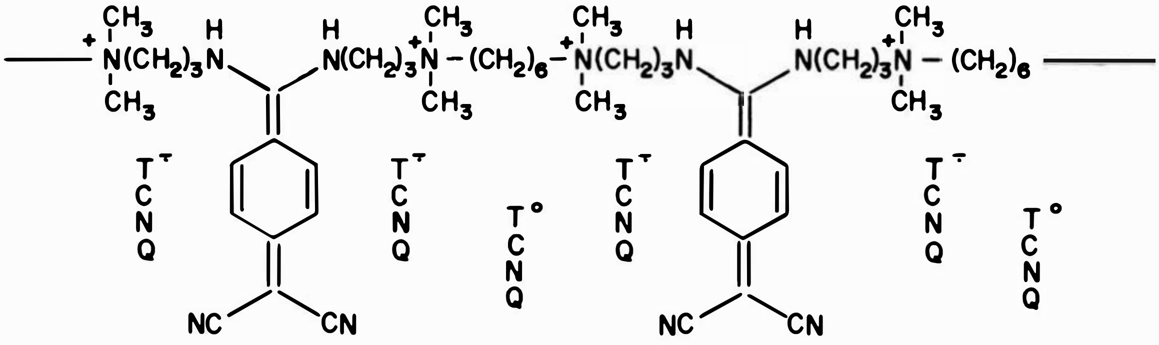


Figure 34: Insertion of TCNQ^{0} Between Adjacent TCNQ$^{\overset{\cdot}{-}}$.

postulated that the second $TCNQ^o$ displaced the TCNE or TCNQ moieties of the polymer from the $TCNQ^o$-$TCNQ^{\overline{\cdot}}$ conducting stacks (Figure 35). As has been indicated previously, the $TCNQ^o$ possesses better conducting properties than either the TCNE or TCNQ moieties of the polymer backbone. Therefore, the conductivities of the polymers would be enhanced if the TCNE or TCNQ moieties were displaced from the conducting stacks by $TCNQ^o$.

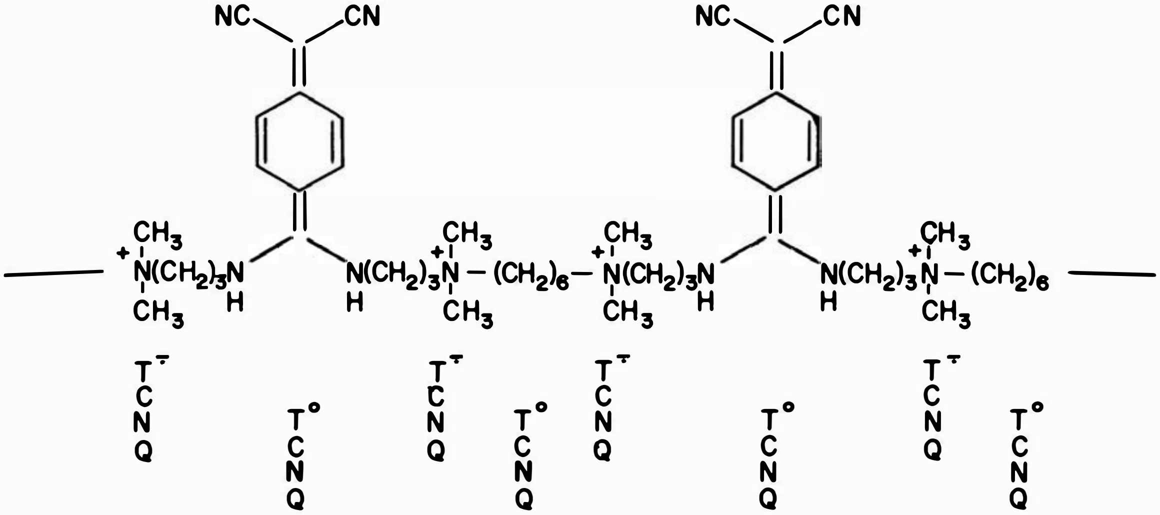


Figure 35: TCNQ Moieties Displaced from Conducting Stacks of the TCNQ 3-6 Polymer by Second $TCNQ^{o}$.

EXPERIMENTAL

General

All starting materials were used as obtained from commercial sources. Unless otherwise indicated, reagent-grade solvents were used in most reactions without further purification.

High resolution proton NMR spectra were recorded on a Varian Model T-60 spectrometer. The spectra were obtained from solutions in one of the following deuterated solvents with tetramethylsilane (TMS) as an internal standard: CD_3COCD_3, CD_3CN, $(CD_3)_2SO$, CD_3OD or $CDCl_3$. Deuterium oxide (D_2O) was used with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the internal standard.

Infrared spectra were recorded on a Perkin-Elmer Model 337 or Model 283 infrared spectrophotometer. Samples were run as KBr pellets. Ultraviolet spectra were recorded on a uv-visible Perkin-Elmer Model 202 or uv-nir Beckmann Acta MVII spectrophotometer using Fisher spectral-grade methanol.

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The carbon, hydrogen and nitrogen elemental analyses were performed by A. H. Robins Company, Richmond, Virginia; Galbraith Laboratories, Inc., Knoxville, Tennessee; or Chemalytics, Inc., Tempe, Arizona. The chemical ionization mass spectra were run by Dr. J. W. Russell at the University of Virginia, Charlottesville, Virginia. The determination of molecular weights by thermoelectric measurements was performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. The electrical conductivity measurements were performed by Dr. A. Rembaum at the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

Synthesis of 1,1,2,2-tetracyanoethylene and Related Compounds

Dibromomalononitrile - Potassium Bromide Complex

The procedure used is that of R. A. Carboni.[57] A mixture of potassium bromide (75.0 g, 0.63 mol), malononitrile (100.0 g, 1.51 mol) and water (900 ml) was placed in a two-liter, three-necked flask equipped with a 250 ml pressure-equalizing dropping funnel, a thermometer and a mechanical stirrer. The mixture was cooled to 5-10° in an ice bath. Bromine (160 ml, ≈490 g) was added over a two-hour period to the mixture via the dropping funnel. The temperature was maintained between 5-10°. A yellow precipitate formed. The mixture was stirred for five hours while the temperature was held between 5-10°. The yellow product was collected by filtration and dried over phosphorous pentoxide in a vacuum desiccator under reduced pressure obtained with a water aspirator. The yield was 355.4 g (92.6%).

1,1,2,2-Tetracyanoethylene (TCNE) (9)

The procedure used for the synthesis of TCNE was similar to that developed by R. A. Carboni.[57] Dibromomalononitrile - potassium bromide complex (254.0 g, 0.25 mol) and dry benzene[a] (1.0 l) were placed in a two-liter, three-necked flask equipped with a condenser, a mechanical stirrer, and a thermometer. The mixture was heated on an oil bath (95°).

