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EXPLORATORY POLYMER SYNTHESIS

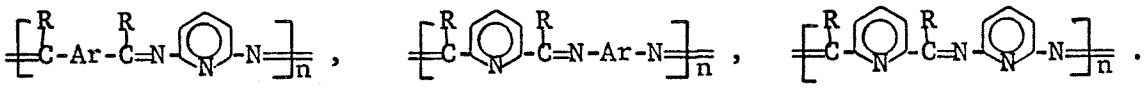
NASA GRANT NGL-004-001

I. Introduction.

This report summarizes the results of research under this grant for the period February 1, 1970 to April 30, 1970.

The research during this period was a continuation of the studies detailed in the Summary Yearly Report under the same grant for the period February 1, 1969 to January 31, 1970. The effort of this research is being directed to the synthesis of polymers of enhanced conductivity and to the exploration of the structural parameters which contribute to conductivity.

As the first approach to achieving this objective, polymeric azomethines which contain heterocyclic aromatic tertiary nitrogen atoms as part of the linear chain were selected as candidates. Typical polymers are the polyazomethines related to the Schiff bases in which the benzene rings are replaced by pyridine rings, for example,

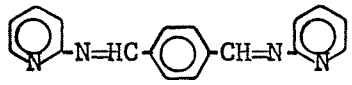


It is believed that these polymers (1) satisfy the requirements as donors in charge-transfer complexes, (2) can be quaternized permitting the attachment of short or long branches, including dipole dye molecules as branches, to the backbone, and (3) the quaternized ionic site can be complexed with acceptors to yield charge transfer complexes.

Since it is important that the parameters that contribute to conduction be understood, and since polymer molecules themselves are complex substances in which the causes for small or subtle changes in properties are difficult to establish, it was considered essential that prototype monomeric molecules, which are similar in structure to the repeating units in the polymer molecules,

be studied first and understood. For this reason the research was divided into two parts. The first part deals with the synthesis of monomers, and selected prototype reactions, which would be related essentially to the reactions contemplated with the polymers.

The second part of the problem deals with the synthesis of pyridine-type Schiff base polymers and of certain specific derivatives therefrom; the synthe sis will be based on chemistry established by prototype studies. Some preliminary studies on polymer synthesis were performed during early 1969, primarily to establish that the pyridine-type Schiff base polymers could be synthesized; the preliminary data confirmed that polymers of this type were feasible. Since then, no effort has been expended on the syntheses of polymers; all effort has been devoted to the study of the reactions of prototype molecules to assure the accuracy of the specific chemistry when it is applied to the pyridine-type Schiff-base polymers. This decision was necessitated by the fact, that the studies on the prototype molecules disclosed previously unknown chemistry for these substituted pyridines, and the type of chemistry encountered was in marked contrast with the chemistry that was expected on the basis of published pyridine chemistry. Substantial progress has been made on the chemistry and understanding of the prototype reactions and reported in the previous yearly summary report. Exploratory experiments had shown that the prototype monomer, p-xylylidene-2-aminopyridine,



DSB

would undergo the type of reactions contemplated for the polymers, namely, that under certain conditions, it can be quaternized with dimethylsulfate and that it would form charge-transfer complexes. The monomer, DSB, is a di-Schiff base of the pyridine type having two pyridine nuclei in its structure and is a highly conjugated prototype molecule. It offers two tertiary nitrogen sites

for derivative formation. Such derivative formation is interesting and important only if it results in an increase in the conductivity of the molecules. Accordingly, a number of derivatives of DSB were prepared and their conductivities at room temperature measured and compared with DSB. This quaterly report covers the synthesis and conductivity measurements of DSB and some of its derivatives.

II. Experimental.

A. p-Xylylidene-2-aminopyridine (DSB).

This monomer was prepared by the procedure previously reported in the Yearly Summary Report.

