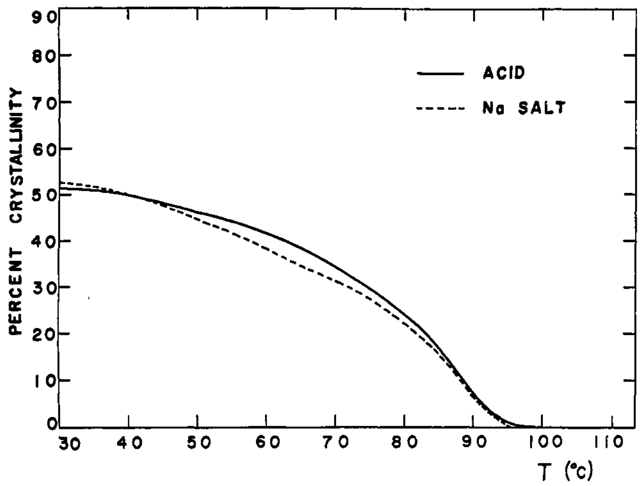


Figure 10. The weight-fraction crystallinity as measured by the differential scanning calorimeter as a function of temperature for the un-ionized copolymer acid and the 55% ionized sodium salt. A crystalline heat of fusion of 33.6 cal/g for branched polyethylene is assumed.

below the softening temperature and that the softening of the ionized regions also leads to an increase in the orientation of the hydrocarbon regions implies a parallel connection between the two.

Microscopic observations and low-angle light-scattering (LALS) studies of the annealed un-ionized acid demonstrate that the structure is spherulitic, probably being composed of chain-folded lamellae.[17] The spherulitic order is almost as good as that in a branched low-density polyethylene. Also, degrees of crystallinity of the annealed acid by X-ray diffraction are of the order of 0.50, again comparable with branched polyethylene. Degrees of crystallinity and spherulitic order of the acid are appreciably decreased for samples quenched from the melt—much more so than for polyethylene itself.

It is apparent that a bulky methacrylic acid group cannot be accommodated within a polyethylene crystal lattice. Thus, if high degrees of crystallinity and spherulitic order can persist for samples containing 4 mol % methacrylic acid, it is likely that the acid groups occur on the irregular fold surface of the ethylene lamellae. For rapidly crystallized samples, there is insufficient time for the chains to arrange themselves so as to allow these groups to occur on lamellae surfaces, so the degree of crystallinity and spherulitic order is suppressed.

While spherulites are not observed for the salt, degrees of crystallinity of the annealed samples as shown in Figure 10 approach those of the un-ionized acid. Also, light-scattering patterns indicate the presence of rod-like aggregates of crystals which may be identified with lamellae.[17] Thus, it seems likely that the ionized regions may occur on lamellae surfaces. This suggests a sandwich type of structure in which the ionized domains may occur between crystalline lamellae. This model would seem consistent with the postulated parallel connectivity between the regions. While the domains may contain some hydrocarbon groups associated with the carboxylate groups, the high crystallizability and spherulitic order suggest that most of the hydrocarbon residues exist outside of the domain in the crystallizable regions. Indeed, there seems to be a competition for the hydrocarbon between the domains and the crystals.

We believe that these infrared studies confirm that the α loss maximum observed for the ionized copolymer is associated with a process which permits greater orientation of amorphous regions of the polymer to take place. The identification of this process with a softening temperature of ionic domains is consistent with this postulate.

(17) R. Prud'homme and R. S. Stein, *J. Polym. Sci.*, in press.

Electrical Properties of 7,7',8,8'-Tetracyanoquinodimethane Salts of Ionene Polymers and Their Model Compounds[1a]

V. Hadek,[1b] H. Noguchi, and A. Rembaum*

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103.

Received January 4, 1971

ABSTRACT: Electrically conducting polymeric salts were prepared by the reaction of ionene polymers with LiTCNQ in the presence or absence of neutral TCNQ. The specific resistivity, the activation energy for conductivity, and the Seebeck coefficient were determined as a function of the number of CH_2 groups between positively charged nitrogens. The wide variations of electrical properties could not be correlated with the length of the polymethylene chain in the polymer. X-Ray analysis of single crystals of model compounds revealed that the electrical properties depend mainly on crystal geometry.

The discovery of highly conducting 7,7',8,8'-tetracyanoquinodimethane (TCNQ) paramagnetic salts constitutes an important advance in the study of electronic conductivity of purely organic materials. This high conductivity is exhibited by mono- or polysalts, provided the TCNQ radical anion ($TCNQ\cdot^-$) is associated with a neutral TCNQ molecule[2,3] ($TCNQ^0$). Although the electronic conductivity of this type of material has already been well established,[4] no data

---

(1) (a) This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract No. NAS 7-100; (b) NRC-NASA Resident Research Associate.