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[a] The benzene was dried either by storing it over sodium ribbon or by azeotroping off the water.

When the temperature of the mixture was above 70°, copper powder (100.0 g) was added. The mixture was heated at reflux and stirred for 12 hours. The hot liquid was filtered and most of the heavy solid was retained in the flask. Additional benzene (300 ml) was added to the residue. The mixture was heated at reflux with stirring for one-half hour and then filtered. The residue was then washed with two portions of hot benzene. The benzene fractions were combined and reduced to approximately 350 ml. The solution was refrigerated (0°) overnight during which time a precipitate formed. The mixture was filtered and the recovered crystals were dried in a vacuum desiccator. The beige-colored crystals weighed 37.79 g (58.9%). The product was purified first by recrystallization from dry chlorobenzene and then sublimation[b] through activated charcoal. (Satisfactory results were also obtained simply by subliming the crude product through activated charcoal.) The sublimed product was white, mp 196.5-197.5° (sealed capillary tube). (Lit.[57] mp 199-200°.)

Dicyanoketene Ethylene Acetal (10)

The following procedure is that of W. J. Middleton and V. A. Engelhardt.[48] A mixture of TCNE (6.40 g, 50 mmol), ethylene glycol (120 ml) and urea (1.00 g) was heated on a steam bath until solution was complete. The solution was then poured into cold water (500 ml). The precipitate was collected by filtration, 6.14 g (90.3%). The product was recrystallized from alcohol-water to yield 3.17 g of white crystals, mp 115-117°. (Lit.[48] 113-114°.)

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[b] The TCNE (5.00 g) was placed in a vial and covered with activated charcoal (3.00 g) 8-12 mesh. A piece of porous filter paper was wired in place over the opening and the vial was placed in the sublimator which was heated on an oil bath at 170-175° under a pressure of approximately 5 torr. The recovery was 82-86%.

1,1-Bis(dimethylamino)-2,2-dicyanoethylene (11)

The title compound was synthesized according to the procedure of W. J. Middleton and V. A. Engelhardt.[48] Dicyanoketene ethylene acetal (1.78 g, 5.73 mmol) was dissolved in dimethylamine (approximately 30 ml). The dimethylamine was allowed to evaporate overnight and the residue was dissolved in a minimum amount of hot water. The hot solution was treated with activated charcoal and filtered. The filtrate was allowed to cool and a precipitate was formed. The precipitate was collected and recrystallized from water to yield 0.52 g (25.8%) of white crystals, mp 133-135°. (Lit.[48] mp 129-130°.)

1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a)

Under an atmosphere of dry nitrogen, TCNE (2.00 g, 15.6 mmol) was dissolved in tetrahydrofuran (40.0 ml, purged with nitrogen) in a 100 ml, three-necked flask equipped with a 50 ml pressure-equalizing dropping funnel, magnetic stirring apparatus and a thermometer (-100 to 50°). The solution was cooled to below -65° in a dry ice - isopropanol bath. Some of the TCNE precipitated out at this temperature. An N,N-dimethyl-1,2-ethanediamine (4.25 g of 95% diamine solution, 45.8 mmol) - tetrahydrofuran (10.0 ml) solution was added to the stirring mixture by means of the dropping funnel at such a rate as to maintain the solution temperature below -65°. The dry ice bath was allowed to degenerate overnight so that the solution temperature rose to room temperature. The solution was then slowly added to 150 ml of a 1:1 mixture of light petroleum ether - ether that had been cooled to approximately -60° and was being rapidly stirred. A precipitate formed which was collected by filtration. The product, 3.61 g (92.4%), was dissolved in hot 95% ethanol and treated with Norite A and filtered. A 1:1 mixture of light petroleum ether - ether was added to the warm solution until it became cloudy. This mixture was allowed to come to room temperature and remain for several hours. The solution was then placed in the freezer (-20°) for two days. A precipitate formed and was collected by filtration. The recrystallized product was straw-colored, 2.57 g, mp 107-110°. The material was further purified by sublimation[a], mp 109-110.5°, or by multiple recrystallization from methanol and ether to yield white crystals, mp 110-111°; NMR (CD_3CN): δ 2.26 (s, 12H), 2.42 (t, 4H), 3.33 (broad m, 4H), 7.70 (broad s, 2H); ir (KBr pellet): 2165, 2195 cm^{-1} (d, CN); uv (CH_3OH): λ_{max} 261 nm (ε 17,800).

Anal. Calcd for $C_{12}H_{22}N_6$: C, 57.57; H, 8.86; N, 33.57.

Found: C, 57.39; H, 8.77; N, 33.80.

1,1-Bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b)

Under an atmosphere of dry nitrogen, TCNE (2.00 g, 15.6 mmol) was dissolved in tetrahydrofuran (40.0 ml, purged with nitrogen), as previously described, and cooled below -65°. The TCNE precipitated at this temperature. An N,N-dimethyl-1,3-propanediamine (5.00 g of 99% diamine, 48.9 mmol) - tetrahydrofuran (10.0 ml) solution was added by means of a dropping funnel to the stirring TCNE mixture at such a rate that the solution temperature did not rise above -65°. The dry ice bath was allowed to degenerate overnight so that the solution temperature gradually rose to room temperature. The solution was then added to a rapidly stirred 1:1 mixture of petroleum ether - ether at dry ice and acetone temperature. A precipitate formed and was collected by filtration. The

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[a] Sublimation was accomplished at a pressure of less than 10^{-3} torr and a temperature of 120-125°. A 2.50 g sample required 11 days to complete the sublimation. The yield was 2.40 g (96.0%).

product, 3.98 g (91.6%), was dissolved in hot isopropanol and treated with Norite A. The hot solution was filtered and a 1:1 mixture of petroleum ether - ether was added to the warm filtrate until it became cloudy. The solution was then placed in the freezer (-20°) overnight. The off-white crystals were recovered and dried, 3.15 g, mp 95-100°. The material was further purified by subliming, mp 104-105.5°, or by multiple recrystallizations from methanol and ether to yield white crystals, mp 106-107°; NMR (CD_3CN): δ 1.65 (m, 4H), 2.16 (s, 12H), 2.40 (t, 4H), 3.35 (q, 4H), 7.83 (broad s, 2H); ir (KBr pellet): 2170, 2190 cm^{-1} (d, CN); uv (CH_3OH): λ_{max} 249.5 (ε 17,300).

Anal. Calcd for $C_{14}H_{26}N_6$: C, 60.40; H, 9.41; N, 30.19.

Found: C, 60.32; H, 9.38; N, 30.32.