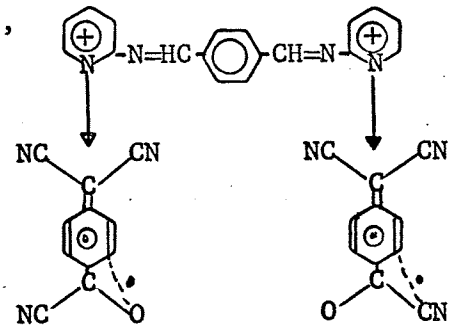
Into a 1000-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed terephthaldehyde (4.82 g, 36.6 mmoles), 2-aminopyridine (6.84 g, 73.2 mmoles), and 450 ml dry toluene. The reaction mixture was heated to reflux and after twenty-four hours a quantitative yield of water was collected. Evaporation of solvent yielded yellow crystals. Recrystallization from toluene yielded p-xylylidene-di-2-aminopyridine, 9.3 g (90%), mp 208°C. Infrared spectrum (KBr disc) was similar to that previously reported.

B. Charge Transfer Complexes Derived from DSB and Tetracyanoquinodimethan (TCNQ).

1. Charge Transfer Complex (DSB.2 TCNQ) in C_2H_5OH.

To a boiling solution of DSB (0.286 g, 1 mmole) in 15 ml of absolute ethanol in a 100 ml three-neck, round-bottom flask equipped with a reflux condenser, a thermometer and stirrer, under a nitrogen atmosphere was added a hot solution of TCNQ (0.408 g, 2 mmoles), in 40 ml of absolute ethanol. The initial color of the reaction mixture was light-green. Then the reaction mixture was heated at 78°C under reflux for seven hours and allowed to stand at room temperature for sixteen hours. After about one-half hour of reaction time,

the color of the reaction mixture changed from green to brown, and all of TCNQ was dissolved in the solvent. At the end of the reaction, the reaction product was soluble in ethanol and the color of the solution was dark-brown. The reaction solution was evaporated to dryness at 0.5 mm Hg pressure and dried at 40°C in a vacuum oven to constant weight for twenty-four hours, yielding a black powder 0.782 g (yield 113%). A portion of this product, 0.500 g, was dissolved in 10 ml of absolute ethanol and precipitated with 100 ml of n-hexane and washed with fresh n-hexane. The precipitated product was recovered by filtration and dried at 40°C in a vacuum oven to constant weight for twenty-four hours, yielding a black powder 0.240 g (yield 48%), m.p. 180-183°C. Its infrared spectrum was identical to the complex previously reported in the Yearly Summary Report, pp 37-38 and Appendix 16, and considered as having the structure, $C_{40}H_{22}N_{10}O_2$,



The specific resistance of this product was measured.

2. Charge Transfer Complex (DSB.2 TCNQ) in CH_3CN.

To a boiling solution of Schiff base (0.143 g, 0.5 mmole) in 20 ml of acetonitrile, in a 100 ml, three-neck, round-bottom flask equipped with a reflux condenser, stirrer and a thermometer, etc., was added a hot solution of TCNQ (0.204 g, 1 mmole) in 25 ml of acetonitrile under a nitrogen atmosphere.

The reaction mixture was heated at 81°C under reflux for five hours; then it was allowed to cool to room temperature and to stand for sixteen hours. Some product precipitated out from the solution.

The color of the initial reaction solution was light-green, but as the reaction proceeded the color deepened and became dark-green. The precipitated product was recovered by filtration, washed with acetonitrile, and dried at 40°C in a vacuum oven to constant weight for twenty-four hours, yielding a dark-green solid, 0.042 g (mp 183~185°C). The filtered dark-green solution was evaporated to dryness at 0.5 mm Hg pressure and dried at 40°C in a vacuum oven to constant weight for twenty-four hours, yielding a dark-green solid, 0.296 g (mp 183-185°C). The material balance was very good.

Infrared spectrum (KBr disc): 2160 (CN broad), 1660, 1580~1560 (broad), 1330, 1150, 830 and 760 cm^{-1}. The infrared spectra of the evaporated and precipitated product were identical and indicated a very broad absorption band for CN groups at 2160 cm^{-1}.

Analysis: Calc'd for $C_{42}H_{22}N_{12}$:

C, 72.62; H, 3.17; N, 24.21.

Found: C, 71.65; H, 4.35; N, 23.14; O < 1.

