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Synthesis of Some Organic Conductive Materials

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SYNTHESIS OF SOME ORGANIC CONDUCTIVE MATERIALS

BY

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1974

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SYNTHESIS OF SOME ORGANIC CONDUCTIVE MATERIALS

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser　　Date

Head, Chemistry Department　　Date

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MHCW

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SUMMARY

The purpose of this experimental work is to study the electronic conductivity of some highly conjugated polycation compounds. In order to attain this goal, the polymer with diazoniapentaphene as the repeating unit and some highly conjugated benzologs of quinolinium tetracyanoquinodimethan (TCNQ) complexes were investigated.

The resistivities of TCNQ complexes which were prepared varied from 10^3 to 10 ohm cm and were dependent on the content of neutral TCNQ in the complex. The low resisitivity of complex salts may be due to the extra TCNQ filling in the spaces in the crystal providing electron conduction through charge transfer complexing. The dication complex, 1,4-bis(1-methylene pyridinium $(\mathrm{TCNQ})_4^{\bar{\cdot}}$) benzene, was synthesized. The resistivity of this dication complex was fairly low. The poly(p-xylene-2,2'-dimethyl-4,4'-dipyridinium) TCNQ complex was also prepared. The resistivity of this complex was fairly high. This could be due to the amorphous nature of the polymer. Attempts were made to synthesize the polymer with diazoniapentaphene as the repeating unit; however, this polymer was not synthesized because of the difficult synthesis of 4,4'-bipyridine-2,2'-aldoxime.

HISTORICAL

The primary goal in conducting the experimental work involved in the formulating of this thesis was to synthesize some organic conducting compounds by utilizing the highly electronegative 7,7,8,8-tetracyanoquinodimethan complexed with some completely conjugated benzologs of the quinolizinium ion. The history is divided into three parts, the first part describing the electronic properties of organic conducting polymers, the second part dealing with anion-radical derivatives and complexes of 7,7,8,8-tetracyanoquinodimethan, the third part describing some benzologs of the quinolizinium ion.

1. Electronic Properties of Organic Conducting Polymers

One of the most important problems of present-day chemistry is the creation of new substances and materials possessing a series of valuable properties. Particularly great prospects have been opened in the synthesis and study of organic compounds possessing extensively delocalized electrons because of the presence in them of highly conjugated double bonds or the formation of charge-transfer complexes. Although in recent years the study of semiconductive properties of organic compounds has made much progress,[1-20] most of the exact mechanisms involved in the electronic conducting processes are at the present time either not known at all or else poorly understood.[21] Generally, the semiconductive polymers can be classified as follows: (a) covalent organic polymers, (b) charge-transfer complexes, (c) metal organic polymers, (d) H-bonded polymers, and (e) mixed polymers, for example, charge-transfer complexes between covalent polymers and low molecular weight donor or acceptor molecules.

The main efforts of synthetic chemists working in this field have been devoted to obtaining stable polymers of low resistance. As a working hypothesis, Pohl proposed the idea of eka- and rubi- conjugation.[8, 22, 23] Rubi-conjugation was defined as a type of structure in which various molecular defects and quantum mechanical effects exist which produce a limited, or broken sequence of electronic delocalization. Such conjugation was to be avoided if strong electronic conduction was desired. In eka-conjugation, molecular defects were absent or suppressed, and full interlinking of the chain atom pi orbitals occurred. Long-range electron orbital delocalization was then possible. The grouping of conjugating macromolecules by class of electronic behavior is shown in Table 1.

Besides quantum mechanical arguments for expecting the two classes of conjugation, Pohl has given experimental evidence.[23] First, the absorbances of the rubi-conjugated even atom chain polyenes were at higher energies, approaching asymptotically a limit of about 2.5eV. Second, the class of eka-conjugated polymers contained those semiconductors with a resistivity less than about 10^9 ohm cm. The other class (rubi-) contained the insulators, with

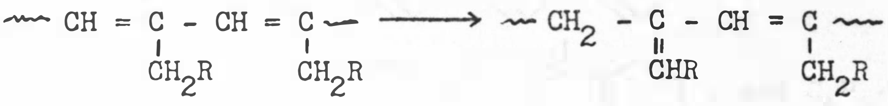
TABLE 1

GROUPS OF CONJUGATED MACROMOLECULES[22, 23]

Polymer	$25^{\circ}C$ ohm cm
Rubiconjugation	
polyhemimidazoles	$10^{13} - 10^{15}$
polyphenyls	$10^{10} - 10^{15}$
polynaphthalenes	10^{16}
poly (alkyl acetylenes)	$10^{10} - 10^{15}$
polydiethynylbenzenes	10^{15}
Ekaconjugation	
polyphthalocyanines	$10^{4} - 10^{7}$
poly (acene quinone radical) polymer	$10^{2} - 10^{9}$
polyxanthenes	$10^{4} - 10^{9}$
pyrographites	$10^{-4} - 10^{-1}$
Graphite	10^{-4}
Pyropolymers	$10^{-3} - 10^{4}$

resistivity greater than about 10^{12} ohm cm. Third, there were some differences in chemical activities and thermal stabilities. The eka-conjugated aryl-substituted polyacetylenes had high thermal stability and were relatively inert to addition reactions, such as hydrogenation with Raney nickel and reaction with maleic anhydride, bromine, $SbCl_3$, perbenzoic acid, oxygen, etc. Fourth, concentrations of delocalized unpaired electrons between the two types of conjugation were different. The eka-conjugated aryl-substituted polyacetylenes exhibited sharp electron spin resonance (ESR) signals characteristic of unpaired electrons delocalized over a conjugated chain. On the other hand, rubi-conjugated poly (alkyl acetylenes) were diamagnetic and did not show ESR spectra characteristic of electron delocalization.

Berlin[24] discussed polymers with systems of conjugated bonds and found that the continuity of the conjugated chain was broken in the poly (alkyl acetylenes) due to the redistribution of the C=C bonds in the macromolecules (Fig. 1).



$$\sim CH = \underset{\displaystyle CH_2R}{\underset{|}{C}} - CH = \underset{\displaystyle CH_2R}{\underset{|}{C}} \sim \longrightarrow \sim CH_2 - \underset{\displaystyle CHR}{\underset{\|}{C}} - CH = \underset{\displaystyle CH_2R}{\underset{|}{C}} \sim$$

Fig. 1 Isomerization of poly(alkyl acetylenes)

Poly (alkyl acetylenes) showed higher resistivities than poly (aryl acetylenes) because the former were not really conjugated. Besides, he synthesized some poly (aryl acetylenes) with molecular weight 1100 - 1700, which showed resistivities $3x10^{18}$ - $3x10^{15}$ ohm cm at room temperature $2.5x10^{17}$ - $3x10^{9}$ ohm cm at $0^{\circ}K$. Poly (alkyl acetylenes) (in Table 1) which were classified as rubi-conjugated and showed resistivities 10^{10} - 10^{15} ohm cm, had even lower resistivities than poly (aryl acetylenes). These data indicated that it was not so easy to classify conjugated systems as eka-conjugated or rubi-conjugated as Pohl proposed.

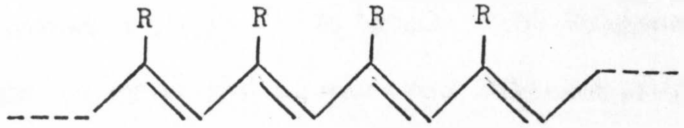
Electronic Properties of Types of Organic Polymers

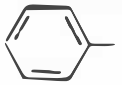
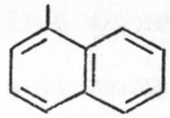
(A) Unmodified Covalent Organic Polymers

Unmodified meant here that the polymers had not undergone any chemical, thermal or radiational modifications after formation. They were normal synthetic polymers in the usual meaning.

(1) Conjugated double bond molecules: Polyacetylenes

The resistivities of these polyacetylenes[25-29] were fairly high. Expected structures were given by this formula:



Where R was CH_3-, C_2H_5-, C_3H_7-, , , and C_4H_9-, etc.

A series of polyacetylenes with exactly known molecular weights and structures were discussed by Schmidt and Hamann.[30] From their data, conductivities of these compounds were dependent on the number of pi electrons, the more pi electrons the higher the conductivities.

(2) Linear molecules that have no double bond in the main chain

Polymer molecules of this type were essentially insulators; in fact, many of them were good insulators. Nevertheless, several studies on polymers of this type have been done, some theoretical and some experimental. Polymers such as polyethylene,[31] nylon 66,[32] and polytrifluorochloroethylene[33] were investigated.

(3) Linear polymers having aromatic rings in the chain

Generally speaking, the polyphenyls (Fig. 2a) had rather high resistivities[34] compared with a fused ring system such as the polyacene polymers (Fig. 2b).

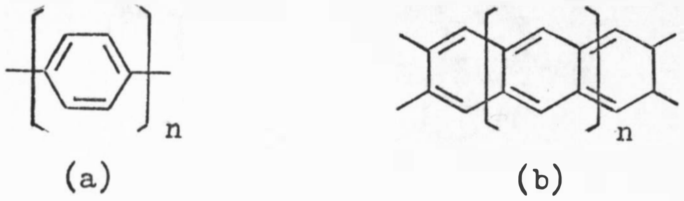


Fig. 2. (a) General formula for the linear polymers having aromatic rings in the chain. (b) Polyacene

This situation might be explained by eka- and rubi-conjugation theory. Since the pi electrons are delocalized through the polyacene polymer chain, higher conductivity is shown.

McNeill and Weiss[35] prepared a series of xanthene polymers, the proposed structure of which was shown in Fig. 3, as the first stage of a study of the potentialities of organic semiconductors for the synthesis of model enzymes and for the development of ion-exchange absorbents capable of direct electrical regeneration. The polymers were found to be p-type semiconductors in accordance with an observed positive Seebeck coefficient. The minimum resistivity was 7×10^3 ohm cm. The conduction probably was due to a resonating carbonium cation, arising from partial ionization of the xanthylium-lactone bond. This might be considered as eka-conjugation.

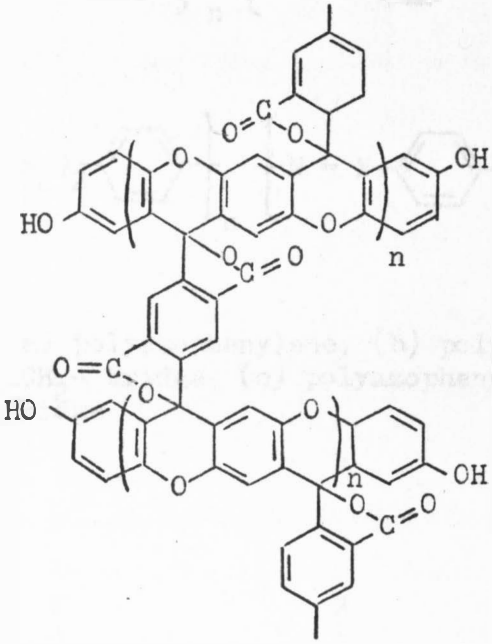


Fig. 3. Xanthene polymers

(4) Linear polymers having heteroatoms in the chain

A series of conducting linear polymers containing azo groups (Fig. 4a) was prepared by Berlin.[36, 37] The effects of incorporating -CH_2- and -CH_2CH_2- bridges into the structure of these polyazophenylenes (Fig. 4b, 4c) were studied by Dulov <u>et al</u>.[38] They concluded that the decrease in activation energy for the polymers having methylene bridges must be due to an increase in

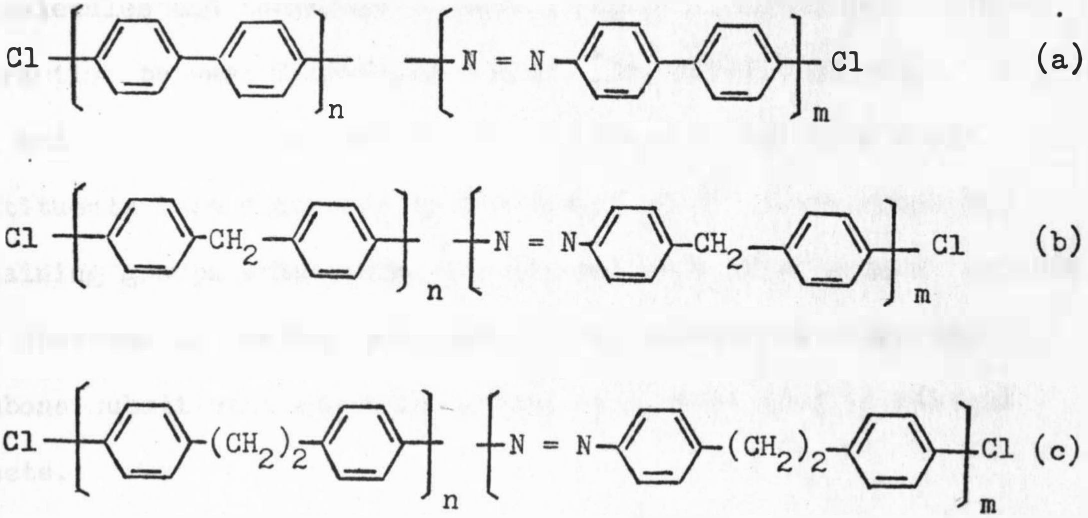


Fig. 4. (a) polyazophenylene, (b) polyazophenylene with $-CH_2-$ bridge, (c) polyazophenylene with $-CH_2-CH_2-$ bridge

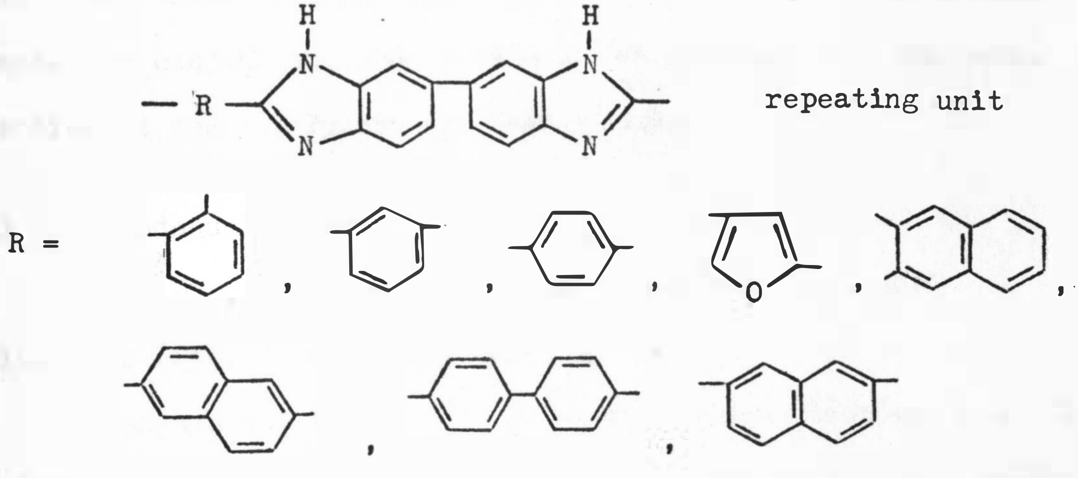


Fig. 5. eight polybenzimidazoles

the flexibility of the polymer chain, leading to a closer packing of the molecules and therefore to easier energy transfer and electron interaction between individual chains. The effects of $-SO_2-$, $-S-$, $-O-$, and $-C{=}C-$ bridges, and of $-NO_2$, $-OCH_3$, and $-Cl$ side chain substituents were discussed by Carlton et al.[39] Those compounds containing groups which were poor transmitters of electronic effects were observed to conduct more poorly than systems in which the backbone substituent was more capable of transmitting electrical effects.