(2) (a) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962); (b) A. Rembaum, A. M. Hermann, F. E. Stewart, and F. Gutmann, *J. Phys. Chem.*, **73**, 513 (1969).

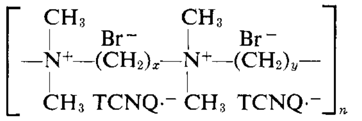
(3) A. Rembaum, *J. Polym. Sci., Part C*, **No. 29**, 157 (1970).

(4) R. G. Kepler in "Phonons and Phonons Interactions," T. A. Bak, Ed., W. A. Benjamin, New York, N. Y., 1964, p 579.

TABLE I
SYNTHESIS OF POLYMERIC TCNQ SALTS (IN THE ABSENCE OF $TCNQ^0$)

				Elemental composition[c]						
				Calcd,[b] %			Found,[c] %			
x–y	[η], dl/g	Temp, °C	Yield,[a] %	C	H	N	C	H	N	Br
3–4	0.154	60–65	85.1	70.69	5.76	23.55	67.01	6.36	19.95	2.13
6–3	0.246	22–30	81.9							
6–3	0.246	60–65	84.7							
6–5	0.482	22–30	82.2							
6–5	0.482	60–65	91.9							
6–6	0.299	22–30								
6–6	0.299	60–65	96.1							
6–8	0.577	22–30	91.0							
6–8	0.577	60–65	97.5							
6–8	0.577	60–65	85.9	72.80	6.98	20.21	68.62	7.68	15.73	3.71
6–10	0.791	22–30	94.4							
6–10	0.791	60–65	90.3	73.30	7.27	19.43	70.23	7.90	15.70	3.23
6–16	0.157	22–30	51.6							
6–16	0.157	60–65	63.0	74.59	8.01	17.40	73.17	8.32	14.71	0.13

[a] The yield refers to polymeric TCNQ salts containing anion radicals only; for sample preparation, see Experimental Section. [b] Calculated for the idealized structure

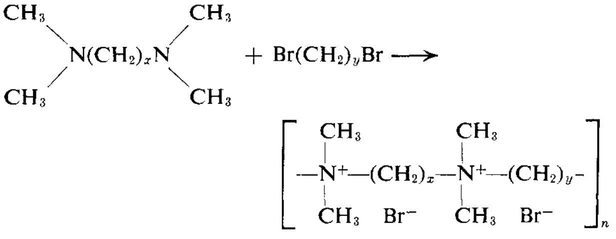


$$\left[-\overset{CH_3\quad Br^-}{\underset{CH_3\ TCNQ\cdot^-}{N^+}}-(CH_2)_x-\overset{CH_3\quad Br^-}{\underset{CH_3\ TCNQ\cdot^-}{N^+}}-(CH_2)_y-\right]_n$$

[c] Discrepancies are due partly to incomplete replacement of Br^- by $TCNQ\cdot^-$ and partly to neutral bromine in the end groups of the polymeric chains. Only traces of Li were found in the products; therefore, the bromine does not originate from residual LiBr.

are available as yet on the electrical properties of polymers containing TCNQ as a function of polymer structure.

The present investigation was undertaken in order to gain insight into the mechanism of electronic conductivity of polymeric TCNQ salts formed from polyelectrolytes the structures of which could be systematically altered. Ionene polymers[5] of well-defined structure seemed to be ideally suited for this purpose. The latter were therefore synthesized by means of the following reaction



$$(CH_3)_2N(CH_2)_xN(CH_3)_2 + Br(CH_2)_yBr \longrightarrow \left[-\overset{CH_3}{\underset{CH_3\ Br^-}{N^+}}-(CH_2)_x-\overset{CH_3}{\underset{CH_3\ Br^-}{N^+}}-(CH_2)_y-\right]_n \qquad (1)$$

x–y ionene bromide

where x and y are integers and n is the number of unit segments. The kinetics of formation and some solution properties of these polymers were recently described.[6]

Electrically conducting polymeric salts were prepared by the reaction of x–y ionene bromides with LiTCNQ in the presence or absence of $TCNQ^0$. It was found that the specific resistivity and the activation energy for conduction of 6–6 ($x = 6, y = 6$) ionene polymeric salts were considerably higher than those of a number of similar polymeric salts with different x and y values. In order to elucidate this anomaly, a homologous series of model TCNQ compounds representing unit segments of the polymers was synthesized from poly[methylenebis(trimethylammonium halides)], and their electrical properties were compared with those of TCNQ polymeric salts. The large variations in electrical properties were found to depend mainly on the geometrical configuration and crystal packing and not on the distances between positively charged nitrogen atoms in the polyelectrolytes.