The elemental analysis of the precipitated product corresponded to a chemical composition of the formula $C_{43.4}H_{31.6}N_{12}O_{0.4}$ against the expected $C_{42}H_{22}N_{12}$. Also its elemental analysis indicated that oxygen content in the complex was less than 1%, and the complex was only partially and slightly oxidized, while the (DSB . 2 TCNQ) prepared in ethanol contained much oxygen, more than 4%.

The ultraviolet spectrum of the complex in acetonitrile showed a very strong absorption band at 392 mμ, but did not give any absorption band at 480 mμ. The 0.296 g of evaporated product was recrystallized from acetonitrile, dried in vacuum, as Complex B.

The electric conductivity of the recrystallized product was measured at room temperature (ca. 25°C) and at 0°C.

3. Charge Transfer Complex (DSB.4 TCNQ) in CH_3CN.

The procedure previously reported in the Yearly Summary Report was used.

A mixture of 0.408 g (2 mmoles) in 25 ml of acetonitrile and 0.143 g (0.5 mmole) of DSB in 15 ml of absolute ethanol was refluxed at 74°C for five hours, and then allowed to stand at room temperature for seventeen hours.

The initial color of the reaction solution was light-green, and as the reaction continued, the color darkened, becoming dark-brown after two hours. The reaction product was soluble in the mixture of ethanol and acetonitrile. The solvent was removed from the reaction mixture by evaporation at 0.5 mm Hg pressure to yield a black powder which dried to constant weight in a vacuum oven at 40°C for twenty-four hours, affording a black solid, 0.624 g.

The product was reprecipitated from ethanol solution with n-heptane, washed with n-haptane and dried at 40°C in a vacuum oven to constant weight, yielding a dark-purple powder (46%), m.p. 181-183°C. Its infrared spectrum (KBr disc): 2180 (CN), 1665 (CO), 1570, 1500, 1350, 1175, 835 and 760 cm^{-1}, was similar to that previously reported and the product showed a very sharp absorption band for CN groups at 2180 cm^{-1}. Its spectrum was identical also to the spectrum of the DSB.2 TCNQ complex. The structure of the complex appears to be the same as that assigned to the 1:2 complex (A) prepared in ethanol.

C. Charge Transfer Complex Derived from Di-N-Methyl-(p-Xylylidene-di-2-aminopyridinium)-Methyl Sulfate (DMPS), and Lithium Tetracyanoquinodimethane, Li.TCNQ.

1. Quaternization of p-Xylylidene-di-2-aminopyridine (DSB) with Dimethylsulfate.

Into a 25-ml, three-neck, round-bottom flask equipped with a reflux condenser, and a thermometer were placed DSB (1.50 g, 4.25 mmoles), dimethylsulfate (1.32 g, 10.5 mmoles), and 30 ml of nitromethane. The reaction mixture was heated under a nitrogen atmosphere at 50°C for one and one-half hours. Evaporation of the solvent yielded 3.24 g of an orange solid.

The product was redissolved in CH_3NO_2 and reprecipitated by the addition of benzene, washed with ether, and dried in vacuum to give the product, DMPS,

mp 66-67°C. Its infrared spectrum (KBr disc): 1660, 1640, 1585, 1230, 1060, 1000 and 760 cm^{-1} was identical to that previously reported in the Yearly Summary Report.

2. Charge Transfer Complex [DMPS.$Li^{+}(TCNQ^{\cdot-})$].

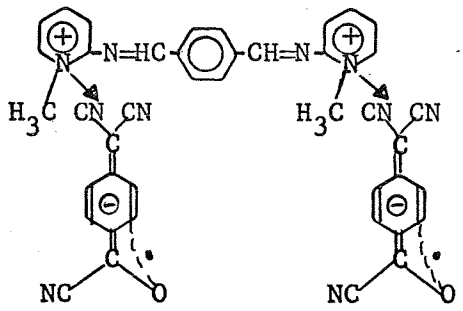
This charge transfer complex was prepared following the procedure previously reported in the Yearly Summary Report.