(5) Polymers having heteroaromatic rings in the main chain

Pohl and Chartoff[25] discussed the electrically conductive nature of polybenzimidazoles (Fig. 5).[40] The data obtained support postulation of the necessity of overlap of pi orbitals for electrical conductivity. Although these polybenzimidazoles were completely conjugated, they were all rubi-conjugated. The resistivities of these polymers are fairly high.

(6) Polycondensed rings

The electrical properties of high molecular weight polyacenes (Fig. 2) are still unknown.

Akamatu and Inokuchi[41] prepared sulfur-containing aromatic semiconductive polymers (Fig. 6) by heating anthracene with sulfur. The measured resistivities ranged from 10^2 to 10^4 ohm cm. Bolto et al.[42] treated hexachlorobenzene with sodium at 300°C. The products, presumably polybenzenes, have resistivities of 0.2 - 25 ohm cm. Some less crosslinked polybenzenes had resistivities some thousand times greater. The higher resistivity of the sulfur-anthracene polymers compared with the polybenzenes may be due to a reduced pi orbital overlap between the aromatic units when these were pushed further apart by bridging sulfur atoms. It may also reflect the ease, compared with anthracene, of building giant crosslinked structures with the smaller, symmetrical benzene rings. Their results suggested that polycondensed ring polymers of good conductivity could be prepared by directly crosslinking small aromatic or heterocyclic units into three-dimensional non-planar structures in which the number of crosslinks should be as large as possible. Either electron-donating or electron-accepting structures, but not both, might be present in the polymer.

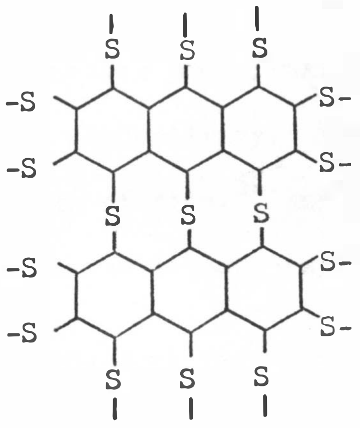


Fig. 6. sulfur-anthracene polymer

(B) Modified Organic Polymers

In this section chemical modifications (except charge-transfer complexes) and effects of ultraviolet and high energy radiation on polymer molecules will be discussed. (Pyrolysis of organic polymers and metal-doped polymers are not included.)

Dehydrohalogenations of poly (vinyl bromide), poly (vinyl chloride) (PVC), chlorinated PVC, poly (vinylidene chloride) were performed for purposes of obtaining semiconductive polymers containing a system of conjugated double bonds.

Poly (acenaphthylene),[43] poly (vinyl carbazole),[44] and poly (vinyl naphthalene)[45] were nitrated. The photoconductivity of these polymers was enhanced by nitration, the degree of enhancement depended on the mole percent of substituted NO_2 groups.

Irradiation of polyethylene,[46] polytetraflouorethylene,[47, 48] polystyrene[49] and polyamide[50] with X-rays or electrons were discussed by many authors. This causes crosslinking or degradation and may also promote electrical conductivity. The enhanced conductivity persists for long periods of time,[51] and the temperature dependence of conductivity obeys the well-known exponential relationship.[50, 52]

(C) Charge-transfer Composed of Low Molecular Weight Donor-Acceptors

Rigorously speaking, the charge-transfer complex composed of low molecular weight components is not a "polymer," at least not a covalent polymer. However, in some cases the donor and acceptor molecules alternated throughout whole crystals, building the stable compounds: DADADA type (D: donor, A: acceptor), not (DAD)/(DAD)/(DAD) or (DA)/(DA)/(DA) type (a bar between parentheses stands for van der Waal forces). This kind of charge-transfer complex could be recognized as "charge-transfer polymer."

(1) Aromatic Hydrocarbon-Halogen

In the charge-transfer complex series, this group was investigated first and is still being studied. The composition of the compounds depends on the molecular size of both donor and acceptor and their chemical and probably crystalline nature. Iodine was one of the most common halogens that complexed with aromatic hydrocarbon. The resistivities of this kind of charge-transfer complexes were fairly low, for example, perylene-I_2 complexes had a low resistivity, 8-9 ohm cm at room temperature.[53, 54]

(2) Amine-Iodine Charge-transfer Complexes

The number of amine-iodine complexes studied so far was not great: indole,[55] acridine,[45] N-methylacridine,[56] N-methylquinoline,[57] and benzidine,[58] and the ions 1-methyl-2-picolinium,[57] tetramethyl ammonium[57, 59] and trimethylphenylammonium.[57] Most of these exist as onium ions in the complexes. Generally speaking the resisitivities of this group of compounds were rather high ($\rho_{20^\circ C} = 10^7$ ohm cm) and varied with iodine content. The activation energy was also relatively high except for the indole-I_2 (E=0.1 eV) and benzidine-I_2 (E=0.48 eV) complexes.

(3) Tetracyanoquinodimethan (TCNQ)

A large variety of conductive compounds have been reported.[60, 61] This series of complexes will be discussed in detail in the second part of the Historical Section.

(4) Tetracyanoethylene (TCNE)

Tetracyanoethylene (TCNE) could also form strong charge-transfer complexes with many donors. The resistivity of these complexes was relatively high (10^8 ohm cm) with the exception of a charge-transfer compound with tetrathiotetracene (ρ_{20^oC} = 15 ohm cm). The resistance of TCNE complexes decreased rapidly with increasing pressure.[62] In the infrared region a broad charge-transfer absorption band was found.[63]

(5) Substituted benzoquinones

p-Fluoro-, p-chloro-, p-iodo-o-chloro-, and o-bromoanil and 2,3-dicyano-5,6-dichloro, and 2,3-dicyano-5,6-dibromobenzoquinone were known as strong acceptors and form a number of charge-transfer complexes.[64] Conductivity of this group strongly depended on the nature of the donor. The relationship between ESR absorption spectra and conductivity of these compounds was discussed in detail[58, 65, 66, 67] as well as their photoconductivity;[68, 69] and pressure effects on the conduction have been investigated by a few groups.[70, 71, 72]

(6) Hydrocarbons and Substituted Hydrocarbons as Acceptors

The electrical resistivities of complexes formed between various aromatic hydrocarbons and trinitrobenzene were found to be fairly high ($\rho_{15^{\circ}C} = 10^{13}$ ohm cm).[73] The research on alkali metal-hydrocarbon semiconductors originated in the studies of graphite-alkali metal lamellar compounds.[74, 75] Since 1954 halogeno-, cyano-, and nitro-substituted hydrocarbons as well as unsubstituted hydrocarbons were reported as acceptors with alkali metal donors (Li, Na, K, Cs), forming organic semiconductors. Surprisingly even acridine derivatives (usually donors) could be acceptors when reacted with sodium metal.[76]

(D) Coordination Polymers

This group could be divided into three types: (1) Those compounds polymerized through coordination, for example a transition metal with a bichelating ligand,[77] such as 2,5-dihydroxyquinone and polynaphthazarin-cobalt and -iron coordination polymers[78, 79] shown in Fig. 7. (2) Polymers composed of metal ions and normal covalent polymers having coordination functional groups. (This type of polymer is a kind of mixed type polymer also.)

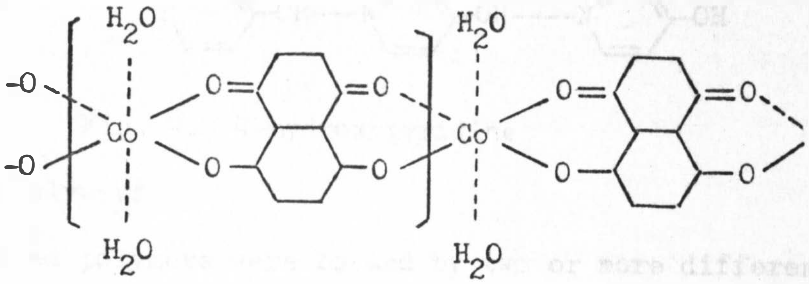


Fig. 7. polynaphthazarin-cobalt coordination polymer

(3) Metal-organic polymers with carbon-metal bonds, such as polyvinylene containing ferrocene substituents,[39] Fig. 8.

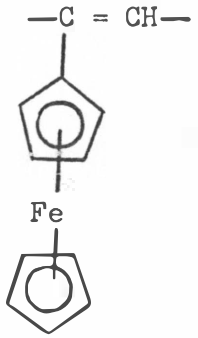


Fig. 8. polyvinylene containing ferrocene substituents

(E) Hydrogen-Bonded Polymers

"Polymer" formation through hydrogen bonding occurred rather widely with examples ranging from water to large organic molecules having both electronegative atoms and labile hydrogen atoms. Aftergut _et_ _al_. reported the possibility of electronic conduction through hydrogen bonds in the molecular chain of 4-hydroxypyridine,[80] (Fig. 9), but they did not obtain enough reliable data to prove their hypothesis.

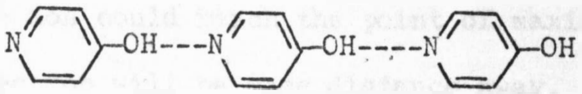


Fig. 9. 4-hydroxypyridine

(F) Mixed Polymers

Mixed polymers were formed by two or more different mechanisms of polymerization,[21] such as charge-transfer polymers having a donor polymer and a small acceptor, coordination polymers having covalent polymer ligands, covalent polymers having hydrogen bonds and charge-transfer complexes having a coordination polymer as an acceptor.

(G) Organic Superconductors

Recently, Little discussed the possibility of synthesizing an organic superconductor.[81] Superconductivity is a kind of electrical property observed only in certain metals cooled to the temperature near absolute zero. When an electric current is induced in such a metal, it flows indefinitely without any loss of power. All resistance to the flow of electrons through it disappeared.

The metal atoms give up some electrons to the Fermi sea and the positive ions form a more or less regular lattice structure. The electrons in the sea are free to move about. As one of these electrons comes close to one of the positive ions (Fig. 10), the electron is attracted to the positive ion via the screened Coulomb interaction. This electron, however, is traveling rather fast, so that before the ion could reach the point of maximum excursion the number one electron will be some distance away. Consequently, some distance behind this electron the lattice would be puckered up in the vicinity of the electron track. In this region there would be a larger density of positive ions than there would otherwise have been. As a result of this there will be an excess positive charge in this region. Now if a second electron approaches this region it will be attracted to this positive charge and may become bound to it. A bound pair of electrons can thus result due to the intermediate interaction with the lattice.

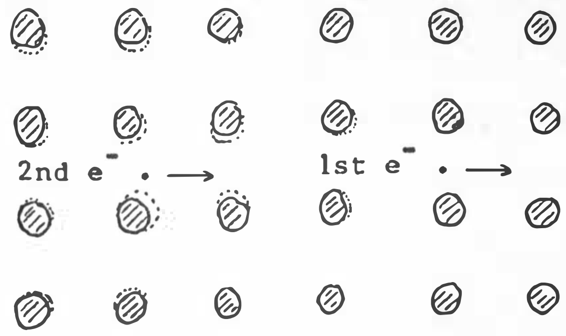


Fig. 10. Model for the superconducting metal

In order for these to be superconducting it appears that two conditions had to be satisfied. First of all there must be some kind of electron-electron attraction which must be large enough so that in spite of the Coulomb repulsion, two electrons could be drawn to one another and form a stable bond pair. Second, in order to remain bound, it seems to be necessary for all the bound pairs to be in identically the same eigen state. Consequently, if the temperature was low enough the system would spontaneously enter this low energy state. Near absolute zero, we should expect a large number of the electrons to pair and organize their motion so as to interfere with one another as little as possible.

From this model of superconductor one can see how it might be possible for superconductivity to occur in some large organic macromolecules. Consider the model of such a molecule shown in Fig. 11. Let A (the spine) be a linear molecule such as a polyene in which charge can move freely from end to end. Let a series of highly polarizable side chains, B, be attached more or less regularly to this molecule A. Now if an electron moves rapidly along A it will interact with the side chains and induce a charge on the side of B nearest A. However, this induced charge will not appear instantaneously at this point but at a slightly later time, a time which will depend on the frequency of vibration of charge in the side chain. Just as before, an excess positive charge will then be induced some distance behind, but in the neighborhood of the track left by this first electron. A second electron can be attracted to this region and may become bound to it and thus indirectly bound to the first electron. In order for this attraction to be effective the other electrons must coordinate their motion with these first two.

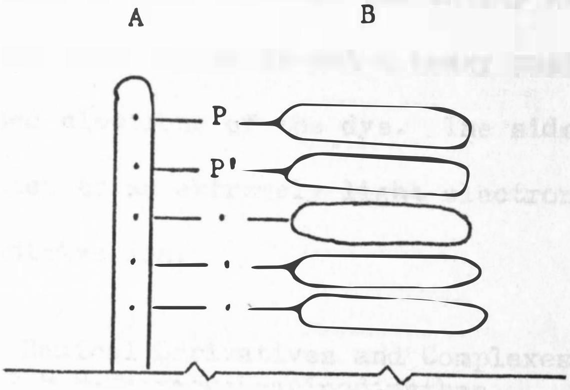


Fig. 11. Model for the superconducting organic compounds

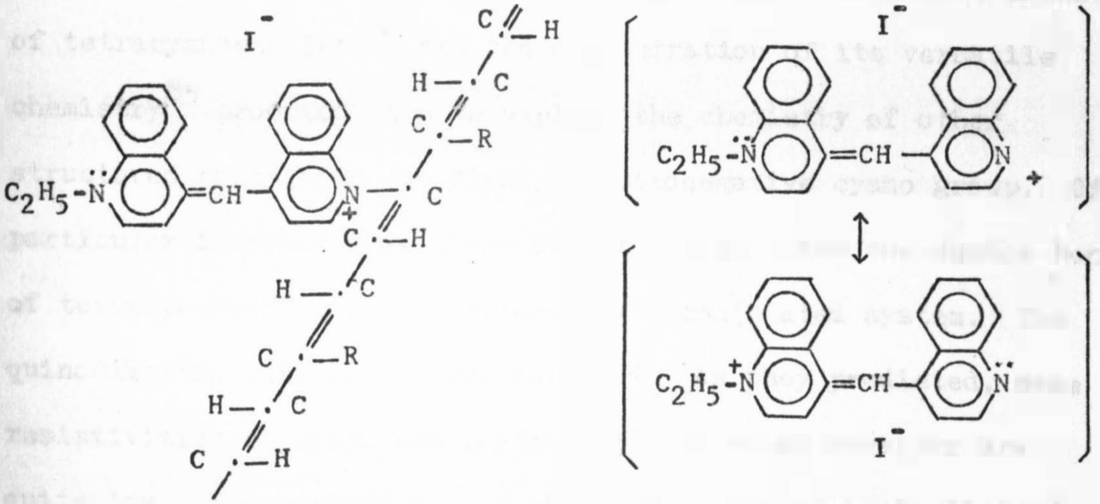


Fig. 12. More realistic model for the superconducting organic compounds

A more realistic model has been proposed by Little[82] where the spine is a conjugated chain of carbon atoms, while the side-chains are part of a diethylcyanine iodide dye (Fig. 12) with the transition temperature (Tc) proposed to be as high as 2000°K. In other words, the superconducting state exists until the temperature rises to 2000°K. The reason why such a high transition temperature may be obtained is that in this molecule the entity which moves to produce the excess positive charge is not a heavy positive ion but one of the delocalized electrons of the dye. The side-chain interaction is mediated by an extremely light electron rather than the usual massive positive ion.

II. Anion-Radical Derivatives and Complexes of 7,7,8,8-Tetracyanoquinodimethan

In 1960, 7,7,8,8-tetracyanoquinodimethan (TCNQ) was synthesized by D. S. Acker, R. J. Harder, W. R. Hertler, W. Mahler, L. R. Melby, R. E. Benson, and W. E. Mochel.[83] The recent discovery of tetracyanoethylene[84] and the demonstration of its versatile chemistry[85] prompted them to explore the chemistry of other structures containing the highly electronegative cyano group. Of particular interest were those structures in which the double bond of tetracyanoethylene was replaced by a conjugated system. The quinodimethan ring system was selected. As they predicted, some resistivities of compounds containing TCNQ as an acceptor are quite low. The resistivity of single crystals of (quinolinium) $(TCNQ^{\overline{\cdot}})(TCNQ^{o})$[60] was the smallest one of those TCNQ compounds that were investigated by Acker *et al*.