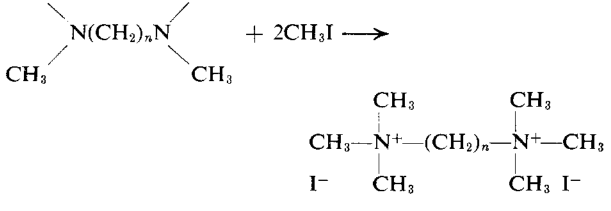
Results

(A) Ionene Polymers. The first series of polymeric TCNQ salts was prepared by treating ionene bromides (intrinsic viscosity $[\eta] = 0.154$–0.791 dl/g measured in 0.4 M KBr aqueous solution) with LiTCNQ, using a molar ratio of unit segment to LiTCNQ of 1:2. The intrinsic viscosities of the polymers, yields, and chemical analyses are recorded in Table I.

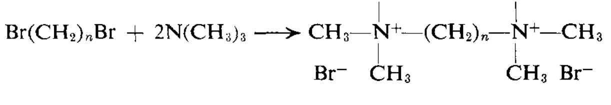
The second series of polymeric salts was prepared by treating ionene bromides with a mixture of LiTCNQ and $TCNQ^0$ using a molar ratio of 1:2:2.

The electrical properties of the polymeric salts, *i.e.*, resistivity (ρ), activation energy (ϵ), and Seebeck coefficient (α), in the absence and presence of $TCNQ^0$, are recorded in Table II. The dramatic changes in resistivity of salts in which $x = 4$ or 6 and $y = 3, 5, 6, 8, 10$, or 16 are shown in Figure 1.

(B) Model Compounds (DiTCNQ Salts). The model compounds, namely poly[methylenebis(trimethylammonium halides)], were prepared by means of reaction 2 or 3. The details



$$(CH_3)_2N(CH_2)_nN(CH_3)_2 + 2CH_3I \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{N^+}}-(CH_2)_n-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3\ \ 2I^- \qquad (2)$$



$$Br(CH_2)_nBr + 2N(CH_3)_3 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{N^+}}-(CH_2)_n-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3\ \ 2Br^- \qquad (3)$$

---

[5] A. Rembaum, W. Baumgartner, and A. Eisenberg, *J. Polym. Sci., Part B*, 6, 169 (1968).

[6] A. Rembaum, H. Rile, and R. Somoano, *ibid., Part B*, 8, 457 (1970).

Table II
Electrical Properties of the TCNQ Polysalts

Numbers of CH_2 groups, x–y	One unit segment to two $TCNQ\cdot^-$ Resistivity, ρ, ohms cm	Activation energy, ϵ, eV	Seebeck coefficient, α, mV/°C	One unit segment to two $TCNQ\cdot^-$, two $TCNQ^0$ Resistivity, ρ, ohms cm	Activation energy ϵ, eV	Seebeck coefficient, α, mV/°C
3–4	2.8×10^4	0.22	+0.12	1.5×10^3	0.20	+0.09
6–3	9.5×10^5	0.30	+0.31	3.4×10^3	0.24	+0.06
6–5	1.5×10^8	0.56	Positive[a]	7.7×10	0.140	−0.027
6–6	3.2×10^8	0.58	Positive[a]	5.2×10^7	0.46	+0.93
6–8	7.2×10^7	0.52	+0.72	1.4×10^7	0.45	+0.66
6–10	3.0×10^6	0.39	+0.39	7.3×10^4	0.29	+0.27
6–16	9.6×10^6	0.48	+0.04	4.7×10^2	0.23	−0.008

[a] The Seebeck coefficient was positive, but its exact value could not be determined because of polarization effects.

Table III
Synthesis of Poly[methylenebis(trimethylammonium halides)]

Reaction			Reaction time, hr	Yield, % I[a]	Yield, % II[b]	Recrystallization solvent	Halogen	Elemental composition Calcd, % C	H	X^-	N	Found, % C	H	X^-	N
	Diamine, mol/ml	CH_3I, mol/ml													
2	0.100/100	0.220/100	120	94.5	4.9	Methanol	I	24.02	5.54	63.44	7.00	24.16	5.47	63.27	6.97
2	0.100/100	0.220/100	120	0	99.6	95% ethanol	I	26.10	5.84	61.29	6.76	26.23	5.87	61.36	6.72
2	0.100/100	0.220/100	120	71.4	28.6	95% ethanol	I	28.05	6.12	59.28	6.54	27.94	6.16	59.20	6.41
	$N(CH_3)_3$, mol	Dibromide–CH_3OH, mol/ml													
3	0.252	0.100/150	260	0	99.2	93% ethanol	Br	37.95	8.11	45.90	8.05	38.03	8.14	45.90	7.99
3	0.244	0.100/200	360	0	99.9	Absolute ethanol	Br	43.09	8.78	40.95	7.18	43.11	8.69	40.95	7.14
3	0.249	0.100/200 + 30 Bz[c]	260	0	113.3	Absolute ethanol	Br	45.95	9.16	38.21	6.70	45.86	9.14	38.08	6.68
3	0.0450	0.0150/40 + 40 Bz	480	0	92.6	1-Butanol	Br	52.59	10.03	31.81	5.58	52.44	10.08	31.85	5.50

[a] I, product filtered off from the mixture at the end of the reaction. [b] II, product isolated from the mother liquor. [c] Bz, benzene.

of synthesis and chemical analysis are shown in Table III.