To a solution at 60°C of DMPS(0.300 g, 0.5 mmole) in 15 ml of absolute ethanol in a 100 ml of 0.5 mmole) in 15 ml of absolute ethanol in a 100-ml three-neck, round-bottom flask equipped with a reflux condenser, a thermometer and stirrer, under a nitrogen atmosphere, was added a boiling solution of $Li^{+}(TCNQ^{\cdot-})$ (0.211 g, 1 mmole) in 15 ml of ethanol. The reaction mixture was maintained at 78°C under reflux for ten minutes. The initial color of the reaction mixture was light-green, but as the reaction proceeded, the color deepened to dark-green. Then the reaction mixture was maintained with stirring at 50°C for five hours and allowed to stand at room temperature for seventeen hours, forming a small amount of precipitate.

The solution was filtered to remove the precipitated product, 0.022 g (4.3%). The filtered solution was then evaporated to dryness at 0.5 mm Hg pressure and dried at 40°C in a vacuum oven to constant weight, yielding a black powder, 0.514 g. The material balance was very good.

A portion of the evaporated product, 0.416 g, was washed eight times with 10 ml of ice-water to dissolve out $Li^{+}CH_3SO_4^{-}$ from the mixture, and dried at 40°C in a vacuum oven to constant weight for twenty hours over phosphorus pentoxide, yielding a dark-green powder, 0.264 g, Complex D.

Its infrared spectrum is substantially identical to that previously reported as Appendix 22 in the Yearly Summary Report and for which, on the basis of analysis, was assigned the structure based on oxidized TCNQ,



D. Formation of the Charge Transfer Complex Derived from Di-N-Methyl-(p-xylylidene-di-2-aminopyridinium)-Methyl Sulfate (DMPS) and Lithium Tetracyanoquinodimethane and Tetracyanoquinodimethan.

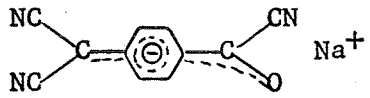
1. Charge Transfer Complex [DMPS.2 $Li^+(TCNQ^{\cdot-})$.2 TCNQ].

To a refluxing solution of the di-quaternized Schiff base (DMPS) (0.300 g, 0.5 mmole) in 15 ml of absolute ethanol, in a 100-ml three-neck, round-bottom flask equipped with a reflux condenser, a thermometer and a stirrer, under a nitrogen atmosphere, was added a boiling solution of $Li^+(TCNQ^{\cdot-})$ (0.211 g, 1 mmole) and neutral TCNQ (0.204 g, 1 mmole) in 25 ml of acetonitrile. The color of the reaction mixture was dark-green. The reaction mixture was heated at 73°C under reflux for one hour, followed by four hours at 50°C, and then allowed to stand at room temperature for sixteen hours. The reaction solution was filtered to remove a small amount of precipitated product, 0.172 g. The filtrate was evaporated to dryness at 40°C under vacuum and dried at 40°C in a vacuum oven to constant weight for twenty-four hours; 0.555 g of evaporated product was obtained. The color of the product was dark-green. The material balance was very good. A portion of the evaporated product, 0.400 g, was washed ten times, each time with 10 ml of ice-water to remove $Li^+CH_3SO_4^-$ from the mixture and dried at 40°C in a vacuum oven to constant weight, yielding a dark-green powder, 0.268 g. The washing was evaporated to dryness and dried at 40°C in a vacuum oven to constant weight, yielding a brown water-soluble solid, 0.102 g, Complex E.

Its infrared spectrum was identical to that previously reported in the

Yearly Summary Report. Its resistance was measured at 25°C

E. Preparation of Sodium Salt of α,α'-Dicyano-p-toluoyl Cyanide, (TCNQO). [JACS, 84, 3392 (1962)].



The procedure given in JACS, 84, 3392 (1962) was used for this synthesis. A solution of 2.000 g of tetracyanoquinodimethan in 500 ml of acetone was added to a solution of 1.400 g of sodium nitrite in 50 ml of water at room temperature. The resulting deep-orange solution was evaporated to dryness at 0.5 mm Hg pressure at room temperature. The dried solid was then treated with 150 ml of acetone, which dissolved the orange compound and left behind an inorganic colorless salt. The acetone solution was evaporated to dryness and the residue extracted with acetone as before. The resulting acetone solution (50 ml) was treated with an excess of methylene chloride (150 ml) and filtered to give 1.455 g of the orange-red sodium salt of α,α'-dicyano-p-toluoyl cyanide (yield 68%).