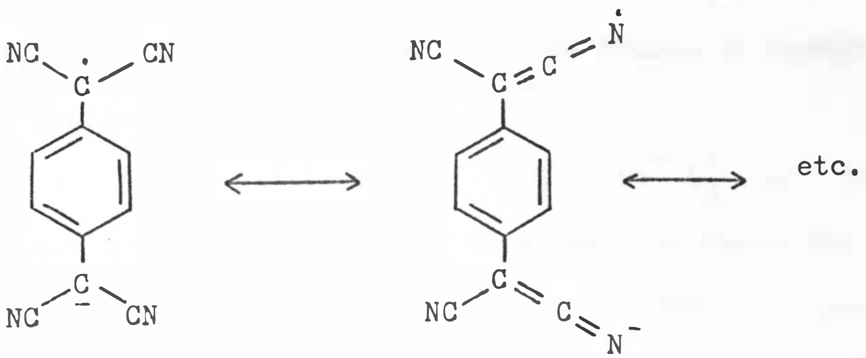
TCNQ formed two types of electronically conducting compounds.

(A) Molecular complexes

The ability of quinones to form stable solid complexes with aromatic amines was known for many decades,[86] and in modern terms such complex formation was ascribed to interaction of the electron-rich pi orbital system of the quinone (pi acid or acceptor) with the electron-rich pi orbitals of the amine (pi base or donor). The pi acid property of TCNQ derives partly from the high electron affinity of the polyene system conferred by the powerful electron-withdrawing effect of the four cyano groups and partly from the planarity and high symmetry of the TCNQ structure. It formed crystalline pi complexes (charge-transfer complexes) with aromatic hydrocarbons, amines and polyhydric phenols. These complexes are characterized by intermediate to high resistivity (10^3 to 10^{14} ohm cm) and very weak EPR (electron paramagnetic resonance) absorption.[87]

(B) Anion-radical salts

TCNQ forms two series of stable, salt-like derivatives, each involving complete transfer of an electron to TCNQ with the formation of the anion-radical $TCNQ^{\overline{\cdot}}$ represented by the resonance hybrid (1).



(1)

(a) Simple salts

The first series is represented by the simple salt formula $M^{+n}(TCNQ^{\overline{\cdot}})_n$ in which M may be a metallic or organic cation, that is, alkali metals, alkaline earth metals, simple transition metals, complexed transition metals, and inorganic or organic ammonium, phosphonium and $\left[(CH_3)_2N\right]_3S+$ ions. TCNQ underwent facile one electron reduction when treated with metal iodides or with certain metals. For example, TCNQ in acetonitrile would react at room temperature with metallic copper or iodide, the TCNQ oxidizes iodide ion to free iodine and took up the electron to form $TCNQ^{\overline{\cdot}}$. With the free metal, direct oxidation/reduction occurs and in the case of copper, the cuprous salt of $TCNQ^{\overline{\cdot}}$ formed (eqs. 1 and 2). The iodide reaction was the more convenient for direct preparation of simple metal $TCNQ^{\overline{\cdot}}$ salts.

$$CuI + TCNQ \longrightarrow Cu^{+}TCNQ^{\overline{\cdot}} + 1/2\ I_2 \qquad \text{(eq. 1)}$$

$$Cu^{0} + TCNQ \longrightarrow Cu^{+}TCNQ^{\overline{\cdot}} \qquad \text{(eq. 2)}$$

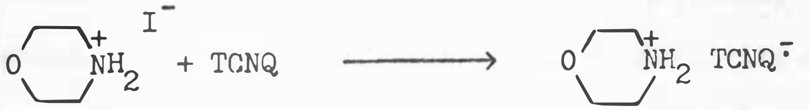
An excess of metal iodide was used so that the iodine by-product can be scavenged as I_3^-, e.g.

$$3\ LiI + 2\ TCNQ \xrightarrow{CH_3CN} 2\ Li^{+}TCNQ^{\overline{\cdot}} + Li^{+}\ I_3^- \quad \text{(eq. 3)}$$

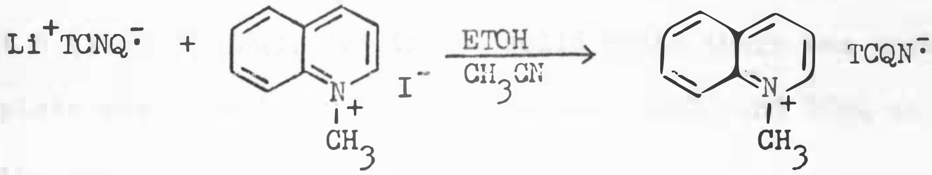
With this stoichiometry, higher yields were realized since the oxidative reverse reaction $1/2\ I_2 + TCNQ^{\overline{\cdot}} \longrightarrow TCNQ + I^-$ was largely obviated. The occurrence of this oxidation was established, since free TCNQ could be isolated by oxidation of $TCNQ^{\overline{\cdot}}$ salts with a large excess of iodine. In this way the lithium, sodium and potassium salts of $TCNQ^{\overline{\cdot}}$ were prepared.[87] The reaction of metal iodides with TCNQ generally afforded simple salts represented by the formula $M^{+}TCNQ^{\overset{-}{\cdot}}$. An exception was cesium iodide which forms the complex salt[88] (1).

$$2\ CsI + 3\ TCNQ \longrightarrow \underset{(1)}{Cs_2^{+}(TCNQ^{\overset{-}{\cdot}})_2(TCNQ)} \qquad (eq.\ 4)$$

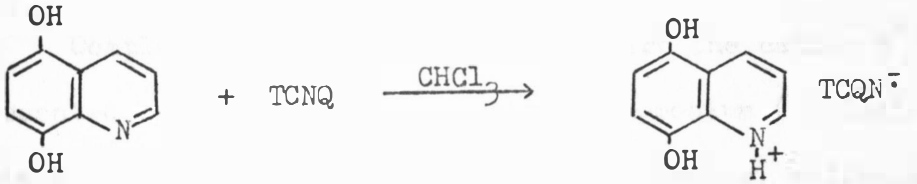
The simple $TCNQ^{\overset{-}{\cdot}}$ salts containing onium cations were prepared by reaction of the onium iodide with TCNQ (eq. 5), metathesis of iodide with $Li^{+}TCNQ^{\overset{-}{\cdot}}$ (eq. 6), or reaction of free base with TCNQ (eq. 7).*



(eq. 5)



(eq. 6)



(eq. 7)

These salts are characterized by weak EPR absorption in the solid state[89] and intermediate resistivity[90] (10^{4} to 10^{12} ohm cm). With few exceptions, the simple salts were obtained in microcrystalline form so that single crystal resistivity measurements were not usually attainable. However, in those instances where sufficiently large single crystals were obtained, the resistivities along three major crystal axes were essentially equivalent

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*The source of the proton required to form the cation is not known but it is probably derived from the base.

(isotropic) in contrast to the marked anisotropy of resistivity observed in single crystals of complex salts described below.

(b) Complex salts

The complex salts are represented by the formulas, $M^+(\text{TCNQ}^{\overline{\cdot}})(\text{TCNQ}^0)$ and $M_2^+(\text{TCNQ}^{\overline{\cdot}})_2(\text{TCNQ}^0)$, containing molar proportions of neutral TCNQ associated with $\text{TCNQ}^{\overline{\cdot}}$ and a cation. Of these two types of complexes the latter was quite rare, and so most of the discussion would be devoted to the $M^+(\text{TCNQ}^{\overline{\cdot}})(\text{TCNQ})$ type. In solution, spectral, polarographic and conductivity data indicated dissociation into the three species formulated in the molecular unit $M^+(\text{TCNQ}^{\overline{\cdot}})(\text{TCNQ})$, but in the solid state there was probably complete electron delocalization between $\text{TCNQ}^{\overline{\cdot}}$ and TCNQ as implied by the formulation $(\text{TCNQ})_2^{\overline{\cdot}}$.[89]

Complex salts were prepared in which the cation M^+ was represented by alkyl or aryl substituted ammonium (including N-heterocycles), phosphonium, arsonium, stibonium, sulfonium and oxonium ions. Neutral TCNQ was usually not incorporated into products containing inorganic cations even when neutral TCNQ was present during synthesis. On the other hand, organic cations generally afforded complex salts under analogous synthesis conditions. There were four major synthetic routes to these complexes, although some methods were more general than others. The four routes were formulated in the equations:

$$\text{Et}_3\text{NH}^+\text{TCNQ}^{\overline{\cdot}} + \text{TCNQ} \xrightarrow{\text{CH}_3\text{CN}} \underset{(2)}{\text{Et}_3\text{NH}^+(\text{TCNQ})_2^{\overline{\cdot}}} \quad (50\%) \quad (\text{eq. } 8)$$

$$3Et_3NH^+I^- + 2\ TCNQ \xrightarrow{CH_3CN} (2) \qquad (50\%) \quad (eq.\ 9)$$

$$2Et_3N + H_2TCNQ + 3TCNQ \xrightarrow{CH_3CN} (2) \qquad (90\%) \quad (eq.\ 10)$$

$$Et_3N + 2TCNQ \xrightarrow{CH_3CN} (2) \qquad (77\%) \quad (eq.\ 11)$$

The first method (eq. 8) probably represented the most general route to the complex anion-radical salts and was dependent only on the availability of the simple salts and on their having a reasonable degree of solubility in acetonitrile.

In method 2 (eq. 9), the iodide ion served as the electron source for the formation of $TCNQ^{\overline{\cdot}}$, the iodide being oxidized to free iodine which was scavenged as triiodide. This method was suitable for virtually all onium iodides including substituted -ammonium, -phosphonium, -arsonium, -stibonium and -sulfonium salts.

Method 3 (eq. 10), in which the H_2TCNQ acts as both proton and electron donor, was particularly suitable for the preparation of trisubstituted ammonium complex salts starting from free amines. The path in this transformation was not certain but two possibilities are included in the sequence.

$$R_3N + H_2TCNQ \xrightarrow{R_3N} 2R_3NH^+ + TCNQ^= \xrightarrow{TCNQ} 2R_3NH^+ + 2TCNQ^{\overline{\cdot}}$$
$$\xrightarrow{2TCNQ} 2\ R_3NH^+(TCNQ)_2^{\overline{\cdot}}$$

$$R_3N + H_2TCNQ \longrightarrow R_3NH^+ + HTCNQ^- \xrightarrow{TCNQ} R_3TCNQ^{\overline{\cdot}} + HTCNQ^{\cdot}$$
$$\xrightarrow{R_3N} 2R_3NH^+ + 2TCNQ^{\overline{\cdot}} \xrightarrow{2TCNQ} 2\ R_3NH^+(TCNQ)_2^{\overline{\cdot}}$$

A variant of this procedure consisted in replacing the H_2TCNQ by another proton-electron source, such as durohydroquinone.

Method 4 (eq. 11) was applicable to tertiary aliphatic amines and is of special interest since the reaction occurred at room temperature in acetonitrile in the absence of added catalyst or proton-electron donor. The course of the ammonium proton was unknown. It was probably derived either from the amine[90] or the solvent. However, Melby et. al.[87] failed to isolate a vinyl-amine derivative or the expected coupling product, succinonitrile.

This series was characterized by exceptionally low electrical resistivity[60] (10^{-2} to 10^{3} ohm cm.) and variable E.P.R. absorption.[91] These resistivities showed the exponential temperature dependence characteristic of intrinsic semi-conductors. And both of these properties were anisotropic as determined by measurements on single crystals.[60, 91]

III. Benzologs of the Quinolizinium Ion

Quinolizinium ion (Fig. 13), in which the carbon at position 4a of the naphthalene nucleus was replaced by a quaternary nitrogen, was synthesized in 1954.[92]

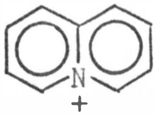
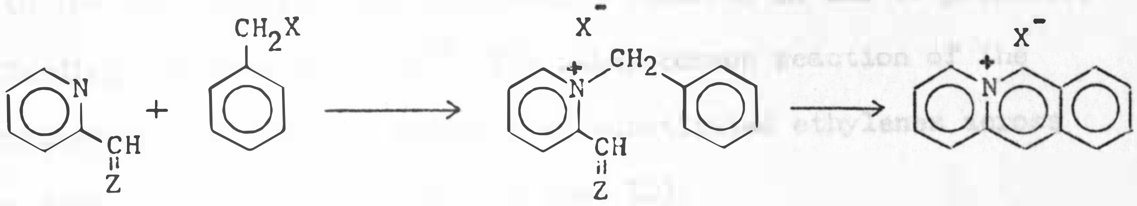


Fig. 13. Quinolizinium ion

In the same year, 4a-azonia-anthracene (acridizinium ion) (3), one of monobenzologs of quinolizinium ion was synthesized by Bradsher and Beavers.[93, 94] They treated benzyl bromide with 2-pyridine-carboxaldehyde (4). The crude salt (7) cyclized in boiling 48% hydrobromic acid to afford acridizinium bromide.



(3)

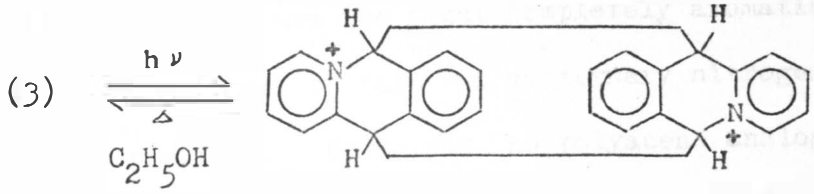
(4) $Z = O$ (7) $Z = O$

(5) $Z = NOH$ (8) $Z = NOH$

(6) $Z = (OCH_2)_2$ (9) $Z = (OCH_2)_2$

They also found that the oxime of 2-pyridinecarboxaldehyde (5) offered the advantages of greater stability and ease of quaternization, and, in addition, the intermediate salt (8) was more easily purified and cyclized more rapidly than the aldehyde salt (7).[95]

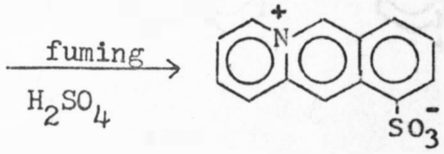
Acridizinium ion was more sensitive to light than is anthracene, and underwent photodimerization through the meso positions.[96] The photodimer (10) disassociated when refluxed in ethanol.



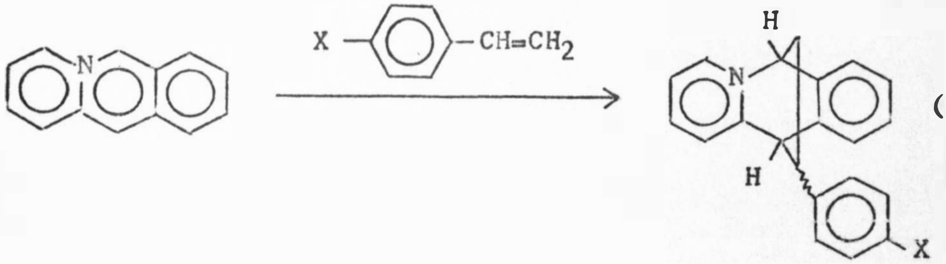
(10)

With the acridizinium ion, sulfonation occurred in the 10 position, affording the betaine (11).[97] The other common reaction of the acridizinium ion was the addition of substituted ethylenes across the meso positions of the nucleus (eq. 12).