The model compounds were subsequently treated with LiTCNQ, and the disalts which were obtained had the composition $M^{2+}(TCNQ\cdot^-)_2$, where M^{2+} represents the poly[methylenebis(trimethylammonium)] dication. This is generally in excellent agreement with the chemical analyses (Table IV). Similarly, when the model compounds were treated with LiTCNQ and $TCNQ^0$ using the three reagents in a molar ratio of 1:2:2, another series of disalts was obtained. The electrical properties of both types of model salts are recorded in Table V and the plot of resistivity *vs.* number of CH_2 groups is shown in Figure 2. The resistivity values of the same batch of materials could be reproduced with an accuracy of ±10%.

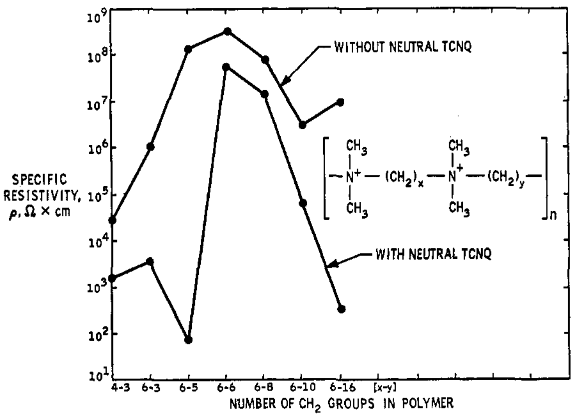


Figure 1. Specific resistivities of the TCNQ salts derived from ionene polymers as a function of the number of CH_2 groups.

The broken line (Figure 2) represents the resistivity of salts prepared at 65° and allowed to crystallize for 15 hr, while the parallel solid line represents the resistivity of salts prepared at room temperature and allowed to crystallize for 3 days. In both cases, the same relation between resistivity and the number of CH_2 groups was found.

The model compounds exhibited a large variation in electrical properties. For the first series with TCNQ radical anions, only the specific resistivity varied in a broad range reaching the maximum of 5×10^{10} ohms cm for the salt with six methylene groups. The positive Seebeck coefficient exhibited by the polymeric salts indicates hole-type conductivity probably due to the electrically active lattice defects.

For the second series of salts with neutral TCNQ, the magnitude of resistivity substantially decreased especially where negative Seebeck coefficients were observed, indicating occurrence of electron conductivity. The same relation between the negative Seebeck coefficient, electron conductivity,

TABLE IV

SYNTHESIS OF THE COMPLEXES WITH TCNQ RADICAL ANIONS FROM POLY[METHYLENEBIS(TRIMETHYLAMMONIUM HALIDES)][a]

							Elemental composition						
							Calcd, %			Found, %			
n	Halogen	Methonium compd, mmol	Li-TCNQ, mmol	CH_3OH,[b] ml	Temp, °C	Yield, %	C	H	N	C	H	N	Halogen
2	I	1.00	2.00	50	Room	97.4							
		1.50	3.00	50	55–60	93.3							
		1.50	3.00	50	60–65	90.6	69.29	5.45	25.25	67.16	5.48	24.94	
3	I	1.50	3.00	50	40–50	76.2	69.70	5.67	24.63	69.32	5.71	24.89	
		1.50	3.00	50	40–50	84.3							
		1.50	3.00	100	60–65	79.9							
4	I	0.75	1.50	50	60–65	80.5							
		1.50	3.00	50	40–50	77.2	70.08	5.88	24.04	70.31	5.83	24.08	
5	Br	0.75	1.50	50	60–65	71.9							
		1.50	3.00	50	40–50	74.0	70.45	6.08	23.47	70.36	6.04	23.68	
6	I	0.75	1.50	50	60–65	78.2				70.60	6.38	22.70	Trace (I)
		1.50	3.00	50	40–50	83.3	70.80	6.27	22.93	70.94	6.20	22.88	
8	Br	0.75	1.50	50	60–65	84.7							
		1.50	3.00	50	40–50	91.5	71.45	6.63	21.93	71.64	6.55	21.92	
10	Br	0.75	1.50	50	60–65	82.7				72.02	7.10	20.68	Trace (Br)
		1.50	3.00	50	40–50	93.4	72.04	6.95	21.00	72.04	6.95	21.03	
16	Br	0.50	1.00	25	Room	91.3							
		0.50	1.00	25	40–50	88.0	73.57	7.78	18.65	73.43	7.80	18.58	
		0.75	1.50	50	60–65	79.3							

[a] The reactions were carried out at room temperature (*ca.* 22°) for 1.5 hr. The reactions at elevated temperatures were carried out for 20 min and left at room temperature for 20 hr before filtration. [b] Amount of methanol used to dissolve each reactant.