Infrared spectrum (KBr disc): 2200, 2160 (CN), 1645, 1590~1560 (broad), 1510, 1450, 1350, 1290, 1230, 1180, 835 (strong) and 750 (sharp) cm^{-1}. The infrared spectrum of the product indicated many absorption bands and was very different from one of TCNQ. The infrared spectrum showed absorption bands at 2160 and 2200 (CN), 1645 (carbonyl), 1590 (conjugated cyano-substituted double bond) and 835 cm^{-1} (1,4-di-substituted benzene).

The ultraviolet spectrum of the product showed a very deep absorption band at 480 m (in acetonitrile); 1.157 g of acetone-insoluble inorganic salt was recovered.

F. Formation of the Charge Transfer Complex Derived from Di-N-Methyl-(p-xylylidene-di-2-aminopyridinium)-Methyl Sulfate (DMPS) and Sodium Salt of α,α'-Dicyano-p-Toluoyl Cyanide (TCNQO).

1. Charge Transfer Complex [DMPS.2 $TCNQO^{\cdot-}$].

To a hot solution of di-quaternized Schiff base (0.300 g, 0.5 mmole) in 15 ml of ethanol, in a 100-ml three-neck, round-bottom flask equipped with a reflux condenser, a thermometer and a stirrer, under a nitrogen atmosphere was added a hot solution of sodium salt of α,α'-di-cyano-p-toluoyl cyanide (0.217 g, 1 mmole) in 15 ml of ethanol. The color of the reaction mixture was red. The reaction mixture was maintained at 78°C for one hour, followed by four hours at 50°C, and then allowed to stand at room temperature for twenty hours. Most of the reaction product was soluble in ethanol. The reaction solution was filtered to remove a small amount of the precipitated product, 0.018 g. Then the filtrate was evaporated to dryness at 0.5 mm Hg pressure and dried at 40°C in a vacuum oven to constant weight over phosphorus pentoxide for twenty-two hours, yielding a red powder, 0.480 g. The material balance was good. This red product was partially soluble in water.

To remove $Na^+CH_3SO_4^-$ from the product, the product was dissolved in acetonitrile and filtered; 0.053 g of insoluble product was collected on a filter. The filtrate was evaporated to dryness at 0.5 mm Hg pressure and dried in a vacuum oven for twenty-four hours, yielding a red powder, 0.358 g, Complex F. This product melted at 63~65°C, was very hydroscopic and sticky; it was not possible to mold a disc from this product.

Infrared spectrum (KBr disc): 2180, 2140 (CN), 1670 (CO), 1590, 1570, 1500, 1450, 1175, 1100, 1000, 840 and 770 cm^{-1}. The infrared spectrum of this product indicated two strong absorption bands for CN groups at 2180 and 2140 cm^{-1}. The broad absorption band for SO_3H groups at 1250~1200 cm^{-1} disappeared.

G. Formation of the Charge Transfer Complex Derived from Di-N-Methyl-(p-xylylidene-di-2-aminopyridinium)-Methyl Sulfate (DMPS) and Sodium Salt of α,α'-Dicyano-p-toluoyl Cyanide (TCNQO) and Tetracyanoquinodimethan (TCNQ).