(3)

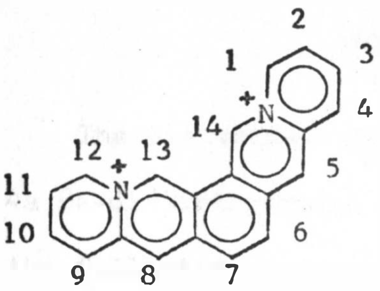


(11)

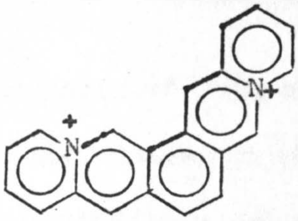


(eq. 12)

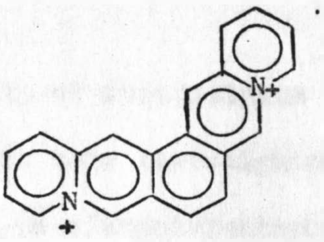
In 1963, 12a,14a-, 4a,12a-, and 4a,8a-diazoniapentaphene salts (12), (13), (14) were synthesized by Bradsher and Parham by replacement of the benzyl halide by o-, m-, p-disubstituted xylene halide.[98] These are the first completely aromatic condensed benzenoid compounds which contain two quaternary nitrogen atoms at bridge head positions. Up to now, no polyacene analogues have been reported. No studies of electrical properties of diazoniapentaphene salts have been reported.



(12)



(13)



(14)

RESULTS AND DISCUSSION

The electrical conductivity of TCNQ salts of acridizinium and 4a,8a-diazoniapentaphene and related polymers were investigated for the following reasons. Acridizinium and 4a,8a-diazoniapentaphene are highly conjugated cationic systems. The addition reaction of alkenes across the meso positions of the acridizinium ion showed the polarizable character of acridizinium ion. Finally, the relatively simple symmetry of these ions compared with N-methylphenazinium ion suggested the possibility of synthesizing some compounds with high density and low resistivities out of acridizinium and 4a,8a-diazoniapentaphene. The reaction between the pyridine and bromomethyl group might proceed in good enough yield to be used in forming the polymer backbone.

First of all, acridizinium and 4a,8a-diazoniapentaphene $TCNQ^{\overline{\cdot}}$ complexes were synthesized. Because the solubility of $Li^+TCNQ^{\overline{\cdot}}$ in water or ethanol is fairly high in contrast to other metal-TCNQ salts which are virtually insoluble in water and organic solvents,[99] the TCNQ anion-radical $(TCNQ)^{\overline{\cdot}}$ was formed by reaction of an excess of lithium iodide with TCNQ in acetonitrile. The TCNQ oxidized iodide ion to free iodine, which was scavenged as I_3^-, and took up the electron to form $Li^+TCNQ^{\overline{\cdot}}$ (15).

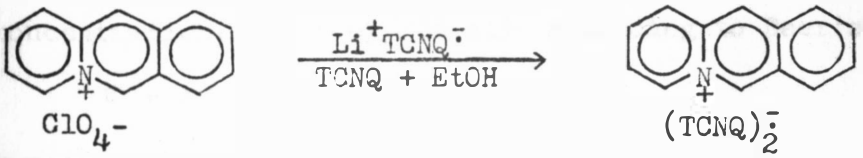
$$3\ LiI + 2\ TCNQ \xrightarrow{CH_3CN} 2\ Li^+TCNQ^{\overline{\cdot}} + Li^+ + I_3^-$$

(15)

Due to the oxidative reverse reaction: $1/2\ I_2 + \mathrm{TCNQ}^{\overline{\cdot}} \longrightarrow \mathrm{TCNQ} + I^-$ and difficulty in recrystalization, $\mathrm{Li}^+\mathrm{TCNQ}^{\overline{\cdot}}$ was isolated as a mixture with neutral TCNQ. Instead of the simple salts of $\mathrm{TCNQ}^{\overline{\cdot}}$ obtained by metathesis of $\mathrm{Li}^+\mathrm{TCNQ}^{\overline{\cdot}}$ with various onium cations, the complex salts $M^{+n}\ (\mathrm{TCNQ})_n^{\overline{\cdot}}(\mathrm{TCNQ})_m$, with different ratios of $\mathrm{TCNQ}^{\overline{\cdot}}$ to TCNQ were obtained.

(1) Acridizinium TCNQ complex

Acridizinium perchlorate was synthesized by the method used by Bradsher.[93] The 1 to 1 ratio complex salt, acridizinium $(\mathrm{TCNQ})_2^{\overline{\cdot}}$, was synthesized by reaction of $\mathrm{Li}^+\mathrm{TCNQ}^{\overline{\cdot}}$ + TCNQ with acridizinium perchlorate. (eq. 13)

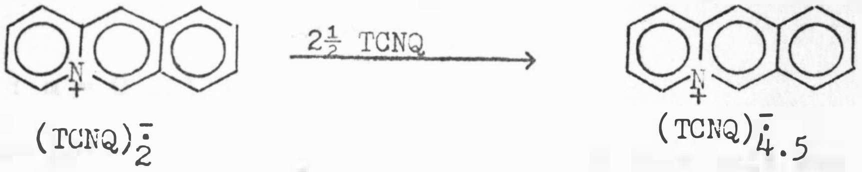


(16)

(eq. 13)

The displacement of perchlorate ion by $\mathrm{TCNQ}^{\overline{\cdot}}$ of acridizinium perchlorate can be seen from the disappearance of characteristic peak of perchlorate at 1100 cm^{-1} in IR spectrum.

The 2 to 7 complex salt (17) was synthesized by reaction of TCNQ with acridizinium $(\mathrm{TCNQ})_2^{\overline{\cdot}}$ (16). (eq. 14)



(eq. 14)

(17)

Ultraviolet spectroscopy was a useful tool for determination of the ratio of TCNQ$^{\overline{\cdot}}$ to TCNQ in complex salts because TCNQ$^{\overline{\cdot}}$ shows two main absorptions around 830 nm and 390 nm with molar extinction coefficients, 43300 l mole^{-1}cm^{-1} and 22000 l mole^{-1}cm^{-1}, while TCNQ shows an absorption at 390 nm with molar extinction coefficient 63600 l mole^{-1}cm^{-1} in acetronitrile.[99] The absorbance of acridizinium (TCNQ)$_2^{\overline{\cdot}}$ at 830 nm and 390 nm was 0.225 and 0.51. (concentration: 0.55 mg/250 ml) According to Beer's law: $A = \varepsilon bc$.

$$\varepsilon = A/bc$$

Where A = absorbance,

b = path length through the sample (1 cm),

c = concentration of solute, in mole/l.

ε = molar extinction coefficient, in l mole^{-1}cm^{-1}.

$$43300 = \frac{0.225}{\frac{n}{250} \times 1} \qquad n = 0.00129$$

Where n = moles of TCNQ$^{\overline{\cdot}}$ in this compound.

At 390 nm, 0.00129 moles of TCNQ$^{\overline{\cdot}}$ showed absorbance 0.11.

$$63000 = \frac{(0.51-0.11)}{\frac{m}{250} \times 1} \qquad m = 0.00157$$

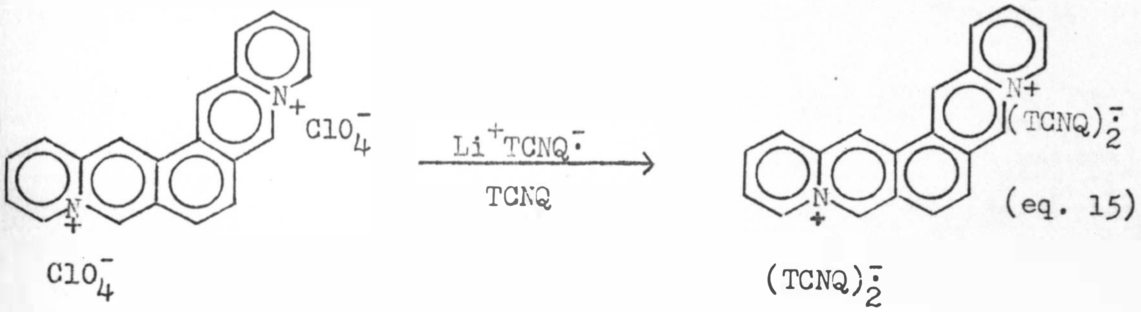
$n : m = 0.00129 : 0.00157 = 1 : 1$

The ratio of $\text{TCNQ}^{\bar{\cdot}}$ to TCNQ in this complex salt was 1 to 1.

All the ratios of complex salts listed in Table 2 were determined by the same method.

(2) 4a,8a-Diazoniapentaphene TCNQ Complex

4a,8a-Diazoniapentaphene perchlorate was synthesized by the method used by Bradsher.[98] The one to one ratio comples salt (18) was synthesized by reaction $\text{Li}^{+}\text{TCNQ}^{\bar{\cdot}}$ and TCNQ with 4a,8a-diazoniapentaphene perchlorate (eq. 15).



(eq. 15)

(18)

The one to three and one to four ratio complex salts, 4a,8a-diazoniapentaphene$(\text{TCNQ})_4^{\bar{\cdot}}$ and 4a,8a-diazoniapentaphene $(\text{TCNQ})_5^{\bar{\cdot}}$, were synthesized by reaction of 18 and TCNQ.

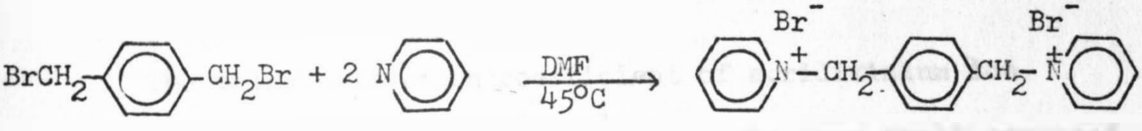
TABLE 2

TABLE OF TCNQ$^{\overline{\cdot}}$ AND TCNQ RATIO FROM ABSORBANCE DATA

Compounds	Absorbance		Ratio n:m
	830	390	
acridizinium $(\mathrm{TCNQ})^{\overline{\cdot}}_{n}(\mathrm{TCNQ})_{m}$	0.225	0.51	1 : 1
	0.15	0.87	2 : 7
4a, 8a-diazoniapentaphene $(\mathrm{TCNQ})^{\overline{\cdot}}_{n}(\mathrm{TCNQ})_{m}$	0.135	0.33	1 : 1
	0.26	0.65	1 : 3
	0.13	0.92	1 : 4
1.4-Bis[1-methylene pyridinium $(\mathrm{TCNQ})^{\overline{\cdot}}_{n}(\mathrm{TCNQ})_{m}$] benzene	0.785	0.23	1 : 1
	0.26	0.48	1 : 3

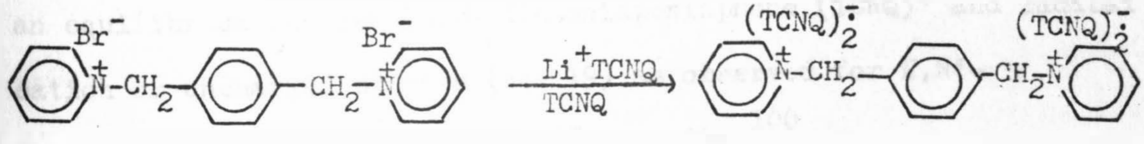
(3) 1,4-Bis(1-methylene pyridinium) benzene TCNQ complex

1,4-Bis(1-methylene pyridinium bromide) benzene (19) was synthesized by reaction of α, α'-dibromo-p-xylene and pyridine in dimethylformamide (eq. 16).



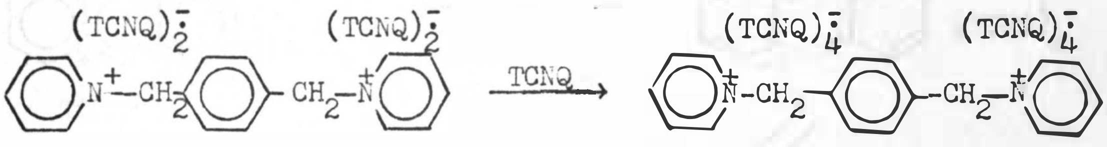
(19) (eq. 16)

The one to one ratio complex salt, 1,4-bis(1-methylene pyridinium $(TCNQ)_2^{\bar{\cdot}}$) benzene (20) was synthesized by reaction of 1,4-bis(1-methylene pyridinium bromide) benzene with $Li^+TCNQ^{\bar{\cdot}}$ and TCNQ (eq. 17).



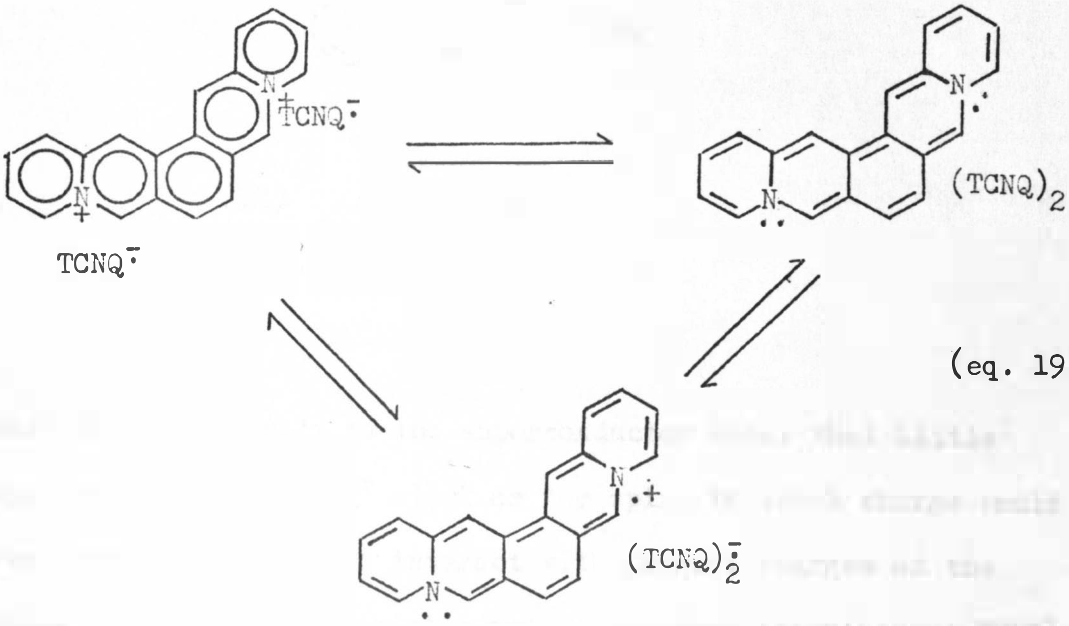
(20) (eq. 17)

The one to three ratio complex salt, 1,4-bis(1-methylene pyridinium $(TCNQ)_4^{\bar{\cdot}}$) benzene (21), was synthesized by reaction (20) with TCNQ (eq. 18).



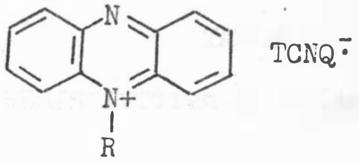
(21) (eq. 18)

The molar extinction coefficient of acridizinium ion around 390 nm was 6170 l mole^{-1} cm^{-1} which was very small compared to the molar extinction coefficients of $\mathrm{TCNQ}^{\overline{\cdot}}$ or TCNQ. In the calculation of the ratio of $\mathrm{TCNQ}^{\overline{\cdot}}$ to TCNQ, it was neglected due to the insignificance. The molar extinction coefficient of 4a,8a-diazoniapentaphene ion at 350 nm was 46200 l mole^{-1} cm^{-1}, and a 1:1:1 ratio of dication and $\mathrm{TCNQ}^{\overline{\cdot}}$ and TCNQ was calculated. Since 4a,8a-diazoniapentaphene ion was a dication, the ratio of cation to $\mathrm{TCNQ}^{\overline{\cdot}}$ should be 1:2. This might be explained as being due to an equilibrium between 4a,8a-diazoniapentaphene $(\mathrm{TCNQ})^{\overline{\cdot}}$ and radical cation or uncharged species (eq. 19) as observed for N,N'-dimethyldihydrophenazinylium $\mathrm{TCNQ}^{\overline{\cdot}}$ by Melby.[100]



(eq. 19)

Melby[100] reported that N-methylphenazinium TCNQ$^{\cdot-}$ simple salt (22a) exhibited the unusually low value of 7×10^{-3} ohm cm measured on single crystals. In marked contrast, the N-ethyl compound (22b) had a single crystal resistivity of 10^{9} ohm cm. X-ray measurements showed that in the N-methyl salt, the TCNQ$^{\cdot-}$ units were stacked one above the other. Furthermore, the compound had a remarkably high density (1.44). These observations suggested that the low steric requirement of the N-methyl group in the cation allows very efficient packing of TCNQ$^{\cdot-}$ units which presumably mediated the electronic conduction.