1,1-Bis(N,N-dimethyl-1,4-butanediamino)-2,2-dicyanoethylene (13c)

Under an atmosphere of dry nitrogen, TCNE (2.00 g, 15.6 mmol) was dissolved in tetrahydrofuran (30 ml, purged with nitrogen), as previously described, and cooled below -60°. The TCNE precipitated at this temperature. The N,N-dimethyl-1,4-butanediamine was added via a pressure-equalizing dropping funnel to the stirred TCNE mixture at such a rate that the solution temperature did not rise above -60°. The solution was stirred overnight and the temperature gradually rose to room temperature. Addition of ether to the solution (in an attempt to precipitate the product) resulted in oiling. The solvent was removed on a rotary evaporator, leaving a brown oil. All attempts to crystallize the product were fruitless. NMR analysis indicated that the oil contained some of the desired product; NMR (CD_3CN): δ 1.53 (m, 8H), 2.20 (s, 12H), 2.33 (t, 4H), 3.28 (m, 4H), 3.36 (s, impurity).

1-(N,N-Dimethyl-1,2-ethanediamino)-1,2,2-tricyanoethylene (12a)

TCNE (2.00 g, 15.6 mmol) was dissolved in tetrahydrofuran (30 ml), as previously described, and cooled to below -60°. A solution of N,N-dimethyl-1,2-ethanediamine (1.37 g, 15.5 mmol) in tetrahydrofuran (5.0 ml) was added. The addition over a 75-minute period was at such a rate as to maintain the solution temperature below -58°. The solution was stirred for another 55 minutes and then poured into a 1:1 mixture of light petroleum ether - ether (150 ml). This mixture was then filtered and 2.68 (91.1%) of light-brown solid was obtained, mp 185-186° dec. A small portion of this material was further purified by sublimation[a], mp 191-193° dec; NMR (CD_3CN): δ 2.70 (s, 6H), 3.12 (t, 2H), 3.72 (t, 2H); ir (NM): 2175, 2200 cm^{-1} (d, CN); uv (CH_3CN): λ_{max} 339 nm (ε 10,764); CI Mass Spec: M+1 peak 190; MW by thermoelectric measurement; 176.

Anal. Calcd for $C_9H_{11}N_5$: C, 57.13; H, 5.86; N, 37.01.

Found: C, 57.00; H, 5.86; N, 37.21.

1-(N,N-Dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene (12b)

TCNE (2.00 g, 15.6 mmol) was dissolved in tetrahydrofuran (40 ml) in a 100 ml, three-necked flask equipped as previously described. This solution was cooled to below -60° in a dry ice - isopropanol bath. A solution of N,N-dimethyl-1,3-propanediamine (1.59 g, 15.6 mmol) in tetrahydrofuran (20 ml) was added. The addition, which required 50 minutes, was at such a rate as to maintain the solution temperature below -60°. Ten minutes after completing the addition, the solution was added to a 1:1 mixture of light petroleum ether - ether. A precipitate

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[a] 0.5 g of the product was sublimed at a pressure of less than 10^{-3} torr and between 90-120° for two months. Approximately 60% of the material was collected.

formed and was collected by filtering the cold solution. The product was recrystallized from methanol and petroleum ether to yield 2.26 g (71.5%) of light-yellow crystals, mp 195-199° dec. The material was further purified by sublimation[a], mp 197-199° dec; NMR (CD_3CN): δ 1.92 (m, 2H), 2.70 (s, 6H), 3.28 (t, 2H), 3.77 (t, 2H), 8.33 (broad s, 1H); ir (NM): 2160, 2198 cm^{-1} (d, CN); uv (CH_3CN): λ_{max} 343.5 nm (ε 10,085); CI Mass Spec: M+1 peak 204; MW by thermoelectric measurement: 199.

Anal. Calcd for $C_{10}H_{13}N_5$: C, 59.10; H, 6.44; N, 34.46.

Found: C, 59.09; H, 6.44; N, 34.31.

1-(N,N-Dimethyl-1,4-butanediamino)-1,2,2-tricyanoethylene (<u>12c</u>)

A mixture of TCNE (2.00 g, 15.6 mmol) in tetrahydrofuran (30 ml) was cooled to -70°, as previously described. N,N-dimethyl-1,4-butanediamine (3.69 g, 31.8 mmol) was added over a one-hour period at such a rate as to maintain the temperature of the stirred mixture below -60°. The temperature of the reaction mixture was allowed to rise to 10° over a seven-hour period, during which time a precipitate formed. The mixture was added to 250 ml of ether which was being stirred at approximately -60° and an oil formed. When the mixture was warmed, the oil solidified and the solid was collected by filtration, 3.15 g (92.9%). The product (1.00 g) was recrystallized from hot methanol and ether, 0.60 g (60.0%), mp 162° dec; NMR (CD_3CN): δ 1.80 (m, 4H), 2.76 (s, 6H), 2.97 (m, 2H), 3.33 (m, 2H), 6.48 (broad s, 1H); ir (KBr pellet): 2160, 2191 cm^{-1} (d, CN).

Anal. Calcd for $C_{11}H_{15}N_5$: C, 60.81; H, 6.96; N, 32.23.

Found: C, 60.90; H, 7.00; N, 31.99.

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[a] Sublimation was carried out at a pressure of less than 10^{-3} torr and between 90-120°. To sublime 0.50 g required approximately one month.

1-(N,N-Dimethyl-1,2-ethanediamino)-1,2,2-tricyanoethylene-N-hydrochloride (22a)

Crude 1-(N,N-dimethyl-1,2-ethanediamino)-1,2,2-tricyanoethylene (12a) (2.53 g, 13.4 mmol) and methanol (50 ml) were placed in an Erlenmeyer flask. Dry HCl was bubbled through the mixture until all of the solid was dissolved. Ether was slowly added to the dark-brown solution until it became cloudy. The mixture remained at room temperature for several hours and then was placed in the freezer (-20°) overnight. A precipitate formed and was collected by filtration yielding a brown solid, 1.36 g (45.1%), mp 166-168°. The material was dissolved in hot methanol and treated twice with Darco G-60. The hot methanol solution was diluted with dioxane until barely cloudy and then was allowed to come to room temperature during which time a precipitate formed. The mixture was refrigerated (0°) overnight and then filtered. Light-tan crystals were obtained, 0.60 g, mp 165-167°; NMR (D_2O): δ 2.96 (s, 6H), 3.51 (t, 2H), 4.08 (t, 2H); ir (NM): 2222 cm^{-1} (s, CN); uv (CH_3CN): λ_{max} 326.5 (ε 13,284).

Anal. Calcd for $C_9H_{12}N_5Cl$: C, 47.90; H, 5.36; N, 31.03; Cl, 15.71.
Found: C, 47.81; H, 5.21; N, 31.05.