1. Charge Transfer Complex [I.2 $TCNQO^{\cdot-}$.2 TCNQ].

To a hot solution of di-quaternized Schiff base (0.300 g, 0.5 mmole) in

15 ml of absolute ethanol was added a boiling solution of sodium salt of α,α'-dicyano-p-toluoyl cyanide (0.217 g, 1.0 mmole) and TCNQ (0.204 g, 1.0 mmole) in 25 ml of acetonitrile, in a 100 ml three-neck, round bottom flask equipped with a reflux condenser, a thermometer and a stirrer, etc., under a nitrogen atmosphere. The reaction mixture was heated at 73°C under reflux for five hours atd then allowed to stand at room temperature for sixty-five hours. The color of the reaction mixture was deep-orange. Then the reaction was filtered to remove an insoluble product from solution. The insoluble product was washed with acetonitrile and dried at 40°C in a vacuum oven to constant weight for twenty-two hours, yielding a purple powder, 0.079 g. The deep-red filtrate was evaporated to dryness at 0.5 mm Hg pressure and dried at 40°C in a vacuum oven to constant weight for twenty-two hours, yielding a deep-red powder, 0.673 g. The total yield was 104% and the material balance was very good. A portion of the evaporated product, 0.400 g, was washed nine times each time with 10 ml of ice-water, to dissolve out $Na^+CH_3SO_4^-$ from the mixture and then dried at 40°C in a vacuum oven over phosphorus pentoxide to constant weight for seventeen hours, yielding a deep-red powder, 0.282 g (mp 100~105°C), Complex G.

Infrared spectrum (KBr disc) of evaporated and washed product: 2190, 2160 (CN), 1710, 1630, 1570, 1500, 1350, 1180, 1010, 840 and 770 cm^{-1}. The infrared spectrum of this product indicated two strong absorption bands for CN groups at 2190 and 2160 cm^{-1}, and did not give a broad absorption band for SO_3H group at 1250~1200 cm^{-1}.

The infrared spectrum of the insoluble purple product was identical to one of $TCNQ^{\cdot-}$ anion radical. This insoluble product was identified as $Na^+TCNQ^{\cdot-}$, which formed by an electron exchange reaction between neutral TCNQ and the sodium salt of α,α'-di-cyano-p-toluoyl cyanide.

The electric conductivity of this complex was measured at 25°C.

H. Measurements of Electrical Conductivities.

One hundred fifty mg of each sample was pressed as a pellet in a KBr disc die at room temperature at a gauge pressure of 2500 lb/sq inch for five minutes to make a sample disc. The conductivities of these discs were measured at room temperature using Keithley Instruments 240A High Voltage Supply and 610C Electrometer. The area of these discs was 1.327 cm^2. The specific resistance, at room temperature, was calculated by use of the following equation:

$$\rho = R \cdot \frac{S}{\ell} = \frac{E}{I} \cdot \frac{S}{\ell} = \text{ohm-cm}$$

E = applied voltage (v)

S = area of disc (1.327 cm^2)

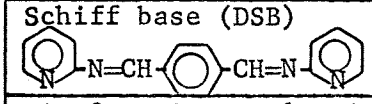
I = current (amp)

ℓ = thickness (cm)

The resistivities of TCNQ and of p-xylylidene-di-2-aminopyridine, pelletized and measured under identical conditions, were used as reference points to determine whether or not derivative formation produced an increase in conductivity. The data are summarized in Table 1.

Table 1

Electric Resistance of the Charge Transfer Complexes at 25°C

Compound	Thick-ness (mm)	Applied Voltage (v)	Current (amp)	Specific Resistance (Ω-cm)
Tetracyanoquinodimethan (TCNQ)	1.0	51	$1x10^{-6}$	$6.8x10^{8}$
Schiff base (DSB) 	1.0	510	$0.7x10^{-10}$	$9.7x10^{13}$
DSB.2 TCNQ; Complex A (prepared in ethanol)	1.1	15	$1x10^{-5}$	$1.8x10^{7}$
DSB. 2 TCNQ; Complex B (prepared in MeCN)	0.7	2	$0.65x10^{-2}$	$5.83x10^{3}$
DSB.4 TCNQ; Complex C (prepared in ethanol)	1.1	54	$1x10^{-3}$	$6.5x10^{5}$
Quaternized Schiff Base, DMPS. 2 $Li^{+}(TCNQ^{\cdot-})$; Complex D	1.1	54	$1x10^{-7}$	$6.5x10^{9}$
Quaternized Schiff Base, DMPS. 2 $Li^{+}(TCNQ^{\cdot-})$. 2 TCNQ; Complex E	1.0	38	$1x10^{-2}$	$5x10^{4}$
Quaternized Schiff Base, DMPS. 2 $Li^{+}(TCNQO^{\cdot-})$; Complex F*	0.33	40	$1x10^{-4}$	$1.6x10^{7}$
Quaternized Schiff Base, DMPS. 2 $TCNQO^{\cdot-}$. 2 TCNQ; Complex G	1.0	38	$1x10^{-3}$	$5x10^{5}$

* This sample was measured by pressing sample between plates of conductivity cell.