(22) a; R = CH_3

b; R = CH_3CH_2

There is a similarity to the superconductor model that Little suggested. Packed TCNQ$^{\overline{\cdot}}$ stack as the spine in which charge could move from end to end and interact with induced charges on the stacked cations. Acridizinium and 4a,8a-diazoniapentaphene TCNQ$^{\overline{\cdot}}$ simple salts might pack tighter than N-methylphenazinium TCNQ$^{\overline{\cdot}}$ simple salt, because the nitrogens of the former compounds are on the bridge head position, giving less hindrance than the one which was quarternized with a methyl group. However, none of the TCNQ$^{\overline{\cdot}}$ simple salts of acridizinium or 4a,8a-diazoniapentaphene were synthesized by metathesis. Maybe the reactions should be carried out in the dry box in order to prevent the oxidizing of TCNQ anion-radical to TCNQ. Great care should also be taken when Li^+TCNQ$^{\overline{\cdot}}$ was synthesized, so that there is not any extra TCNQ combined with Li^+TCNQ$^{\overline{\cdot}}$. Another method could be tried where the onium iodide is reacted with TCNQ to form simple salt directly.

The resistivities of those complex salts listed in Table 3 were determined on pellets prepared by mechanical compaction of microcrystalline products at room temperature. Resistivity, given

TABLE 3

RESISTIVITIES OF COMPLEX SALTS

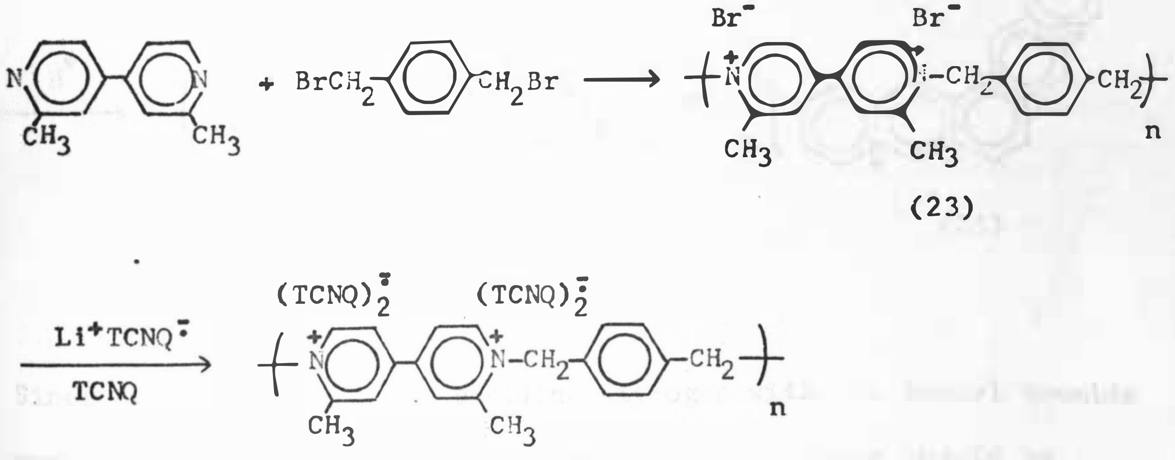
Compounds	n : m	Resistivities, ohm cm
acridizinium $(TCNQ)_n^{\dot{-}}(TCNQ)_m$	1 : 1	$3.8x10^3$
	2 : 7	427
4a.8a-diazoniapentaphene $(TCNQ)_n^{\dot{-}}(TCNQ)_m$	1 : 1	$19x10^4$
	1 : 3	14.1
	1 : 4	11.9
1.4-Bis[1-methylene pyridinium $(TCNQ)_n^{\dot{-}}(TCNQ)_m$] benzene	1 : 1	large
	1 : 3	16.5

the symbol ρ, was defined by the relationship $\rho = (RxA)/L$ where R is the electrical resistance (ohms), A is the area (cm^2), and L is the length (cm) of the pellet being examined.

The following conclusion can be drawn from the resistivity data; the more neutral TCNQ combined with onium cation in these complex salts, the lower the resistivity. This may be explained as being due to the extra TCNQ filling in the spaces in the crystal providing electron conduction through charge transfer complexing. The resisitivities of the one to one complex salt of acridizinium and 4a,8a-diazoniapentaphene were fairly close; however, the resistivities of the one to three 4a,8a-diazoniapentaphene TCNQ complex was almost forty times lower than the acridizinium TCNQ complex. This could be attributed to better conduction through the more conjugated 4a,8a-diazoniapentaphene TCNQ complex or to the greater extent of charge transfer complexing in the larger 4a,8a-diazoniapentaphene complex with its higher content of TCNQ. Recently the charge transfer TCNQ compound (tetrathiofulvalene-tetracyanoquinodimethan) has been shown to have good conductive properties.[101] Thus the charge-transfer between TCNQ radical anions and acceptor TCNQ may be more important to conductivity in our complex salts than the polar bonding between the cation and TCNQ radical anion.

The resistivities of 4a,8a-diazoniapentaphene TCNQ complex salts were also measured by cooling the pellets down to 77°K. The resistivities were inversely proportional to the temperature. This indicated that 4a,8a-diazoniapentaphene TCNQ complex salts are semiconductors. More of the electrons of the semiconductor cross the activation energy barrier at high temperature than at low temperature.

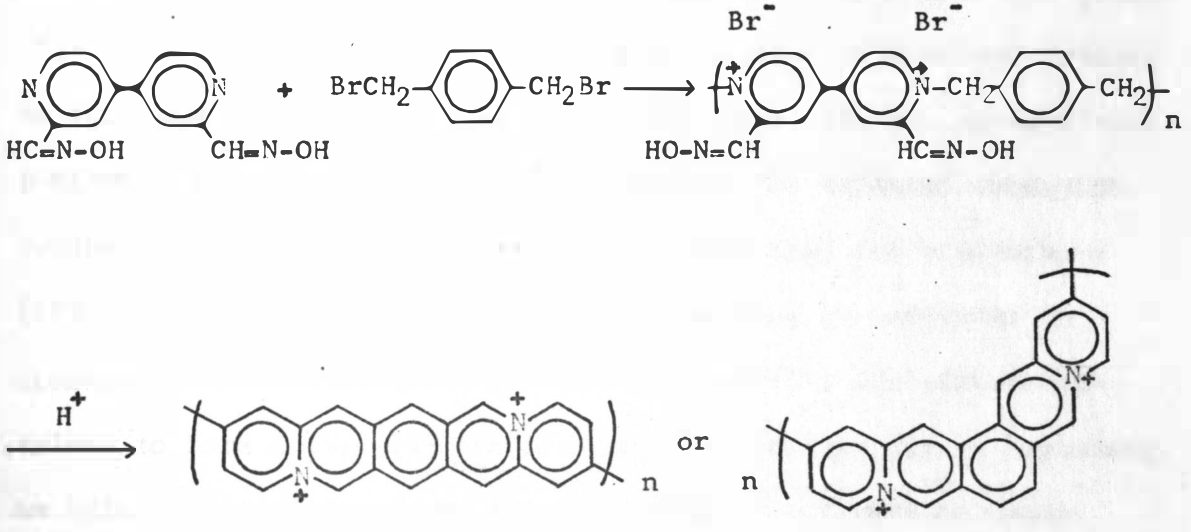
The 4,4'-bipicolinium polymer TCNQ complex (24) was also prepared. The resistivity of this complex was fairly high. This could be due to the amorphous nature of the polymer.



(23)

(24)

Attempts were made to synthesize the polymer with diazoniapentaphene as the repeating unit (25) or (26), because the conducting properties of these highly conjugated system TCNQ complexes should be quite interesting. Conduction through polarizable polycation as well as through $\mathrm{TCNQ}^{\bar{\cdot}}$ or $\mathrm{TCNQ}^{\bar{\cdot}}$ complexes could occur. This polymer might be considered as a superconductor; part of the diazoniapentaphene acts as the spine for electron conduction and the other part of diazoniapentaphene furnishes cations needed for Cooper pairing of electrons.

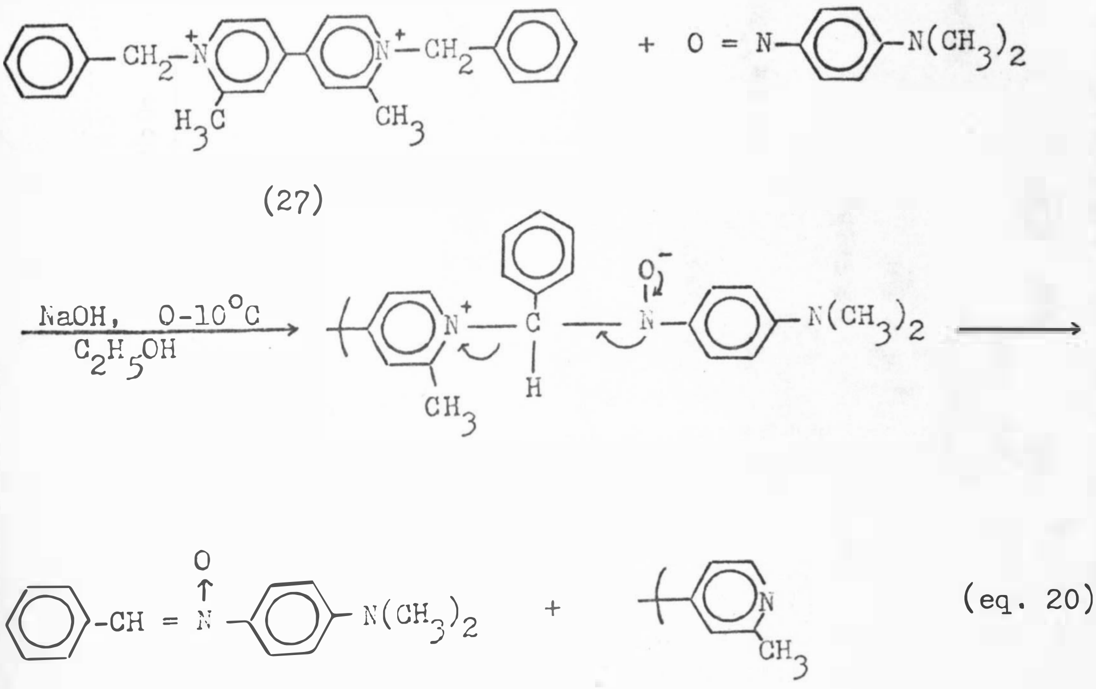


(26) (25)

Since the reaction of the pyridine nitrogen with the benzyl bromide proceeded in high yield, the backbone of the polymer should be synthesized with the reaction of a bispyridine derivative with α,α'-dibromoxylene as described above. The major problem was to effect the synthesis of a bispyridine with an ortho aldehyde or derivative (Fig. 13) or to find a method to convert ortho methyl groups in the polymer (23) to aldehyde groups quantitatively.

In a model system to explore the possibility of the later method, 4,4'-bipicoline was treated with α-bromotoluene in DMF to form the bipicolinium salt (27). IR absorption bands showed at 3050 cm^{-1}(aromatic C-H), 2980, 2940, 2860 (aliphatic C-H), 1635

(C=N stretching). N.M.R. (DMSO-d_6)showed δ 9.5, 9.3, 8.85, 8.7 (mult. pyridinium CH), 7.4 (s. phenyl CH), 5.9 (s. N-CH_2-), 2.8 (s. picoline -CH_3). Since only one absorption for the methyl group was observed, the two methyl groups on the bipyridine are equivalent. This showed that both pyridine nitrogens reacted with benzyl bromide to form the bipicolinium salt. Then this salt (27) was treated with p-nitroso-N,N-dimethylaniline.[102] However, the expected condensed product (28) was not obtained. It was hoped that the bisaldimine (27) could be cyclized to a biacridizinium ion, or subjected to cleavage of the benzyl group and then treated with α,α'-dibromo-p-xylene to form a bipyridinium polymer. The failure may be explained as being due to the nitroso group attacking the methylene group instead of attacking the methyl group of bipicolinium salt (27).[103] (eq. 20)



(27)

(eq. 20)