TABLE V

ELECTRICAL PROPERTIES OF THE TCNQ COMPLEXES DERIVED FROM POLY[METHYLENEBIS(TRIMETHYLAMMONIUM HALIDES)]

	With negative TCNQ			With negative and neutral TCNQ		
Number of CH_2 groups, n	ρ, ohms cm	ϵ, eV	α, mV/°C	ρ, ohms cm	ϵ, eV	α, mV/°C
2	1.9×10^{3}	0.12	+0.12	9.0×10	0.10	+0.043
3	1.3×10^{5}	0.24	+0.59	4.2×10^{2}	0.16	−0.060
4	3.1×10^{7}	0.41	+0.52	6.5×10^{2}	0.26	+0.132
5	4.0×10^{6}	0.29	+0.41	1.2×10^{2}	0.22	−0.150
6	5.0×10^{10}	0.73	Positive[a]	1.0×10^{2}	0.21	−0.143
8	3.7×10^{7}	0.41	+0.72	7.0	0.090	−0.010
10	3.6×10^{7}	0.44	+0.69	4.1×10^{5}	0.28	+0.64
16	1.4×10^{9}	0.46	+0.75	1.5×10^{2}	0.16	0

[a] The Seebeck coefficient was positive, but its exact value could not be determined because of the high impedance.

low resistivity, and low activation energy of conductivity was observed for polymeric salts (Table II and Figure 1).

(C) Spectral Properties. The spectra of all salts containing $TCNQ\cdot^-$ only exhibited two typical major bands at 420 and 842 mμ. The intensity ratio of the two bands, *ca.* 0.57, was independent of the number of CH_2 groups. The ratio at λ_{max} 395 mμ to that at λ_{max} 842 mμ for salts containing $TCNQ^0$ varied from 0.9 to 1.6, the highest value representing the most conducting salt (with eight CH_2 groups).

(D) X-Ray Analysis. The materials investigated by single-crystal X-ray diffraction methods were TCNQ salts of model compounds of the following composition: I, $[(CH_3)_3N^+(CH_2)_5N^+(CH_3)_3](TCNQ\cdot^-)_2(TCNQ^0)$; II, $[(CH_3)_3N^+(CH_2)_5N^+(CH_3)_3](TCNQ\cdot^-)_2$; III, $[(CH_3)_3N^+(CH_2)_6N^+(CH_3)_3](TCNQ\cdot^-)_2(TCNQ^0)$; IV, $[(CH_3)_3N^+(CH_2)_6N^+(CH_3)_3](TCNQ\cdot^-)_2$.

Other crystals, listed in Table V, were twinned and too small to yield satisfactory diffraction patterns. I and IV yielded the most distinct and intense patterns. These two salts were found to have triclinic unit cells (Table VI). The dimensions of the unit cell of IV were substantially smaller than those of I, evidently due to the effect of two extra TCNQ molecules in the unit cell. Two other salts, II and III, gave less satisfactory diffraction patterns, which indicated nevertheless one-dimensional structures.

The unit cell parameters of I are recorded in Table VI. The *h*0*l* precession photograph showed a strong series of spots in the ($\bar{1}04$) direction (*i.e.*, spots $\bar{1}04$, $\bar{2}08$, $\bar{3}$,0,12 were very intense). This could be interpreted as stacking of electron density regions roughly perpendicular to the *C* axis and separated by a repeat distance of 3.21 Å.

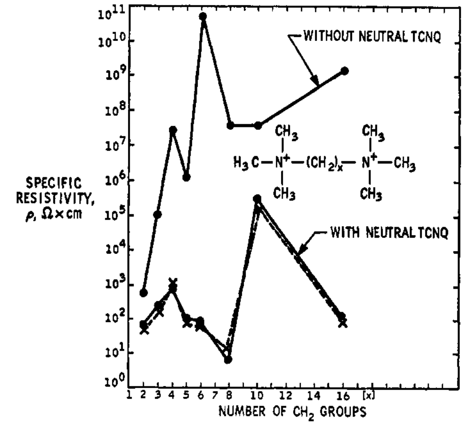


Figure 2. Specific resistivities of the TCNQ salts derived from the model compounds as a function of the number of CH_2 groups.