1-(N,N-Dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene-N-hydrochloride (22b)

Dry HCl gas was bubbled through a mixture of methanol (10 ml) and 1-(N,N-dimethyl-1,3-propanediamino)-1,2,2-tricyanoethylene (12b) (1.40 g, 6.88 mmol) until all of the solid dissolved. The solution was warmed and, as it cooled to room temperature, a precipitate formed. The solid was collected by filtration and washed with dioxane. The product weighed 1.49 g (90.2%), mp 202°. The material was dissolved in hot methanol and treated with decolorizing charcoal. As the solution cooled to room temperature, a precipitate formed. The mixture was refrigerated (0^o) overnight. White crystals were collected by filtration, 1.03 g, mp 201-204^o; NMR (CD_3CN): δ 2.20 (m, 2H), 2.85 (s, 6H), 3.13 (q, 2H), 3.67 (q, 2H); ir (Nujol): 2227 cm^{-1} (s, CN); uv (CD_3CN): λ_{max} 330.5 nm (ε 13,297).

Anal. Calcd for $C_{10}H_{14}N_5Cl$: C, 50.11; H, 5.89; N, 29.21; Cl, 14.29.

Found: C, 50.09; H, 5.82; N, 29.27.

Attempt to Synthesize 1,1-Bis(trimethylammonium)-2,2-dicyanoethylene Diiodide

Procedure A

A solution of 1,1-bis(N,N-dimethylamino)-2,2-dicyanoethylene (11) (0.30 g, 1.9 mmol) in methanol (2.0 ml) and methyl iodide (4.0 ml) was refluxed for two days. Enough ether was added to the solution to make it cloudy and it was then placed in the refrigerator (0^o) overnight. A precipitate formed and was collected by filtration, 0.16 g, mp 133-134^o. NMR analysis indicated the product to be starting material.

Procedure B

A solution of 1,1-Bis(N,N-dimethylamino)-2,2-dicyanoethylene (0.50 g, 3.2 mmol) in methanol (4.0 ml) and methyl iodide (4.0 ml) was stirred at room temperature for 30 days. The solvents were removed on a rotary evaporator, yielding 0.44 g of off-white solid. NMR analysis indicated that the product was starting material.

1,1-Bis(2-trimethylammoniumethylamino)-2,2-dicyanoethylene Diiodide (14a)

In a dry box with a nitrogen atmosphere, methyl iodide (5.00 ml) was added to a stirring suspension of 1,1-bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a) (5.00 g, 20.0 mmol) in absolute ethanol (75.0 ml). After the addition of the methyl iodide, the solid material dissolved. A precipitate started to form after one-half hour and the mixture was allowed to stir for 24 hours. A white, hygroscopic material was collected by filtration and dried in a vacuum desiccator at 70° for 24 hours, 10.31 g (96.6%), mp 198.5-202° dec. This material was recrystallized from methanol, mp 203-206° dec; NMR (D_2O): δ 3.22 (s, 18H); 3.75 (m, 8H); ir (KBr pellet): 2185, 2205 cm^{-1} (d, CN).

Anal. Calcd for $C_{14}H_{28}N_6I_2$: C, 31.48; H, 5.28; N, 15.73; I, 47.51.
Found: C, 31.54; H, 5.39; N, 15.39.

1,1-Bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene Diiodide (14b)

In a dry box under a nitrogen atmosphere, 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b) (5.00 g, 18.0 mmol) was added over a 15-minute period to methyl iodide (25.0 ml). The reaction was exothermic and soon formed a white precipitate. An excess of methyl iodide (5.0 ml) was added and the mixture was allowed to stir at room temperature for three days. The product was isolated by filtration and washed with anhydrous ether. The hygroscopic salt was dried in a vacuum desiccator at 70° for 24 hours, 9.74 g (96.5%), mp 208-210°; NMR (D_2O): δ 2.08 (m, 4H), 3.16 (s, 18H), 3.43 (m, 8H); ir (KBr pellet): 2165, 2195 cm^{-1} (d, CN).

Anal. Calcd for $C_{16}H_{32}N_6I_2$: C, 34.18; H, 5.73; N, 14.95; I, 45.14.
Found: C, 33.88; H, 5.74; N, 14.90.

1,1-Bis(2-trimethylammoniumethylamino)-2,2-dicyanoethylene Di(tetracyanoquinodimethanide) (15a)

Lithium tetracyanoquinodimethanide (0.8445 g, 4.0 mmol) was dissolved in refluxing methanol (100 ml). This solution was added to a refluxing solution of 1,1-bis(2-trimethylammoniumethylamino)-2,2-dicyanoethylene diiodide (14a) (1.0685 g, 2.0 mmol) in methanol (225 ml).

The resulting solution was refluxed for 30 minutes and then allowed to cool and stand at room temperature for 12 days. The precipitate that formed was collected by filtration. The dark-blue powdery product was washed thoroughly with methanol and then water until no iodide ion could be detected by 0.10 M silver nitrate. The product was dried in vacuo at room temperature to yield 1.07 g (38.8%). Recrystallization of 0.2000 g from methanol (1000 ml) and ether (500 ml) yielded 0.0864 g of pure product, 243^{o} dec; ir (KBr pellet): 2200 cm^{-1} (s, CN); ρ: 5.5×10^{6} ohm cm.

Anal. Calcd for $C_{38}H_{36}N_{14}$: C, 66.26; H, 5.27; N, 28.47.

Found: C, 66.14; H, 5.19; N, 28.23.

1,1-Bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene Di(tetracyanoquinodimethanide) (15b)

Lithium tetracyanoquinodimethanide (0.8445 g, 4.0 mmol) was dissolved in refluxing methanol (100 ml). This solution was added to a refluxing solution of 1,1-bis(3-trimethylammoniumpropylamino)-2,2-dicyanoethylene diiodide (14b) (1.1205 g, 2.0 mmol) in methanol (10 ml). Refluxing the resultant solution was continued for 30 minutes during which time a precipitate formed. The mixture was allowed to cool to room temperature and to stand for 68 hours. The product was collected by filtration and washed, first with methanol and then with water, until no iodide ion could be detected by a 0.10 M silver nitrate solution. The product, 1.15 g (40.1%), was dried in vacuo at room temperature; 225^{o} dec; ir (KBr pellet): 2170, 2200 cm^{-1} (d, CN); ρ: 6.6×10^{5} ohm cm.

Anal. Calcd for $C_{40}H_{40}N_{14}$: C, 67.01; H, 5.62; N, 27.36.

Found: C, 66.94; H, 5.66; N, 27.18.

Synthesis of 7,7,8,8-Tetracyanoquinodimethan and Related Compounds

2,5-Dicarbethoxy-1,4-cyclohexanedione

The procedure used is similar to that of A. T. Nielsen and W. R. Carpenter.[58] A sodium ethoxide solution was prepared by adding small pieces of sodium (61.3 g, 2.66 mol) as rapidly as possible to commercially available absolute ethanol (600 ml) in a two-liter, two-necked flask equipped with a condenser and a drying tube. The mixture was heated under reflux for four hours. Diethyl succinate (232.1 g, 1.33 mol) was then added to the solution and this mixture was heated under reflux for six hours during which time a thick, pink precipitate formed. The ethanol was removed on a rotary evaporator and a sulfuric acid solution (2 N, 1390 ml) was added to the warmed residue. This mixture was stirred overnight. The solid material which remained was removed by suction filtration and air-dried. This product (138.4 g) was dissolved in boiling ethyl acetate (1.0 l) and suction filtered, while hot, through a heated funnel. The filtrate was cooled and cream-colored crystals precipitated which were recovered by filtration. The filtrate was reduced to one-half its original volume and refrigerated (0°) to yield additional product. The total yield was 115.8 g (67.8%), mp 127-129°. (Lit.[58] mp 126.5-128.5°.)