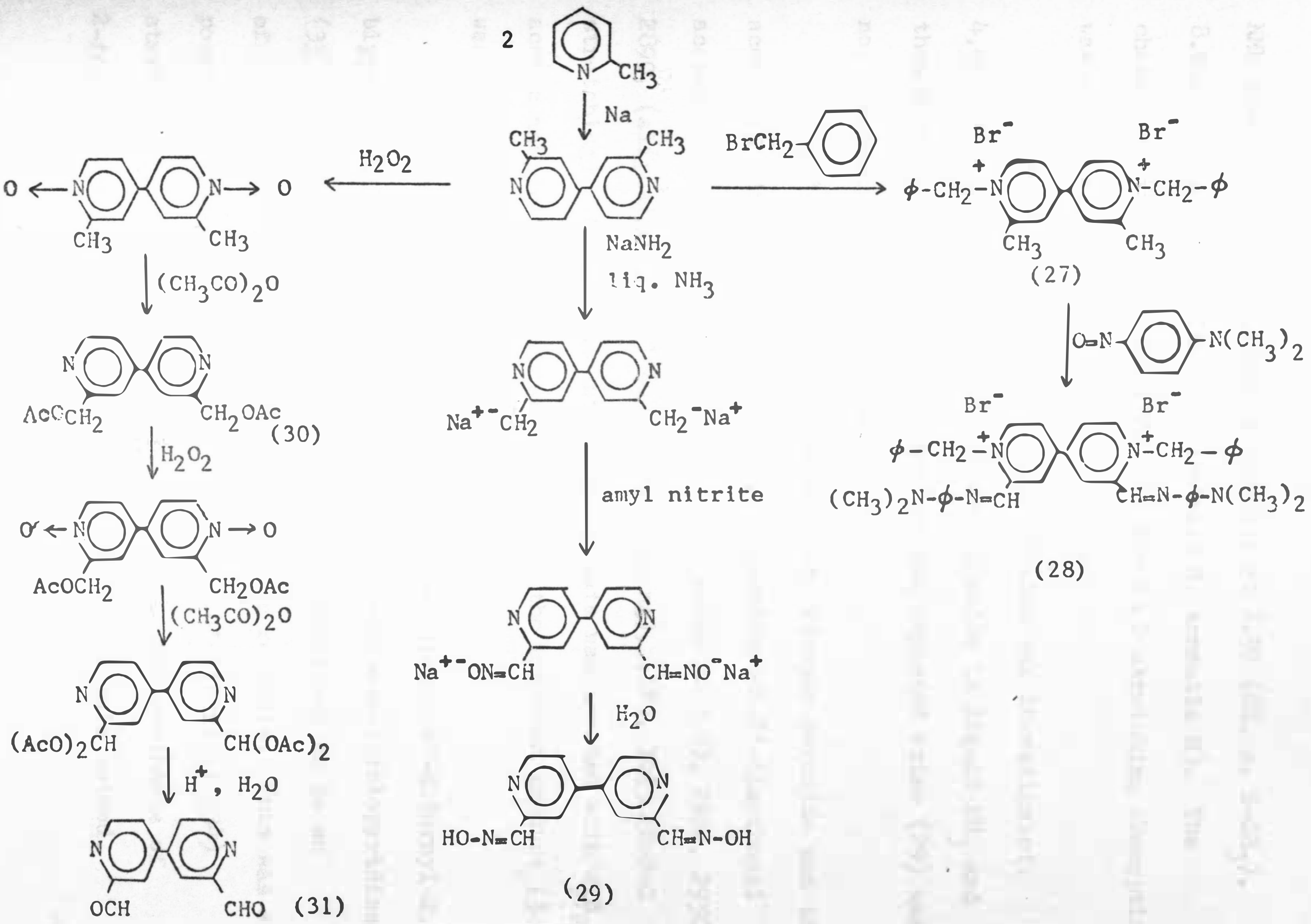


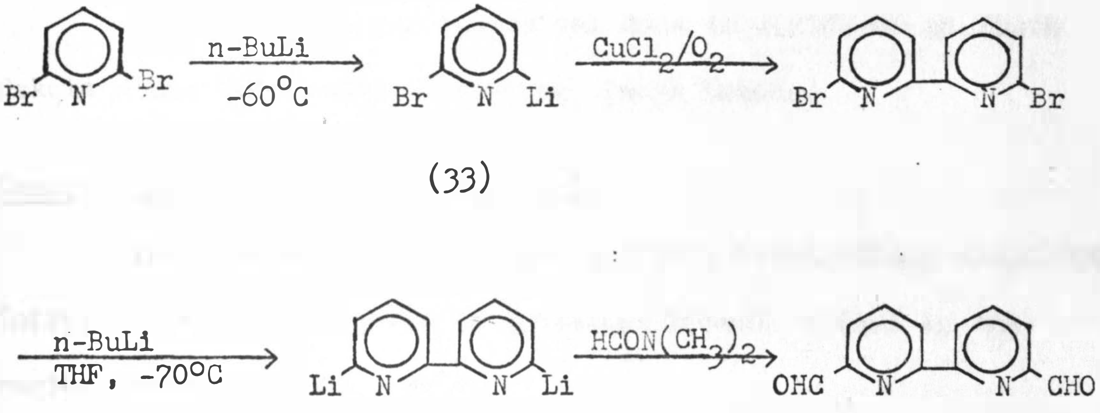
Fig. 14. Synthesis of 4,4'-bipyridine-2,2'-aldoxime and it's related derivatives

NMR spectrum ($CDCl_3$) showed absorption at 2.97 (6H, s, N-CH_3), 8.95, 6.6, 6.45 (10H, mult., aldehydic H, aromatic H). The characteristic IR peak at 1380 cm^{-1} for N→O stretching absorption was also observed.

The synthesis of bispyridinaldoxime was investigated. 4,4'-Bipicoline was treated with sodium amide in liquid NH_3 and then with isoamyl nitrite,[104] however the expected oxime (29) was not obtained.

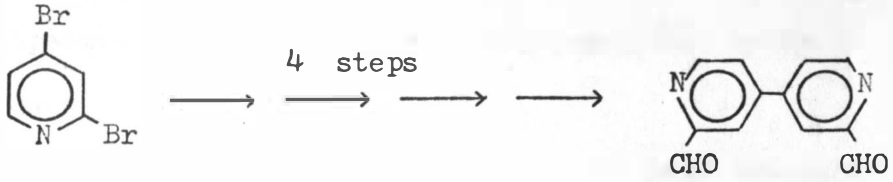
4,4'-Bipicoline was treated with hydrogen peroxide and then acetic anhydride[105,106] to form 4,4'-bipyridine-2,2'-dimethanol acetate (30). IR spectrum showed 3070 (aromatic C-H), 2980, 2950, 2890, (aliphatic C-H), 1680 (C=O stretching), 1120, 1095 (C-O-C stretching). A small amount of the acetate was treated with H_2O_2, acetic anhydride again, however, none of the expected product (31) was obtained.

Parks, Wagner and Holm[107] reported that 6,6'-diformyl-2,2'-bipyridyl (32) was synthesized employing 6-bromo-2-lithiopyridine (33) as an intermediate. Cupric chloride was found to be an effective coupling agent for lithiopyridine reagents. This was a possible method to prepare 2,2'-diformyl-4,4'-bipyridyl (34) starting with 2,4-dibromopyridine. However, the synthesis of 2-formyl pyridine (35) could not be repeated by this method.

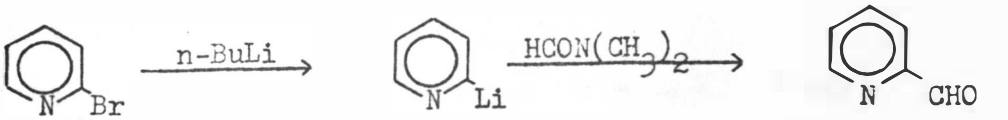

n-BuLi
-60°C
CuCl2/O2
Br
N
Li
n-BuLi
THF, -70°C
HCON(CH3)2
OHC
CHO

(33)

(32)


Br
N
4 steps
CHO

(34)


n-BuLi
HCON(CH3)2
N
Br
Li
CHO

(35)

EXPERIMENTAL

The work reported herein was done in residence at South Dakota State University, Brookings, South Dakota.

Description of Instrumentation Used:

Infrared spectra were obtained on a Perkin-Elmer Model 700 Infrared Spectrophotometer as potassium bromide wafers in the region from 650 to 4000 cm^{-1}.

Ultraviolet-Visible spectra were done on a Beckman DK-2A Spectrophotometer.

Nuclear magnetic resonance spectra were obtained on a 60 MHz Varian A-60A Spectrometer using tetramethylsilane (TMS) as an external standard.

The resistivities of all the complex salts were measured by EICO Model 555 volt ohm meter on pellets which were prepared by mechanical compaction of microcrystalline products at 20000 lbs. for half minute at room temperature. Pellets were placed between two copper plates which were connected to the two leads of the volt ohm meter.

Melting points of all compounds were measured with Fisher-Johns melting point apparatus.

Lithium tetracyanoquinodimethan (15)

The formation of $Li^+TCNQ^{\overline{\cdot}}$ salt was carried out in the same manner as employed by Melby et al.[87] To a boiling solution of 0.82 g (0.004 mole) of TCNQ in 80 ml of acetonitrile was added a boiling solution of 1.6 g (0.012 mole) of lithium iodide in 5 ml of acetonitrile. The mixture stood for 4 hours at room temperature. The purple solid was collected and washed on the filter with acetonitrile until the washings were bright green, and then washed with a large volume of ether, m.p. over 300°C.

Infrared absorption bands at 2200 cm^{-1}(C≡N stretching).

Yield = 0.79 g % Yield = 93.6%

Acridizinium perchlorate

The procedure used was the same as that used by Bradsher.[93,94] Pyridine-2-oxime (1.22 g) was mixed with 1.71 g of α-bromotoulene in 40 ml of acetone and allowed to stand at 50°C for 24 hours. At the end of this time, the precipitate was filtered and washed with ether, and then dissolved by warming gently in 10 ml of 48% hydrobromic acid, and transferred with the aid of 5 ml of 48% hydrobromic acid to a 25 ml flask equipped with a ground glass condenser. After 15 hours of refluxing under a nitrogen atmosphere, the solution was evaporated under reduced pressure until only 5 ml residue remained. This was dissolved in 30 ml of hot water (Norite), filtered and again concentrated under reduced pressure until a volume of approximately 10 ml remained. Ten ml of 3M perchloric acid were added to that solution. It gave light yellow prisms. The precipitate was recrystalized from methanol, m.p. 204-206°C (lit[94] 205-206°C)

Infrared absorption bands at 3120 cm^{-1} (C-H aromatic), 1660 (C=N stretch), 1100 (ClO_4^-), 920, 790, 750 (C-H bending). Ultraviolet absorption (95% ethanol) maxima (and log molar extinction coefficients) 240 nm(4.59), 360(3.91), 376(3.91), 396(3.82). lit[2] 242(4.68), 361(3.99), 379.5(4.01), 399(3.93).

Yield = 1.08 g % Yield = 36.6%

Acridizinium $(TCNQ)_2^{\cdot}$ (16)

To a boiling solution of 0.13 g (0.0005 mole) of acridizinium perchlorate in 10 ml acetronitrile was added a filtered boiling solution of 0.11 g (0.0005 mole) of $Li^+TCNQ^{\cdot}$ in 20 ml acetonitrile The mixture stood for 2 hours. The solution was evaporated under reduced pressure until precipitate formed. The dark green powder was collected. (254-255°C dec.) The yield was poor due to the low solubility of $Li^+TCNQ^{\cdot}$ in acetronitrile.

Ultraviolet absorption (CH_3CN) concentration: 0.55mg/250ml maxima (absorbance) 830 nm(0.25), 390(0.5).

UV. spectrum, page 58

Yield = 0.03 g % Yield = 10.4%

Acridizinium $(TCNQ)_{4.5}^{\cdot}$ (17)

To a boiling solution of 0.03 g (0.00005 mole) of acridizinium $(TCNQ)_2^{\cdot}$ in 30 ml acetonitrile was added a boiling solution of 0.016 g (0.000079 mole) of TCNQ in 5 ml acetonitrile. The mixture stood at room temperature and then cooled with ice-bath. The shiny, black, feather-like precipitate was collected and washed with cold acetronitrile, m.p. over 300°C.

Ultraviolet absorption (CH_3CN) concentration : 1.1mg/250ml, maxima (absorbance) 830 nm(0.15), 390(0.85).

UV. spectrum, page 59

Yield = 0.04 g % Yield = 72.7%

4a,8a-diazoniapentaphene bromide

The procedure used was the same as that used by Bradsher.[94,98] Pyridine-2-oxime (1.22 g, 0.01 mole) was mixed with 1.32 g (0.005 mole) α,α'-dibromo-p-xylene in 10 ml dimethylformamide and allowed to stand at 45°C for 16 hours. The solid mass of salt was broken up and washed thoroughly with acetone. This yielded 2.11 g white precipitate which was 1,4-bis(1-methylene-2-aldoxime pyridinium bromide) benzene. 1,4-bis(1-methylene-2-aldoxime pyridinium bromide) benzene (0.76 g, 0.0015 mole) was dissolved by warming gently in 20 ml of 48% hydrobromic acid. After 18 hours of refluxing under a nitrogen atmosphere, the solution was evaporated under reduced pressure until only 10 ml residue remained. This was dissolved in 20 ml of hot water, then cooled in ice-bath. The yellow-orange precipitate was collected and recrystalized from acidic water, m.p. over 300°C.

Ultraviolet absorption (H_2O) maxima (and log molar extinction coefficients) 293 nm(4.41), 337(4.67), 350(4.67), 360(4.50), 380(4.59), 418(3.75), 445(3.70). lit^3 2.97.5(4.35), 341(4.67), 354.5(4.68), 362(4.51), 384(4.59), 422(3.73), 447(3.72).

Yield = 0.44 g % Yield = 65.8%

The perchlorate

4a,8a-Diazoniapentaphene bromide (0.44 g) was dissolved in 10 ml of hot water and 8 ml 3.5M perchloric acid. Brown-orange precipitate 0.47g was collected, with gradual charring above 280°C.

Infrared absorption bands at 3090 cm^{-1}(aromatic C-H), 1640(C=N stretch), 1100(ClO_4^-), 900,770(C-H bending).

4a,8a-Diazoniapentaphene $(\mathrm{TCNQ})_2^{\bar{\cdot}}$ (18)

To a boiling solution of 0.098 g (0.0002 mole) of 4a,8a-diazoniapentaphene perchlorate in 25 ml acetonitrile was added a filtered boiling solution of 0.084 g (0.0004 mole) of $Li^+TCNQ^{\bar{\cdot}}$ in 15 ml absolute ethanol. The mixture stood for 2 hours. The black powder was collected and washed with acetronitrile, m.p. over 300°C.

Infrared absorption bands at 3050 cm^{-1}(C-H aromatic), 2200(C≡N stretching). Ultraviolet absorptions (CH_3CN) concentration : 0.75 mg/250 ml maxima (absorbance) 830 nm(0.21), 390(0.4), 350(0.16).

UV. spectrum, page 60

Yield = 0.12 g % Yield = 86.3%

4a,8a-Diazoniapentaphene $(\mathrm{TCNQ})_4^{\overline{\cdot}}$

To a boiling solution of 0.17 g (0.0008 mole) of $\mathrm{Li}^{+}\mathrm{TCNQ}^{\overline{\cdot}}$ in 35 ml absolute ethanol was added a boiling solution of 0.2 g (0.0004 mole) of 4a,8a-diazoniapentaphene bromide in 7 ml of water and a boiling solution of 0.17 g (0.0008 mole) of TCNQ in 40 ml of acetonitrile. The mixture stood for 2 hours. The black powder was collected and washed with acetonitrile, m.p. over 300°C.

Ultraviolet absorptions (CH_3CN) concentration : 900-600 nm 1.6 mg/250 ml, 600-300 nm 1.6 mg/500 ml maxima (absorbance) 830 nm(0.3), 390(0.74).

UV. spectrum, page 61

Yield = 0.34 g % Yield = 77.2%

4a,8a-Diazoniapentaphene $(\mathrm{TCNQ})_5^{\overline{\cdot}}$

To a filtered boiling solution of 0.11 g (0.000157 mole) of 4a,8a-diazoniapentaphene $(\mathrm{TCNQ})_2^{\overline{\cdot}}$ in 60 ml of acetonitrile was added a boiling solution of 0.065 g (0.000316 mole) of TCNQ in 20 ml acetonitrile. The mixture stood for 2 hours. The black glistening crystals were collected and washed with acetonitrile, m.p. over 300°C.

Ultraviolet absorptions (CH_3CN) concentration : 1.0 mg/250 ml maxima (absorbance) 830(0.2), 390(1.0).

UV. spectrum, page 62

Yield = 0.07 g % Yield = 51.1%

1,4-Bis(1-methylene pyridinium bromide) benzene (19)

The solution of 1.32 g (0.005 mole) of α, α'-dibromo-p-xylene and 0.79 g (0.01 mole) of pyridine in 30 ml acetone was stirred for 4 hours. The precipitate was collected and washed with acetone and recrystalized from methanol-absolute ethanol, m.p. 289-290°C.

Infrared absorption bands at 3025 cm^{-1}(aromatic C-H), 2970,2850(aliphatic C-H), 1630(C=N stretch).

Yield = 1.38 g % Yield = 65.4%

1,4-Bis(1-methylene pyridinium $(TCNQ)_2^{\overline{\cdot}}$) benzene (20)

To a filtered solution of 0.21 g (0.001 mole) $Li^+TCNQ^{\overline{\cdot}}$ in 50 ml of boiling acetonitrile was added a boiling solution of 0.21 g (0.0005 mole) of 1,4-bis(1-methylene pyridinium bromide) benzene in 30 ml absolute ethanol-methanol. The mixture stood for 2 hours at room temperature. The shiny, deep-purple needles were collected on a funnel and washed with acetonitrile, 253-255°C dec.

Infrared absorption bands at 3075 cm^{-1}(aromatic C-H), 2200(C≡N stretch). Ultraviolet absorption (CH_3CN) concentration : 2.4 mg/625 ml maxima (absorbance) 830 nm(0.1), 390(0.24).

UV. spectrum, page 63

Yield = 0.31 g % Yield = 92.5%

1,4-Bis(1-methylene pyridinium $(TCNQ)_4^{\overline{\cdot}}$) benzene (21)

To a boiling solution of 0.11 g (0.0005 mole) of TCNQ in acetonitrile was added a boiling solution of 0.17 g (0.0005 mole) of 1,4-bis(1-methylene pyridinium $(TCNQ)_2^{\overline{\cdot}}$) benzene in 40 ml acetonitrile. The mixture stood for 2 hours at room temperature. The black needles were collected and washed with acetonitrile, m.p. over 300°C.