Table VI
Crystal Structure

Model Compound $(CH_3)_3N^+(CH_2)_6N^+(CH_3)_3(TCNQ\cdot^-)_2$
Unit Cell Triclinic
$a = 11.500$ Å $\alpha = 93°\ 33'$
$b = 11.690$ Å $\beta = 125°\ 17'$
$c = 7.675$ Å $\gamma = 95°\ 40'$
$V = 829.53$ Å^3

Model Compound $(CH_3)_3N^+(CH_2)_5N^+(CH_3)_3(TCNQ\cdot^-)_2(TCNQ^0)$
Unit Cell Triclinic
$a = 14.151$ Å $\alpha = 98°\ 29'$
$b = 7.829$ Å $\beta = 108°\ 07'$
$c = 13.813$ Å $\gamma = 72°\ 28'$
$V = 1384.39$ Å^3

Salt II also showed evidence of 3.21 Å stacking as in salt I, but unfortunately crystal disorder effects prevented determination of unit cell dimensions.

As in the previous case, salt III showed a one-dimensional stacking effect (this time with a repeat distance of 3.11 Å), but further analysis was hampered by crystal twinning.

Salt IV gave very good diffraction patterns, but no evidence of any stacking phenomena was observed (*i.e.*, no intense series of spots could be found in the diffraction pattern). The unit cell parameters are shown in Table VI.

Discussion

The values of ρ, ϵ, and α have been found to be reproducible within 30%. Further confidence in the accuracy of the results was gained by the use of di- or polymeric salts synthesized under different experimental conditions, *i.e.*, varying the temperature or solvent system. Essentially the same results were obtained, indicating that the trends depicted in Figures 1 and 2 are correct. The high values of specific resistivities of 6–6 ionene polymers were independent of molecular weight (samples of approximate weight average molecular weight of 10,000, 25,000, and 80,000 were tested). In addition, the properties of x–y ionenes were identical with those of y–x ionenes.

In general, the examination of Figures 1 and 2 and Tables I, II, III, and IV leads to the following conclusions. (1) The highest specific resistivity and activation energy were observed for salts derived from model compounds or polymers containing six CH_2 groups. (2) The salts with both negative and neutral TCNQ derived from the model compounds with 16 CH_2 groups and 6–16 ionene bromide exhibited very low specific resistivities, in spite of the fact that they contain the longest methylene chain between positive nitrogen atoms. (3) The salts from the model compounds and the polymers with high specific resistivities invariably exhibited hole-type conductivity or positive Seebeck coefficients, while those with low specific resistivities were characterized by electron-type conductivity or negative Seebeck coefficients. (4) The salts with 16 CH_2 groups exhibited low Seebeck coefficients. The lowest concentrations of the charge in these salts gave rise to a mixed type of conductivity with the same concentration of holes and electrons. (5) The characteristic variations of specific resistivity as a function of the number of CH_2 groups can be attributed to the conformations of polymethylene chains in the solid state, the high conductivity being due to electron delocalization in one-dimensional TCNQ columns. Salts containing odd numbers of CH_2 groups are generally more conducting than those that contain even numbers of CH_2 groups. In the former case, the TCNQ molecules will tend to be on the same side of the chain in a conformation more favorable for conduction. This condition is not valid as the number of CH_2 groups becomes larger than six, in which case the chains become more flexible and TCNQ molecules may be arranged in a columnar configuration in spite of the fact that the number of CH_2 groups is even. However, when the distance between TCNQ molecules becomes relatively large, the resistivity increases considerably.[6]

The resistivity value of the polymeric salt containing six CH_2 groups between positive nitrogens and only $TCNQ\cdot^-$ is also the highest of those of the analogous model salts (Figure 2). The fact that the TCNQ salt of the model compound (salt III; section D) exhibits a resistivity value of the order of 10^2 ohms cm seems to be out of line. It can be understood on the basis of the X-ray investigations. The geometry of the salts formed is the dominant factor in the electrical values of the materials under investigation, and it is only when one-dimensional column stacking of the TCNQ moiety occurs that a very high electronic conductivity is observed. It is, therefore, not surprising to note that a decrease of concentration of positive charges in the polymeric chain or in the model compounds does not necessarily increase the values of ρ or ϵ (Figures 1 and 2 and Tables I and II).

The preliminary X-ray data support the anomalously high resistivity of salt IV as compared with salt II. Salts I and III have even lower resistivities and lower activation energies of conductivity. This is consistent with the X-ray results, for salt IV is the only one of the four compounds studied which shows no evidence of one-dimensional stacking.