1,4-Cyclohexanedione

The following procedure, adapted from that of A. T. Nielsen and W. R. Carpenter,[58] was used. Water (113.0 ml) and 2,5-dicarbethoxy-1,4-cyclohexanedione (113.0 g, 0.44 mol) were placed in a Parr pressure vessel of one-liter capacity. The vessel was sealed and heated as rapidly as possible to 185-195° and maintained at this temperature for 15 minutes. The reaction vessel was removed from the heat source and rapidly cooled to room temperature in an ice bath. The resulting orange-colored liquid was distilled under reduced pressure. (Lit.[58] mp 77-79°.)

1,4-Bis(dicyanomethylene)-cyclohexane

The procedure of D. S. Acker and W. R. Herther[22] was followed. A mixture of 1,4-cyclohexanedione (100.0 g, 0.89 mol) and malononitrile (119.1 g, 1.80 mol) was melted by warming on a steam bath. To this melt was added a solution of β-alanine (1.0 g in 200 ml of water). The resulting solution was warmed and swirled over the steam bath until a precipitate started to form and then was allowed to cool to room temperature. The product was collected by filtration and washed with water and ether to yield 178.1 g (95.9%) of white crystals, mp 216-221°. (Lit.[22] mp 216-217°.)

7,7,8,8-Tetracyanoquinodimethan (TCNQ) (1)

The following procedure is a modified version of that described by D. S. Acker and W. R. Herther.[22] Acetonitrile (200 ml) was placed in a 500 ml, three-necked flask equipped with a mechanical stirrer, a thermometer (-100 to 50°) and a 60 ml pressure-equalizing dropping funnel. The acetonitrile was purged by bubbling dry nitrogen through it for 15-20 minutes. Then, 1,4-bis(dicyanomethylene)-cyclohexane (12.00 g, 0.058 mol) and bromine (19.3 g, 0.12 mol) were added to the flask. This mixture was stirred under a nitrogen atmosphere and cooled to -22° in a dry ice - ethylene glycol bath. A pyridine solution (20 ml in 30 ml of acetonitrile) was added, via the dropping funnel, at such a rate that the temperature of the solution did not increase during the addition. The resulting solution was stirred overnight and the temperature of the solution rose to -3°. The bath was removed and the solution was allowed to warm to room temperature. The solution was diluted with 300 ml of ice water to precipitate the product which was then recovered by filtration. The product was recrystallized from acetonitrile which had been purged with nitrogen. This procedure yielded 9.74 g (82.8%) of red-brown crystals, mp 185-190°. (Lit.[22] mp 193.5-196°.)

Lithium Tetracyanoquinodimethanide

The procedure by L. R. Melby et al[24] was followed. A solution of lithium iodide (40.0 g, 0.3 mol) in boiling acetonitrile (100 ml) was added to a boiling solution of TCNQ (20.4 g, 0.1 mol) in acetonitrile (2 1). A purple, powdery precipitate separated from the dark-brown solution. The mixture was allowed to stand at room temperature for two days. The precipitate was collected by filtration and washed with acetonitrile until the washings were bright green. The product was washed with one liter of ether and dried, 20.2 g (95.8%).

7,7-Bis(dimethylamino)-8,8-dicyanoquinodimethan (16)

The procedure used was similar to that of D. S. Acker and D. C. Blomstrom.[42] To a solution of TCNQ (4.00 g, 0.020 mol) in tetrahydrofuran (350 ml) was added a solution of dimethylamine (5.41 g, 0.12 mol) in tetrahydrofuran (150 ml). The dark solution was allowed to stand at room temperature for 68 hours. The mixture was filtered to recover 3.58 g of a yellow solid. The filtrate was reduced to one-fourth of its original volume and an additional 0.45 g of product was obtained. The total yield was 4.03 g (85.6%). The product (2.99 g) was dissolved in methanol (135 ml) heated to 55°. Ether (30 ml) was added to the warm solution and on cooling, 2.58 g of yellow crystals were obtained, mp 235-236° dec. (Lit.[42] mp

232-236° dec.) NMR ($(CD_3)_2SO$): δ 3.10 (s, 12H), 6.90 (d, 2H), 7.13 (d, 2H); ir (KBr pellet): 2140, 2175 cm^{-1} (d, CN): uv (CH_3OH): λ_{max} 403 nm (ε 28,000).

Anal. Calcd for $C_{14}H_{16}N_4$: C, 69.97; H, 6.71; N, 23.31.

Found: C, 69.73; H, 6.79; N, 23.60.

7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a)

To a solution of TCNQ (2.00 g, 9.79 mmol) in tetrahydrofuran (250 ml) was added 95% N,N-dimethyl-1,2-ethanediamine (4.23 g, 45.6 mmol). After stirring for three hours, the above solution showed evidence of a precipitate. The mixture was allowed to stand at room temperature for two days. The solvent was removed on a rotary evaporator and the residue was recrystallized twice from methanol and ether to yield 2.36 g (96.2%) of yellow crystals, mp 253-254°; NMR ($(CD_3)_2SO$): δ 2.10 (s, 12H), 2.35 (t, 4H), 3.40 (t, 4H), 6.86 (d, 2H), 7.30 (d, 2H); ir (KBr pellet): 2130, 2175 cm^{-1} (d, CN); uv (CH_3OH): λ_{max} 206 nm (ε 32,300).

Anal. Calcd for $C_{18}H_{26}N_6$: C, 66.23; H, 8.03; N, 25.74.

Found: C, 66.20; H, 8.15; N, 25.71.

7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b)

To a solution of TCNQ (2.00 g, 9.79 mmol) in tetrahydrofuran (250 ml) was added 99% N,N-dimethyl-1,3-propanediamine (4.30 g, 41.7 mmol). This solution was stirred for three hours and then allowed to stand at room temperature for two days. No precipitate was observed. The solvent was removed on a rotary evaporator and the solid residue was recrystallized from methanol and ether to yield 2.31 g (66.5%) of yellow crystals. These were recrystallized a second time from methanol and ether to give 2.18 g of product, mp 157.5-159.0°; NMR (CD_3CN): δ 1.70 (m, 4H), 2.23 (s, 12H), 2.43 (t, 4H), 3.41 (unresolved t, 4H), 6.97 (d, 2H), 7.26 (d, 2H); ir (KBr pellet): 2130, 2175 cm^{-1} (d, CN); uv (CH_3OH): λ_{max} 369 nm (ε 22,600).