The data of Table 1 show that the Schiff base, DSB, is an excellent insulator having a specific resistance of almost $1x10^{14}$ ohm-cm, and that TCNQ is also a good insulator with a specific resistance approaching $1x10^{9}$.

Complex A, prepared in ethanol from DSB and TCNQ, showed a much lower resistance of $2x10^{7}$ which is 100 times lower than TCNQ; however, the product was shown to have been partially oxidized, most probably by reaction with ethanol and air and apparently the $TCNQO^{\cdot-}$ anion radical that results contributes less to conductivity than does the $TCNQ^{\cdot-}$ anion radical, but it does cause a drop in the resistance. This type of oxidation is retarded and substantially eliminated when the complex is formed in acetonitrile, as for example, Complex B. The resistivity of Complex B prepared from DSB and TCNQ in CH_3CN was found to be $5.83x10^{3}$, which is the order of magnitude found in semi-conductors; compared to $6.8x10^{8}$ for the TCNQ, this value corresponding to an improvement in conduc-

tivity of 10^5 over TCNQ and 10^{10} over the di-Schiff base, DSB. Yet, when an excess of TCNQ is complexed with DSB, in the presence of ethanol, even though oxidation of the TCNQ to TCNQO occurs, an improvement in conductivity is observed with a specific resistance, as in Complex C, of $6x10^5$, which is 10^2 higher than Complex B prepared in CH_3CN but in the absence of excess neutral TCNQ.

The conductivity of Complex D prepared by the reaction of quaternized di-Schiff base, DMPS and Li(TCNQ$^{\cdot}$) in the absence of excess TCNQ was $6.5x10^9$ and lies closer to the $6.8x10^8$ value for TCNQ than to the $9.7x10^{13}$ value for the DSB. In contrast, when the same reaction was performed with the addition of neutral TCNQ as in Complex E, a marked improvement was observed with a value for the resistance of $5x10^4$ ohm-cm.

The related Complex F, prepared by the reaction of DMPS and Li(TCNQO$^{\cdot}$) showed resistance of $1.6x10^7$ compared to $6.5x10^9$ for its unoxidized analogue, Complex D, and may be considered as comparable. However, when the reaction with Li(TCNQ$^{\cdot}$) was performed in the presence of added neutral TCNQ, as in Complex G, the conductivity increased and the specific resistance dropped to a value of $5x10^5$ compared to its analogue, Complex E, of $5x10^4$.

It is recognized that the measurement of the conductivity of pressed powders depends on many factors and due to the limitations of the available equipment, the pressures used in preparing the discs for conductivity measurements were probably not high enough, since, after pressing some increase in the thickness of the discs was observed on standing. The resistance measurements of all discs were made immediately after pressing and under comparable conditions. Nonetheless, the trend in the changes of conductivity is considered significant; the value of $5.8x10^3$ for the Complex of DSB and TCNQ prepared in acetonitrile in the absence of excess TCNQ were surprising.

It also appears to be significant that $TCNQO^{\cdot}$ as an ion radical can be substituted for the TCNQ ion radical as in Complexes F and D, to give conductivity value within an order of one, and that when neutral TCNQ is added to either of these systems, a marked improvement in conductivity occurs. The technical literature on the use of TCNQO, alone or in the presence of TCNQ, on the formation of conductive monomeric or polymeric molecules appears to be non-existent.

It is postulated that on the basis of the prototype studies, the complexes of the poly-pyridine-type Schiff bases will show much higher conductivities than the parent polymers.

Acknowledgment. The contribution of the conductivity cell by Professor Allan Hermann, Physics Department, Tulane University, New Orleans, Louisiana is acknowledged and gratefully appreciated.