Ultraviolet absorption (CH_3CN) concentration: 900-550 nm, 4.8 mg/625 ml, 550-300 nm, 9.6 mg/3125 ml, 830 nm(0.27), 390(0.48.

UV. spectrum, page 64

Yield = 0.21 g % Yield = 77.8%

4,4'-(2,2' - dimethyl) bipyridine

The procedure used was the same as that used by Smith.[108] Sodium 1 g (0.0434 mole) was allowed to react with about 85 ml. (excess) of completely dried and purified 2-picoline for 24 to 48 hours. The mixture was then slowly heated at 80°C under a reflux condenser for 10 to 16 hours. The flask was then removed and the condenser was replaced quickly by a dry cork stopper carrying an inlet tube for the introduction of oxygen and an outlet tube for release of pressure and the subsequent distillation of the excess of 2-picoline. The end of the oxidation was clearly indicated by the disappearance of the blue color which changed to reddish-brown. The temperature was now increased and the excess of 2-picoline was distilled and recovered in a condition ready for a new treatment with sodium.

In order to separate the dipyridyls, ether was added to the residue, lumps were broken up with a flattened rod, and finally 1.5 ml. of water was added in small portions. This caused the separation of resins on the bottom of the flask and left the ether clear to be poured off. Fresh ether was added to extract more material. The combined ether solutions were dried with potassium hydroxide, the ether was evaporated and the residue of mixed dipyridyls distilled; the fraction distilling from 190° - 230°C was collected. (at 3 mmHg.)

Infrared absorption bands 3070 cm^{-1}, 3030 (aromatic C-H), 2950, 2870 (aliphatic C-H), 1600,1480, 1440(C=C stretching).

Yield = 1.8 g % Yield = 44.9%

Poly(p-xylylene-2,2'-dimethyl-4,4'-dipyridinium bromide) (23)

0.62 g (0.034 mole) of 4,4'-(2,2'-dimethyl)bipyridine was mixed with 0.88 g (0.0034 mole) of α,α'-dibromo-p-xylene in 20 ml of acetone at 45°C for 24 hours. At the end of this period, the crude product was filtered and washed with ether, and then recrystalized from methanol-ethanol solution.

Infrared absorption bands 3050 (aromatic C-H), 2950,2880 (aliphatic C-H), 1640 (C=N stretching).

Yield = 0.15 g % Yield = 10%

Poly p-xylene-2,2'dimethyl-4,4'-dipyridinium (TCNQ)$_2^{\overline{\cdot}}$ (24)

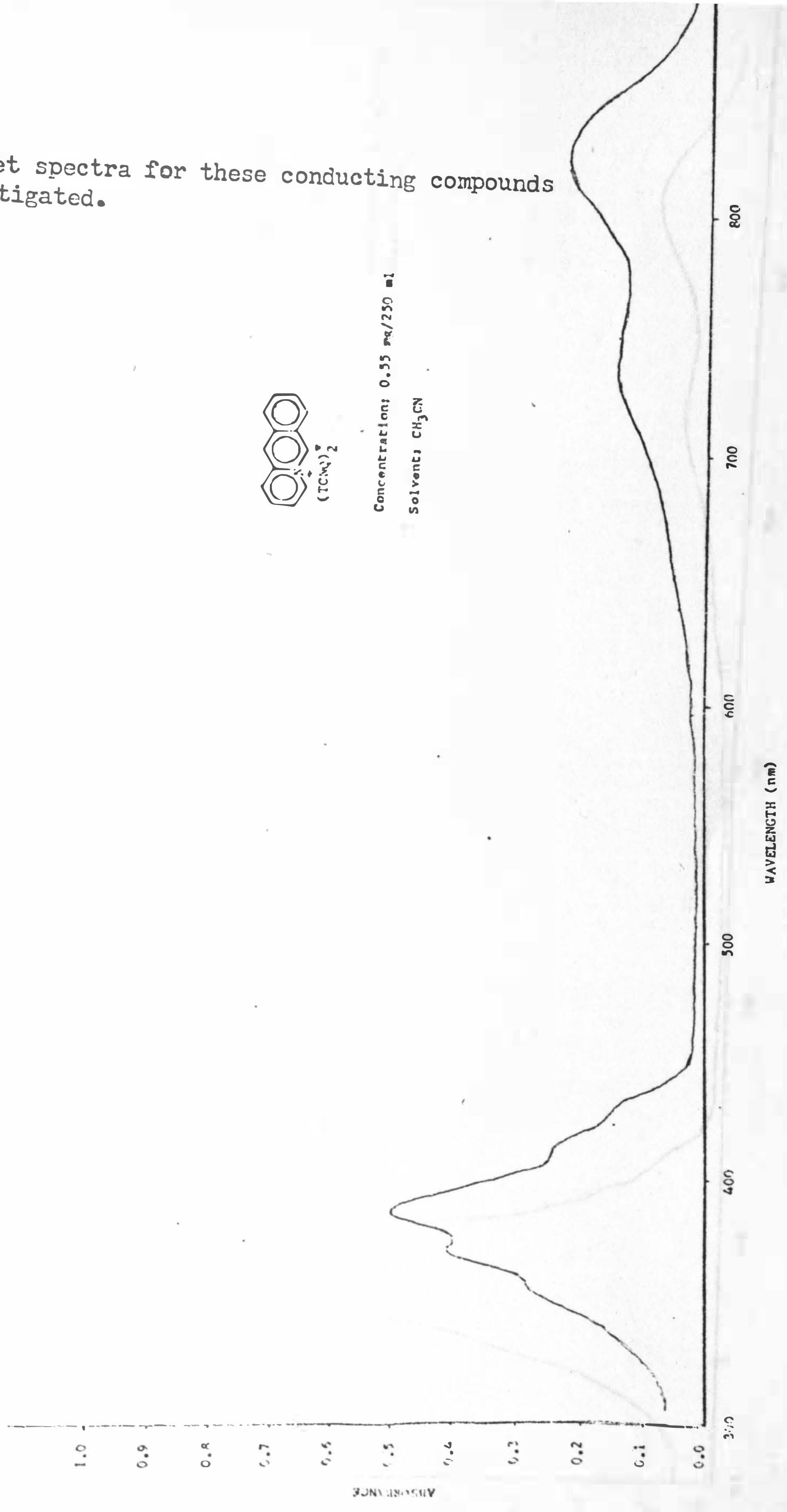
To a filtered solution of 0.006 g (0.000125 mole) of poly 1,4-bis(1-methylene 4,4'-(2,2'-dimethyl)bipyridinium bromide) benzene in 20 ml of ethanol-methanol was added a boiling solution of 0.05 g (0.00025 mole) of Li^{+}TCNQ$^{\overline{\cdot}}$ in 20 ml absolute ethanol. The mixture stood for 2 hours at room temperature. The blue green powder was collected on a funnel and washed with ice cold ethanol. This powder dissolved in 20 ml of acetonitrile, then was added to a boiling solution of 0.018 g (0.000094 mole) of TCNQ in 20 ml of acetonitrile. The mixture stood for 2 hours at room temperature. The solution was concentrated under reduced pressure until the precipitate formed. The black powder was collected.

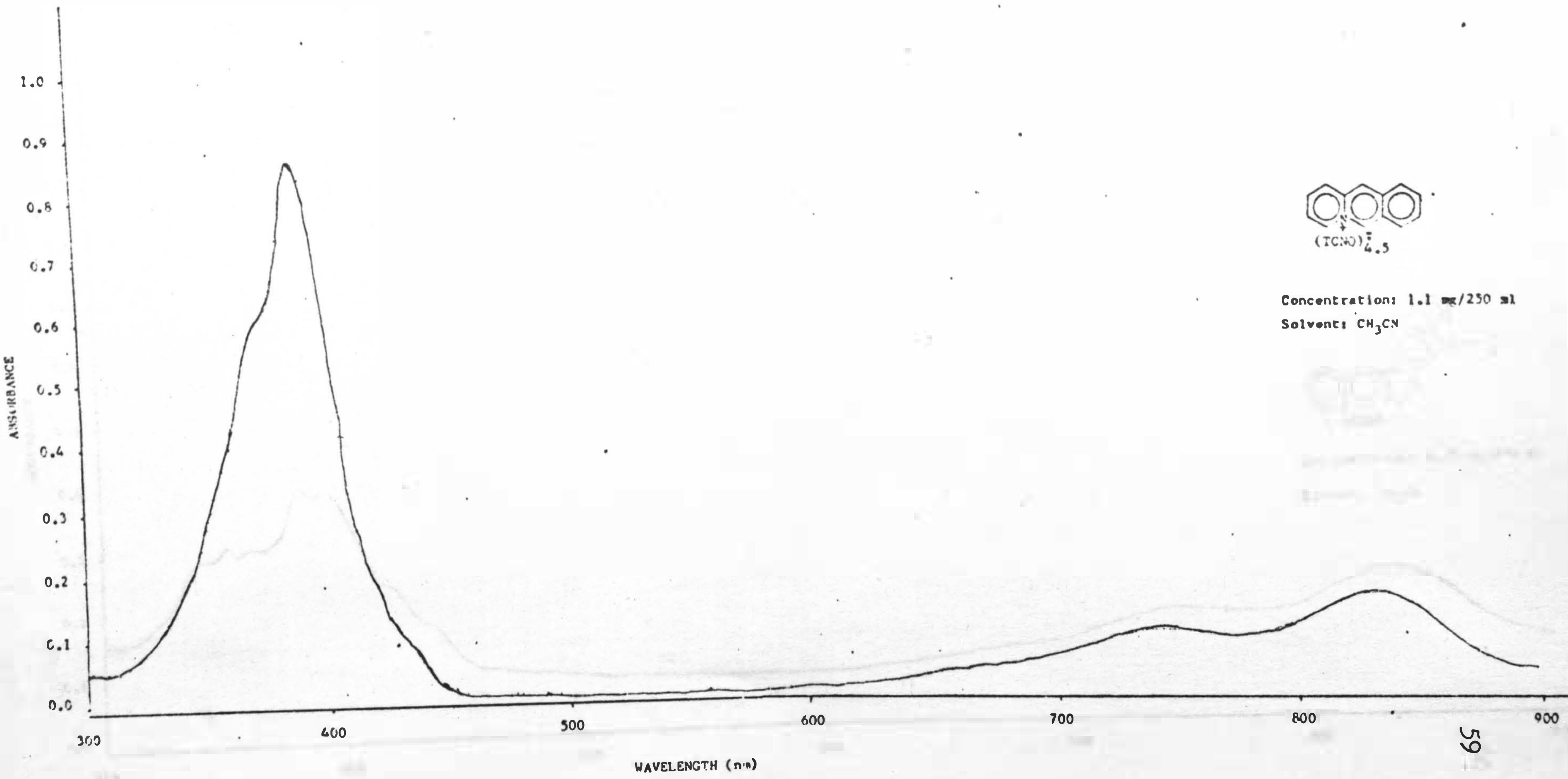
Infrared absorption bands 2200 broad (C≡N stretching), 1635 (C=N stretcing). Ultraviolet absorption (CH_3CN), concentration : 900-600 nm 0.2 mg/50 ml, 600-300 nm 0.2 mg/250 ml. Maxima (absorbance), 830(0.23), 390(0.41).

UV spectrum, page 65

Yield = 0.03 g % Yield = 18.2%

Ultraviolet spectra for these conducting compounds are investigated.