Anal. Calcd for $C_{20}H_{30}N_6$: C, 67.76; H, 8.53; N, 23.71.

Found: C, 67.58; H, 8.59; N, 23.61.

7,7-Bis(N,N-dimethyl-1,4-butanediamino)-8,8-dicyanoquinodimethan (<u>18c</u>)

The N,N-dimethyl-1,4-butanediamine (3.50 g, 30 mmol) was added to a warm solution of TCNQ (2.00 g, 10 mmol) in tetrahydrofuran (200 ml). The solution was allowed to come to room temperature and to stand for three and one-half days. The solvent was removed on a rotary evaporator leaving an oil. All attempts to crystallize the oil were fruitless. NMR analysis indicated that the oil contained the desired product; NMR (CD_3CN): δ 1.61 (m, 8H), 2.25 (m, 16H), 3.31 (t, 4H), 6.50 (broad s, 2H), 6.97 (d, 2H), 7.27 (d, 2H).

7-(N,N-Dimethyl-1,2-ethanediamino)-7,8,8-tricyanoquinodimethan (<u>17a</u>)

N,N-Dimethyl-1,2-ethanediamine (0.42 g, 4.9 mmol) was added with stirring to a solution of TCNQ (1.00 g, 4.9 mmol) in tetrahydrofuran (200 ml). The solution was allowed to stand for two days at room temperature. A precipitate formed and was collected by filtration. The dry product weighed 1.01 g (77.7%), mp 118^{o} dec; NMR ($(CD_3)_2SO$): δ 2.90 (s, 6H), 3.52 (t, 2H), 4.10 (t, 2H), 6.90 (d, 2H), 7.67 (d, 2H); ir (KBr pellet): 2125, 2180 cm^{-1} (d, CN).

Anal. Calcd for $C_{15}H_{15}N_5$: C, 67.90; H, 5.70; N, 26.40.

Found: C, 63.23; H, 6.21; N, 18.70.

7-(N,N-Dimethyl-1,3-propanediamino)-7,8,8-tricyanoquinodimethan (17b)

N,N-Dimethyl-1,3-propanediamine (0.49 g, 4.8 mmol) was added with stirring to a solution of TCNQ (1.00 g, 4.9 mmol) in tetrahydrofuran (200 ml). The solution was allowed to stand at room temperature for two days. A precipitate formed and was collected by filtration. The reddish-brown product was dried in vacuo at room temperature, 1.25 g (91.2%). A portion of the product (0.5022 g) was recrystallized from hot methanol (200 ml) to yield 0.0763 g (15.2%) of reddish-brown crystals, mp 181-182° dec; NMR ($(CD_3)_2SO$): δ 2.10 (m, 2H), 2.86 (s, 6H), 3.28 (t, 2H), 3.87 (t, 2H), 6.89 (d, 2H), 7.64 (d, 2H); ir (KBr pellet): 2125, 2175 cm^{-1} (d, CN).

Anal. Calcd for $C_{16}H_{12}N_5$: C, 68.80; H, 6.13; N, 25.07.

Found: C, 68.58; H, 5.90; N, 24.95.

7-(N,N-Dimethyl-1,4-butanediamino)-7,8,8-tricyanoquinodimethan (17c)

N,N-Dimethyl-1,4-butanediamine (0.57 g, 4.9 mmol) was added to a warm solution of TCNQ (1.00 g, 4.8 mmol) in tetrahydrofuran (125 ml). A precipitate formed after ten minutes. The mixture was allowed to stand at room temperature for two days. The product was collected by filtration and dried in vacuo at room temperature, 1.35 g (95.7%). The product (0.50 g) was recrystallized from hot methanol (100 ml) to yield 0.27 g of brown crystals, mp 183-185° dec; NMR ($(CD_3)_2SO$): δ 1.75 (m, 4H), 2.80 (s, 6H), 2.63 (t, 2H), 3.83 (t, 2H), 6.89 (d, 2H), 7.64 (d, 2H); ir (KBr pellet): 2140, 2180 cm^{-1} (d, CN).

Anal. Calcd for $C_{17}H_{19}N_5$: C, 69.60; H, 6.53; N, 23.87.

Found: C, 69.20; H, 6.29; N, 23.32.

7-(N,N-Dimethyl-1,3-propanediamino)-7-(n-propylamino)-8,8-dicyanoquinodimethan

TCNQ (4.00 g, 19.6 mmol) was dissolved in tetrahydrofuran (400 ml). N,N-Dimethyl-1,3-propanediamine (2.00 g, 19.6 mmol) was added to the stirring TCNQ solution. Stirring was continued for five hours at room temperature during which time a reddish-brown precipitate formed. n-Propylamine was added to the stirred mixture and stirring was continued for an additional five hours. During this time, the precipitate, which had previously formed, dissolved. The volume of the solution was reduced to approximately 50 ml and a yellow precipitate appeared which was collected by filtration and washed with ether, 5.00 g (82.0%). The product was recrystallized twice from methanol and ether to yield 2.76 g of light-yellow crystals, mp 164°; NMR ($CDCl_3$): δ 1.22 (t, 3H), 1.75 (m, 4H), 2.33 (s, 6H), 3.41 (q, 4H), 6.92 (d, 2H), 7.25 (d, 2H): ir (KBr pellet) 2130, 2175 cm^{-1} (d, CN).

Anal. Calcd for $C_{18}H_{25}N_5$: C, 69.42; H, 8.09; N, 22.49.

Found: C, 68.89; H, 8.13; N, 23.74.

7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan Diiodide (20b)

In a dry box under a nitrogen atmosphere, methyl iodide (5.0 ml) was added to a stirred mixture of 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) (5.00 g, 14.1 mmol) and absolute ethanol (75 ml). The 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanodimethan dissolved. After stirring for 24 hours, a precipitate formed which was collected by filtration and dried in vacuo at 50° for 48 hours, 7.55 g (83.9%). The product was recrystallized from methanol and ether, mp 199-202° dec; NMR (D_2O): δ 2.30 (m, 2H), 3.20 (s, 18H), 3.58 (m, 8H), 6.98 (d, 2H), 7.45 (d, 2H); ir (KBr pellet): 2125, 2170 cm^{-1} (d, CN).

Anal. Calcd for $C_{22}H_{36}N_6I_2$: C, 41.39; H, 5.68; N, 13.16; I, 39.71.

Found: C, 41.27; H, 5.87; N, 12.82.