Experimental Section

Reagents. Dibromides were purified by distillation. Methyl iodide was refluxed over copper wire for 5 hr and then distilled. Trimethylamine was obtained from Matheson Co., Norwood, Ohio, and used without any pretreatment. Lithium tetracyanoquinodimethane was synthesized according to the previously established procedure.[2a] Tetracyanoquinodimethane was obtained from E. I. du Pont de Nemours aud Co., Wilmington, Del., and was recrystallized from acetonitrile. Solvents were reagent or spectroscopic grade, and were used without further purification.

Elemental Analyses. Total elemental analyses were carried out by the Spang Microanalytical Laboratory, Ann Arbor, Mich., and by the Elek Microanalytical Laboratories, Torrance, Calif. Ionic bromine and iodine contents were also determined by the Mohr method in our laboratory.

Electronic Absorption Spectroscopy. The electronic absorption spectra of the complexes derived from the model compounds were taken with a Cary spectrophotometer, Model 14CM, using acetonitrile as a solvent.

X-Ray Diffraction. X-Ray studies were carried out by means of a standard precession camera with Mo Kα radiation (λ 0.7107 Å). Crystals were grown at room temperature in a U tube in which the reagents were separated by means of a medium-sized sintered-glass filter.

Measurements of Electrical Properties. The experimental technique for measuring the electrical properties of the TCNQ salts has been described in detail elsewhere.[7] All samples were measured *in vacuo* and under a pressure of 1000 atm between room temperature and −100° or liquid nitrogen temperature. The activation energy for conductivity refers to these temperature ranges and the values of the Seebeck coefficient refer to room temperature.

Poly[methylenebis(trimethylammonium halides)]. Hexamethylenebis(trimethylammonium iodide) was obtained from the K & K Laboratories, Plainview, N. Y., and was recrystallized from absolute ethanol and dried *in vacuo* at 40°. *Anal.* Calcd for $C_{12}H_{30}I_2N_2$: I (ionic), 55.64. Found: I (ionic), 55.8. The other model compounds were synthesized by one of the following two general procedures.

---

(7) V. Hadek, *Rev. Sci. Instrum.*, **42**, 393 (1971).

(a) A solution of methyl iodide in methanol was added with stirring to a solution of *N,N,N′,N′*-tetramethyl-α,ω-diaminoalkane in methanol. The mixture was cooled initially with ice water for a short time. It became pale yellow on standing at room temperature. The precipitated colorless crystal was filtered, washed with a small amount of methanol and then with benzene, and dried *in vacuo* at 40° (fraction II). Both fractions were analytically pure. The main fraction was further recrystallized and then analyzed for elemental composition. When *n* was 1, the isolated product consisted of tetramethylammonium iodide.

(b) Pure trimethylamine was added with stirring to a solution of α,ω-dibromoalkane in methanol or in a mixture of methanol and benzene. After standing at room temperature, the mixture was evaporated to dryness. The residue was triturated with *n*-hexane to remove the remaining dibromide. The solid product was filtered, washed with hot *n*-hexane, and dried *in vacuo* at 40°. It was recrystallized and then analyzed for elemental composition.

When *n* was 8 and 10, the ionic bromine contents of the crude products were lower than the calculated values. After recrystallization and drying *in vacuo* at 40°, the ionic bromine contents were lowered even further. However, by drying *in vacuo* at 100° overnight, the elemental compositions agreed well with the calculated values.

Reaction of *N,N,N′,N′*-Tetramethyldiaminomethane with Methyl Iodide. To a solution of 10.38 g (0.102 mol) of tetramethyldiaminomethane in 100 ml of methanol was added 34.72 g (0.245 mol) of methyl iodide in 110 ml of methanol, with stirring. The mixture was cooled initially with ice water for a short time. After 24 hr of reaction at room temperature, the precipitate was filtered, washed three times with a small amount of methanol and then with benzene, and dried *in vacuo* at room temperature. The yellowish filtrate was not examined; yield, 10.91 g (53.4% based on the diamine[8]). It was recrystallized from a 3:1 mixture (by volume) of methanol and water: mp >360° dec (lit.[9] >230° dec); nmr τ 6.80 (singlet, 12 H, N^+–CH_3; lit.[10] τ 6.82). *Anal.* Calcd for $C_4H_{12}IN$ (tetramethylammonium iodide): C, 23.90; H, 6.02; I (ionic), 63.12; N, 6.97. Found: C, 23.89; H, 5.97; I (ionic), 63.13; N, 6.99.

Tsatsas and Damiens[11] obtained the same resulting using ether as solvent.