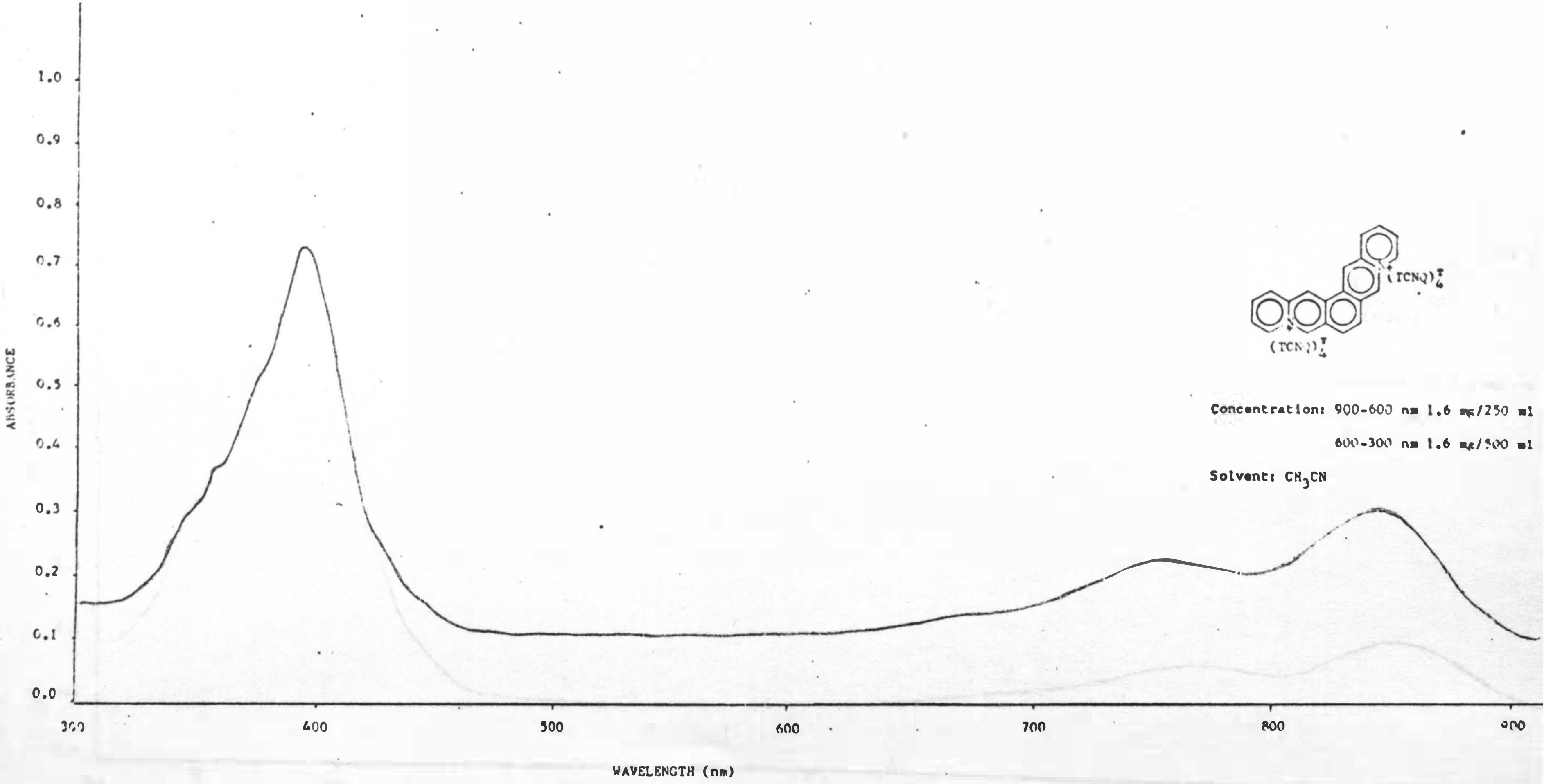


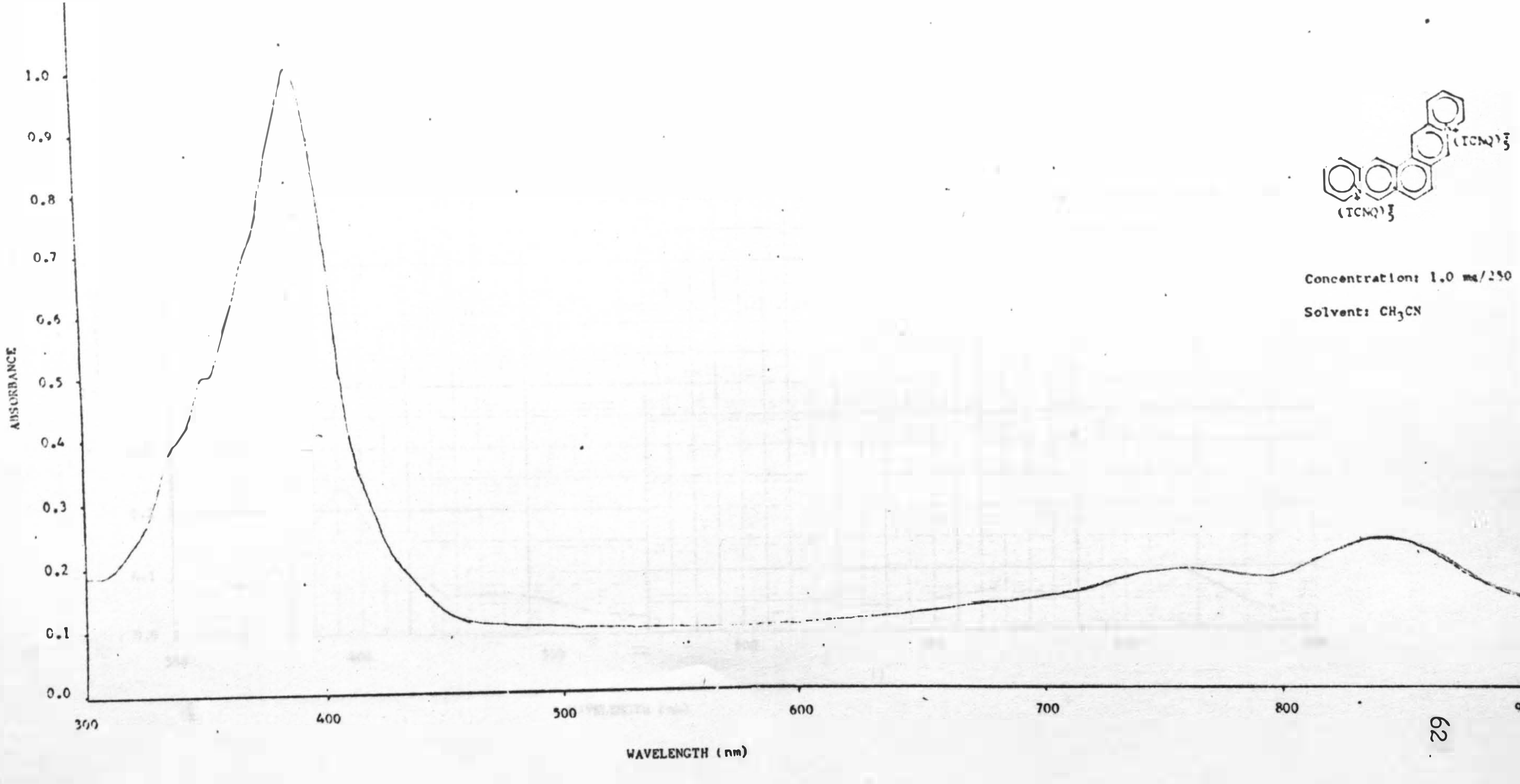
Concentration: 1.1 mg/250 ml

Solvent: CH_3CN

Concentration: 0.75 mg/250 ml

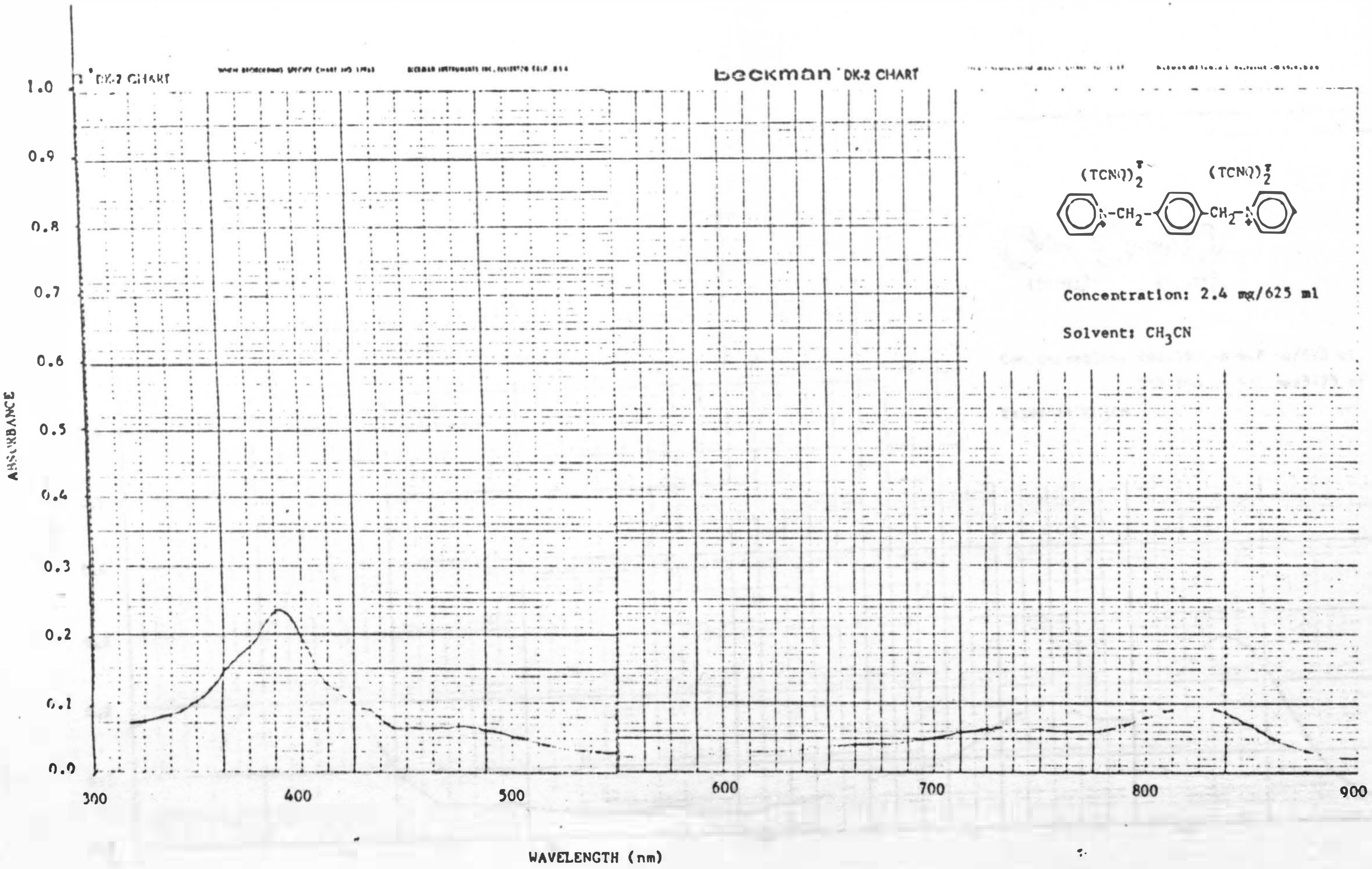
Solvent: CH_3CN


ABSORBANCE
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
300
400
500
600
700
800
900
WAVELENGTH (nm)
(TCNQ)$_4^{\mp}$
(TCNQ)$_4^{\mp}$
Concentration: 900-600 nm 1.6 mg/250 ml
600-300 nm 1.6 mg/500 ml
Solvent: CH$_3$CN



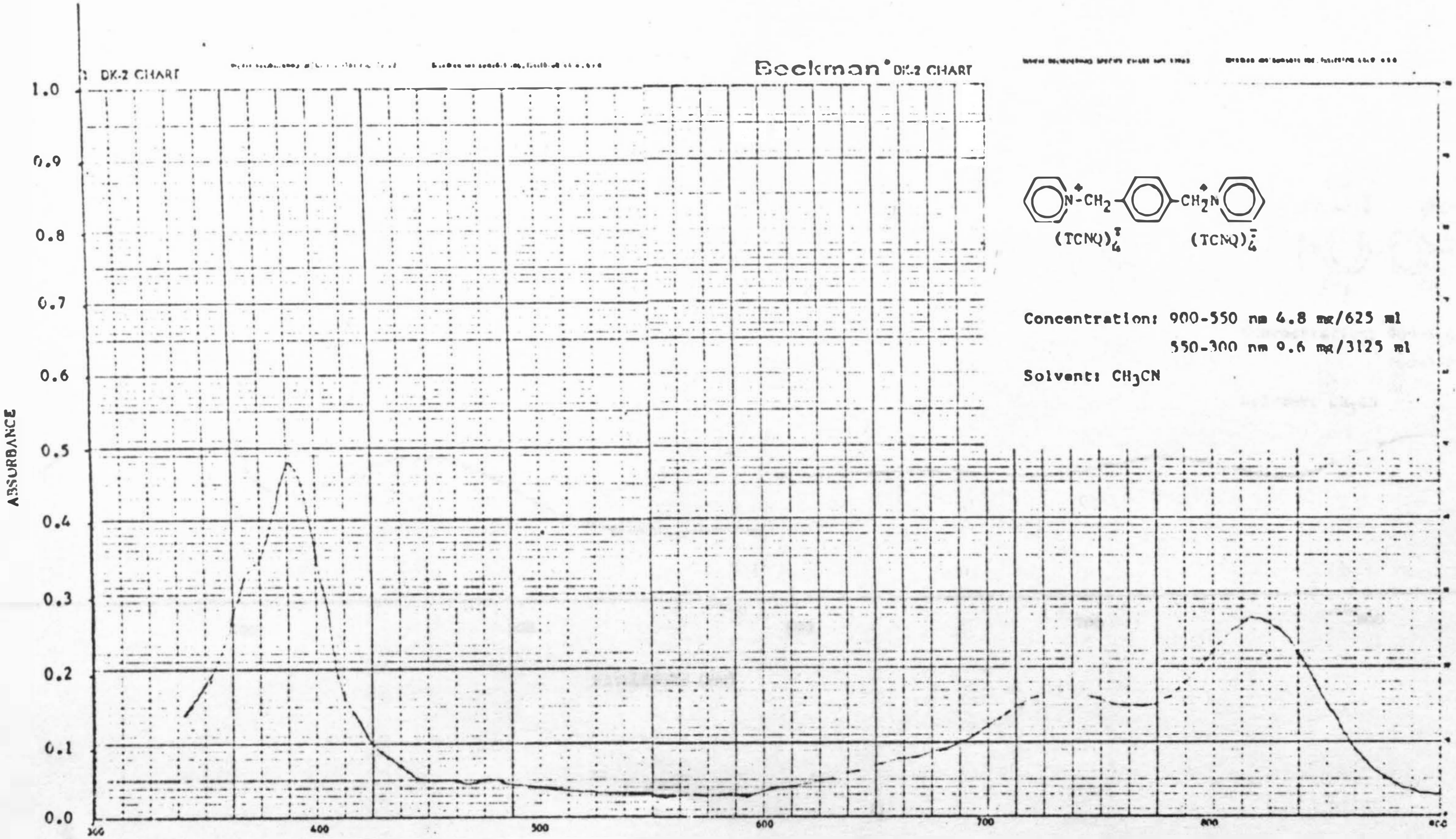
Concentration: 1.0 mg/250

Solvent: CH_3CN



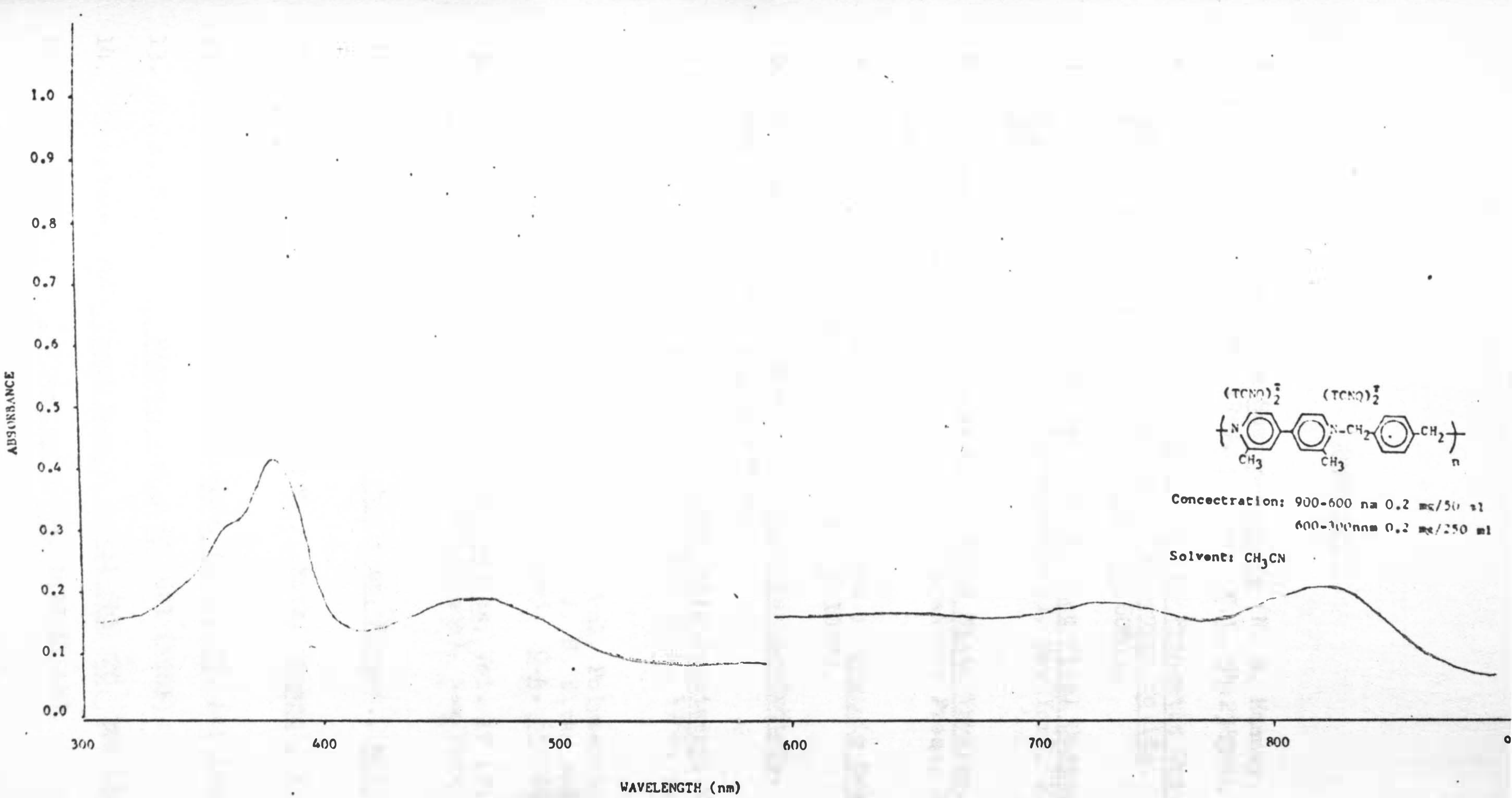
Concentration: 2.4 mg/625 ml

Solvent: CH_3CN



Concentration: 900-550 nm 4.8 mg/625 ml
550-300 nm 9.6 mg/3125 ml

Solvent: CH_3CN



ABSORBANCE
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
300
400
500
600
700
800
WAVELENGTH (nm)
$(TCNQ)_2^{\overline{\cdot}}$
$(TCNQ)_2^{\overline{\cdot}}$
N
N-CH2
CH2
CH3
CH3
n
Concectration: 900-600 nm 0.2 mg/50 ml
600-300nm 0.2 mg/250 ml
Solvent: CH3CN

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