7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan Di(tetracyanoquinodimethanide) (<u>21</u>)

A refluxing solution of lithium tetracyanoquinodimethanide (0.8446 g, 4.00 mmol) in methanol (100 ml) was added to a refluxing solution of 7,7-bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan diiodide (<u>20b</u>) (1.2768 g, 2.00 mmol) in methanol (50 ml). The resulting solution was heated for an additional ten minutes. The solution was allowed to come to room temperature and to stand for 24 hours. A precipitate formed and was collected by filtration. The purple solid, after being washed with methanol and water until no iodide ion could be detected by 0.01 M silver nitrate, weighed 1.1915 g (75.1%). The product (0.7500 g) was recrystallized from hot methanol (450 ml) to yield 0.2515 g of purified product, mp 214° dec; ir (KBr pellet): 2130, 2170, 2182, 2203 cm^{-1} (CN).

Anal. Calcd for $C_{46}H_{44}N_{14}$: C, 69.68; H, 5.59; N, 24.73.

Found: C, 68.48; H, 5.75; N, 23.90.

7,7-Bis(N,N-dimethylamino)-8,8-dicyanoquinodimethan - Methyl Iodide Complex (<u>16a</u>)

A mixture of 7,7-bis(dimethylamino)-8,8-dicyanoquinodimethan (<u>16</u>) (0.50 g, 2.1 mmol) and methyl iodide (20.0 ml) was refluxed for 93 hours. The methyl iodide was removed on a rotary evaporator. The red residue was dissolved in ethanol and sufficient ether was added to make the solution cloudy. The solution was placed in the freezer (-20°) overnight. A precipitate formed and was collected by filtration, 0.78 g (97.5%), mp 119-123°; NMR (CD_3CN): δ 2.23 (s, 3H), 3.20 (s, 12H), 7.93 (s, 4H); ir (KBr pellet): 2140, 2160 cm^{-1} very weak (d, CN); uv (CH_3OH): λ_{max} 223 nm (ε 21,200).

Anal. Calcd for $C_{15}H_{19}N_4I$: C, 43.13; H, 5.01; N, 14.66; I, 33.20.

Found: C, 46.12; H, 5.16; N, 14.41.

7,7-Bis(2-trimethylammoniumethylamino)-8,8-dicyanoquinodimethan Diiodide - Methyl Iodide Complex (19a)

A mixture of 7,7-bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a) (5.00 g, 15.3 mmol) and methyl iodide (25 ml) were stirred in a sealed 50 ml flask under a nitrogen atmosphere at room temperature. After 28 days, a solid was collected by filtration, washed with anhydrous ether and dried in vacuo at room temperature, 10.83 g (94.0%), softened at 150°; NMR (D_2O): δ 2.30 (s, 3H), 3.24 (d, 18H), 3.97 (m, 8H), 8.00 (s, 4H); ir (KBr pellet): 2130, 2175 cm^{-1} (d, CN); uv (CH_3OH): λ_{max} 218 nm (ε 39,700).

Anal. Calcd for $C_{21}H_{35}N_6I_3$: C, 33.53; H, 4.69; N, 11.17; I, 50.61.

Found: C, 33.67; H, 5.30; N, 10.64.

7,7-Bis(3-trimethylammoniumpropylamino)-8,8-dicyanoquinodimethan Diiodide - Methyl Iodide Complex (19b)

A mixture of 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) (0.50 g, 1.4 mmol) and methyl iodide (10 ml) was put in a 25 ml flask. The flask was sealed and allowed to stand at room temperature for two months. A thick, paste-like material remained. It was dried in vacuo at room temperature for three days, 0.87 g (80.6%), softened at 58°; NMR (CD_3CN): δ 2.23 (s, 3H), 2.30 (m, 4H), 3.23 (d, 18H), 3.71 (m, 8H), 7.97 (s, 4H); uv (MeOH): λ_{max} 219 nm (ε 49,510).

Anal. Calcd for $C_{23}H_{39}N_6I_3$: C, 35.40; H, 5.04; N, 10.77; I, 48.79.

Found: C, 33.62; H, 4.95; N, 10.49.

Synthesis of N,N-Dimethyl-1,4-butanediamine

4-Dimethylaminobutyronitrile

The procedure used was adapted from that of A. Lespagnol et al.[59] A mixture of 4-chlorobutyronitrile (208.0 g, 2.01 mol), benzene (240 ml) and dimethylamine (254.5 g, 5.64 mol) was placed in a one-liter Parr pressure vessel. The vessel was sealed and heated at 100° for 24 hours. After the reaction mixture cooled to room temperature, the white crystals which had formed were collected, washed with benzene and discarded. The benzene washings and the filtrate were combined and the solvent removed by a rotary evaporator. The remaining liquid was distilled at 22 torr. A clear distillate was collected between 70-73°, 87.24 g (38.7%). (Lit.[59] bp 92°/18 torr.)

4-Hydroxybutyramide

The title compound was prepared by the procedure of A. Lespagnol et al.[59] A solution of γ-butyrolactone (172.0 g, 200 mol), methanol (100.0 ml) and liquid ammonia (170 ml) was placed in a one-liter Parr pressure vessel and heated at 100° for 16 hours. The solution was filtered through a fritted glass filter. The solvent was removed from the filtrate by means of a rotary evaporator. The resulting melt solidified upon standing at room temperature. The product was hygroscopic and required drying under reduced pressure to yield 199.07 g (96.6%).

4-Chlorobutyronitrile

The following procedure is that of A. Lespagnol et al.[59] A mixture of 4-hydroxybutyramide (100.0 g, 0.97 mol) and chloroform (200 ml) was placed in a one-liter, three-necked flask equipped with a condenser, a 250 ml pressure-equalizing dropping funnel and a mechanical stirrer.

Thionyl chloride (260 g, 2.18 mol) was added slowly to the stirring mixture from the dropping funnel. The reaction was exothermic and the addition required 30 minutes. The stirred mixture was then heated by means of an oil bath at 60° for 24 hours. The reaction mixture was filtered and the residue was discarded after it was washed with chloroform. The filtrate and the washings were combined and the solvent was removed on a rotary evaporator. The remaining liquid was distilled under reduced pressure (1.2-1.8 torr) and the product was collected between 60-63° as a clear liquid, 58.0 g (57.8%). (Lit.[59] bp 81°/16 torr.)

N,N-Dimethyl-1,4-butanediamine

The following procedure was adapted from that of W. A. Lott and John Krapcho.[60] Lithium aluminum hydride (19.00 g, 0.50 mol) was added to anhydrous ether (500 ml) in a three-necked, one-liter flask equipped with a mechanical stirrer, condenser, calcium chloride drying tube and 60 ml pressure-equalizing dropping funnel. 4-Dimethylaminobutyronitrile (50.00 g, 0.45 mol) was added, drop-wise, to the stirring lithium aluminum hydride suspension. After the addition was complete (approximately 30 minutes), the stirred solution was heated on an oil bath at 50° for 18.5 hours. The solution was then cooled to room temperature and an aqueous sodium hydroxide solution (4.5 g NaOH in 85 ml of H_2O) was added. The resulting mixture was filtered and the white, inorganic solid was washed with ether. The filtrate and washings were combined and dried over anhydrous magnesium sulfate. The ether was removed on a rotary evaporator and the liquid residue was distilled under reduced pressure. A clear distillate was collected at 45-50° at a pressure of 2-5 torr, 13.47 g (26.0%). (Lit.[61] bp 49-50°/7 torr.)