Hexadecamethylenebis(trimethylammonium bromide). Method A. To a solution of 21.06 g (0.0548 mol) of 1,16-dibromohexadecane in 210 ml of benzene was added 10.2 g (0.173 mol) of trimethylamine, with stirring. After a few minutes, small needles separated out. The mixture was left for 164 hr at room temperaature. The crystalline product was filtered, washed with benzene to remove the remaining dibromide, and dried *in vacuo* at room temperature; yield, 22.86 g (94.1% based on the dibromide). *Anal.* Calcd for $C_{19}H_{41}Br_2N$ (ω-bromohexadecyltrimethylammonium bromide): C, 51.47; H, 9.32; Br (ionic), 18.02; Br (total), 36.04; N, 3.16. Found: C, 51.64; H, 9.43; Br (ionic), 18.06; Br (total), 35.94; N, 3.24.

To a solution of 19.52 g (0.0440 mol) of ω-bromohexadecyltrimethylammonium bromide obtained as above in 140 ml of methanol was added 12.7 g (0.215 mol) of trimethylamine, with stirring. The reaction was carried out for 115 hr at room temperature. The homogeneous mixture was then evaporated to dryness, and the residue was triturated with benzene. The solid product was filtered, washed with benzene, and dried *in vacuo* at 40°; yield, 22.32 g (100.9% based on the monoammonium salt). *Anal.* Calcd for $C_{22}H_{50}Br_2N_2$: Br (ionic), 31.81. Found: Br (ionic), 31.15.

These results indicated that the product contained a small amount of methanol. It was recrystallized from 2-propanol. The purified product was dried *in vacuo* at 100° overnight prior to analysis. *Anal.* Calcd for $C_{22}H_{50}Br_2N_2$: C, 52.59; H, 10.03; Br (ionic), 31.81; N, 5.58. Found: C, 52.45; H, 10.02; Br (ionic), 31.70; N, 5.49.

Method B. To a solution of 5.76 g (0.0150 mol) of 1,16-dibromohexadecane in 40 ml of benzene were added 40 ml of methanol and then 2.66 g (0.0450 mol) of trimethylamine, with stirring. The reaction was left for 20 days at room temperature. The homogeneous mixture was then evaporated to dryness, and the residue was triturated with benzene to remove the remaining dibromide. The solid product was filtered, washed with benzene, and dried *in vacuo* at 40°; yield, 6.98 g (92.6% based on the dibromide). *Anal.* Calcd for $C_{22}H_{50}Br_2N_2$: Br (ionic), 31.81. Found: Br (ionic), 31.41.

This result indicated that the product contained a small amount of methanol. It was recrystallized from 1-butanol. The purified product was dried *in vacuo* at 100° overnight prior to analysis. *Anal.* Calcd for $C_{22}H_{50}Br_2N_2$: C, 52.59; H, 10.03; Br (ionic), 31.81; B, 5.58. Found: C, 52.44; H, 10.08; Br (ionic), 31.85; N, 5.50.

Complexes with TCNQ·$^-$. A solution of an ammonium compound in methanol was poured into a solution of LiTCNQ in methanol, with stirring, at room temperature or after heating both solutions to a given temperature. A deep blue product separated immediately in most cases. The reaction was continued at the given temperature for 20 min, with stirring. Then the mixture was left at room temperature. The deep blue crystalline or powdery product was filtered or, if necessary, centrifuged. It was washed thoroughly, first with methanol, then with water, until no halogen ion could be detected with a silver nitrate solution, and finally it was washed with methanol, and dried *in vacuo* at room temperature.

Complexes with both Negative and Neutral TCNQ. A solution of TCNQ in acetonitrile heated to 60–65° was added, with stirring, to a solution of LiTCNQ in methanol heated to the same temperature. Into the mixed solution was then poured, with stirring, a solution of an ammonium compound in methanol heated to 60–65°. A deep blue product precipitated immediately. The reaction was continued at this temperature for 20 min, with stirring, and left at room temperature for 12 hr. The deep blue crystalline or powdery product was filtered, washed successively with acetonitrile, methanol, and water until no halogen ion could be detected, and dried *in vacuo* at room temperature.

Acknowledgment. V. Hadek and H. Noguchi are grateful to the National Academy of Sciences–National Research Council, Washington, D. C., for the Postdoctoral Resident Research Associateships supporting this research. The authors wish to express their thanks to Dr. R. Bau for helpful discussions and assistance in the X-ray investigations.

---

(8) H. Bohme and W. Lehners, *Justus Liebigs Ann. Chem.*, **595**, 169 (1955).

(9) I. Heilbron and H. M. Bunbury, Ed., "Dictionary of Organic Compounds," Vol. IV, Eyre and Spottiswoode, London, 1953, p 463.

(10) K. Tori, T. Iwata, K. Aono, M. Ohtsuru, and T. Nakagawa, *Chem. Pharm. Bull.*, **15**, 329 (1967).

(11) G. Tsatsas and R. Damiens, *Ann. Pharm. Fr.*, **7**, 444 (1949).