Polymers

Reagents

The solvent for the polymerizations was Fisher reagent-grade N,N-dimethylformamide (DMF) which was purified by stirring over potassium hydroxide for 24 hours and distillation under nitrogen from calcium oxide. The alkyldibromides, obtained from the Aldrich Chemical Company, were distilled under reduced pressure directly before use. The TCNQ and TCNE monomer derivatives were prepared and purified by methods previously described in the Experimental section.

Polymerizations of 1,1-Bis(N,N-dimethyl-1,2-ethanediamino)-2,2-dicyanoethylene (13a), 1,1-Bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b) and 7,7-Bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan (18b) with α,ω-Alkyldibromides

The polymers in Tables 14, 15 and 17 were prepared by a procedure similar to that described below for the copolymerization of 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b) and 1,5-dibromopentane. All solutions were prepared with 50 percent monomers by weight.

Copolymerization of 1,1-Bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b) and 1,5-Dibromopentane

A mixture consisting of 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene (13b) (3.4800 g, 12.5 mmol), 1,5-dibromopentane (2.8739 g, 12.5 mmol) and N,N-dimethylformamide (6.3231 g) was sealed in a one-ounce, screw-cap jar with a magnetic stirring bar. All solid material dissolved after 15 minutes of stirring at room temperature. The stirring was continued at room temperature for seven days. In a nitrogen atmosphere, the polymer was precipitated by adding dry acetone, isolated and powdered by stirring in approximately 150 ml of dry acetone for several days. The polymer was collected by filtration and initially dried for 24 hours in vacuo at 50°. The polymer was then dried at 110°, 0.6 torr, for three days, 6.2805 g (98.84%).

Polymerizations of 7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a) with α,ω-Alkyldibromides

The polymers in Table 16 were prepared by essentially the same procedure as that given below for the copolymerization of 7,7-bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a) and 1,4-dibromobutane. All solutions were 50 percent monomer by weight.

Copolymerization of 7,7-Bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a) and 1,4-Dibromobutane

A mixture consisting of 1,1-bis(N,N-dimethyl-1,2-ethanediamino)-8,8-dicyanoquinodimethan (18a) (3.2640 g, 10.0 mmol), 1,4-dibromobutane (2.1592 g, 10.0 mmol) and N,N-dimethylformamide (5.5223 g) was sealed in a 50 ml screw-cap vial with a magnetic stirring bar. The mixture was stirred at 50°; after 14 hours all of the solid had dissolved. Stirring was continued for seven days at 50°. Under a nitrogen atmosphere, the polymer was precipitated by adding dry acetone and powdered by stirring in approximately 150 ml of dry acetone for several days. The polymer was collected by filtration and initially dried in vacuo at 50°. The polymer was then dried at 110°, 0.6 torr, for three days, 4.9419 g (91.13%).

Polymer Complexes with $TCNQ^{\cdot}$

The polymer complexes in Table 20 were derived from the 1,1-bis-(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoethylene monomer. The complexes were prepared by the procedure given below for the $TCNQ^{\cdot}$ complex of the 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene-1,4-dibromobutane copolymer (TCNE 3-4).

TCNQ$^{\overline{\cdot}}$ Complex of 1,1-Bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene-1,4-dibromobutane Copolymer (TCNE 3-4)

The copolymer (1.000 g, 2.02 mmol based on repeating unit) was dissolved in methanol (50 ml). The solutions were heated to 60^{o} and the LiTCNQ solution was added to the stirred polymer solution. The resulting mixture was heated at 60-65^{o} with stirring for 20 minutes. The mixture was allowed to cool to room temperature and stand for 24 hours. The resulting precipitate was filtered and washed thoroughly with methanol and water until no halide ion could be detected by a 0.01 M silver nitrate solution. The product was dried in vacuo at room temperature for seven days, 1.2148 g (65.5%).

The polymer complexes in Table 21 were derived from the 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan monomer. The complexes were prepared by essentially the same procedure as above for the 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene-1,4-dibromobutane copolymer. The only difference was that the polymer remained dissolved in 50 ml of the 10 percent (by volume) N,N-dimethylformamide - methanol solution.

Polymer Complexes with TCNQ$^{\overline{\cdot}}$ and TCNQ^{0}

The TCNQ$^{\overline{\cdot}}$-TCNQ^{0} complexes of the 1,1-bis(N,N-dimethyl-1,3-propanediamino)-2,2-dicyanoethylene-1,5-dibromopentane copolymer (TCNE 3-5) and the 7,7-bis(N,N-dimethyl-1,3-propanediamino)-8,8-dicyanoquinodimethan-1,6-dibromohexane copolymer (TCNQ 3-6) were prepared by a procedure similar to that for the respective TCNQ$^{\overline{\cdot}}$ complexes, the main difference being that a TCNQ solution in acetonitrile was heated to the same temperature as the LiTCNQ solution and the polymer solution. The TCNQ solution was added to the LiTCNQ solution and the resulting solution was then added to the polymer solution.

Viscosities

Viscosity measurements were made using Cannon-Ubbelohde semimicro dilution viscometers. The age of the solutions, up to one week, did not affect their viscosities.

Solutions for the viscosity studies in varying concentrations of KBr were prepared in one of two ways:

Method 1: Solution A was prepared by dissolving the polymer (1.0000 g) in water to make a 10.00 ml solution. Solution A was then passed through a fritted glass filter. Samples (1.00 ml) of solution A were then pipetted into each of nine 10.00 ml volumetric flasks. The appropriate volume of 1.00 M KBr was pipetted into each volumetric flask in order to obtain the desired molarity of KBr when the solution was diluted to 10.00 ml with water. After they were thoroughly mixed and temperature equilibrium had been established, the elution times were measured.

Method 2: Solution B was prepared by dissolving the polymer (1.00 g) in water, followed by dilution to make a 10.00 ml solution. Solution B was then passed through a fritted glass filter. A 2.00 ml sample of solution B was pipetted into a 10.00 ml volumetric flask. To prepare solution C, enough 1.00 M KBr solution was pipetted into the volumetric flask to make the maximum molarity of KBr, and water was added to bring the volume to 10.00 ml. Solution D was prepared by pipetting 5.00 ml of solution B into a 50.00 ml volumetric flask and diluting to 50.00 ml with water. Solutions C and D contained the same concentrations of polymer. Solution D was used to dilute solution C and, thus, change the salt concentration of solution C. The elution times of the polymer at various KBr salt concentrations were obtained in this manner.

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