

Properties of Conducting 7,7,8,8-Tetracyano-*p*-quinodimethane Salts with 1,*n*-Bis[1-(γ -picolinio)]alkane Dication Homologues

L. J. Yu,* F. C. Lang, and J. S. Lee

Department of Chemistry, Tamkang University, Tamsui, Taipei 25137, Republic of China
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1,*n*-Bis[1-(γ -picolinio)]alkane-(TCNQ)_{*m*} salts are nonstoichiometric with *m* varying from 3.4 to 4.7 for *n* = 2-7. The conductivity (compressed pellet, four-probe method, in the temperature range 230-310 K) varies with the alkyl chain length of the dications, the highest being 2 S cm⁻¹, for *n* = 4 and *m* = 4.6, with the lowest activation energy (0.033 eV). FT-IR and electronic absorption spectra are presented and discussed. On the basis of the results observed, a possible structure is proposed for these homologous salts.

Introduction

There are numerous organic conducting 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) salts with various conductivities and conduction mechanisms.¹ The variations are mainly associated with differing cation structures that induce different crystal structures. High conductivities are observed for salts with highly π -conjugated planar cations. In these salts, the cations and anions form segregated columns.^{2,3} A mixed stacking of cations and anions results in low conductivity.⁴ A third type of crystal structure consists of cations arranged in an ordered or disordered array in the channels between the TCNQ columns. Ashwell and co-workers reported several studies of TCNQ-dipyridinium salts having crystal structures of the third type with conductivities in the range of 10⁻⁴-100 S cm⁻¹.⁵⁻⁷

Considering the solid as a whole, the conduction electrons are moving in the conduction chains and experiencing the electric potential exerted from the nearby counterions. Thus, the periodicity and strength of the potential and the structural variations induced by the counterions are important in determining the movement of conduction electrons. For TCNQ salts, these factors are mainly associated with the variations among the cations used. We have studied TCNQ salts of a homologous series of dications having differing lengths of nonbranched alkyl chains as the central segments with the same charged moieties as the terminals. Provided the crystal structures are of the same type (the third type mentioned above) for these salts, the periodicity of electric potential is therefore varied with the alkyl chain length. We report here the results of these salts with *N*-alkylated γ -picoliniums as the charged terminals.

Experimental Section

The typical synthetic procedures of these salts are as follows. A mixture of 1,*n*-dibromoalkane, γ -picoline (4-methylpyridine), and 2-propanol (or dimethylformamide (DMF) for higher *n* values) is refluxed for 2 h. The obtained dibromide salts are recrystallized from methanol/acetone to give colorless crystals. After metathesis with 2 equivalent amounts of LiTCNQ,⁸ the product is mixed with neutral TCNQ in hot acetonitrile. Upon slow cooling of the mixture, dark precipitates of irregular shapes are obtained. The final product obtained is designated as C_{*n*}2*Pm*T, where subscript *n* stands for the number of carbon atoms of the

alkyl linkage, P for γ -picolinium, and *m* for the number of TCNQ molecule (T) incorporated.

Proton spectra of the dibromide salts were taken with a Bruker WP 100 SY FT NMR spectrometer. Electrical conductivity was measured on compressed pellets of these salts by a four-probe method⁹ via a Keithley 617 electrometer and a 485 picoammeter. A sample is placed in a sample holder equipped with a Haake Q thermostat for temperature control, and temperature is measured with a copper-constantan thermocouple. Optical measurements were carried out on pellets composed of ground samples and KBr with a Bomem DA 3.002 FT-IR and a Hitachi 330 UV-vis near-IR spectrometer.

Results and Discussion

Elemental Data and Conductivity. The dibromide salts obtained are sensitive to moisture and hence are not analyzed elementally. However, the proton NMR spectra of these salts (dissolved in D₂O) give chemical shifts and proton ratios consistent with the structures for the desired formulas. The results of elemental analysis for C_{*n*}2*P*2T are consistent with those expected. For the salts of C_{*n*}2*Pm*T with *m* > 2, on the basis of the results of elemental analysis, it is found that the number of TCNQ molecules accommodated by the dication is nonstoichiometric. Similar behaviors were observed for other salts by Ashwell and co-workers.^{6,7} Some results of analysis are listed in Table I with the best-fit *m* values. Composition percentage is not sensitive to stoichiometry for these salts. Therefore, the stoichiometry was determined solely from the results of elemental analysis and cannot be taken too seriously. The melting points of all these salts (*m* > 2) listed are higher than 390 °C.

Electrical conductivity for salts with *m* = 2 is of the order of 10⁻⁸ S cm⁻¹. The conductivity is increased by 6-8 orders of magnitude when extra neutral TCNQ molecules are introduced. In a plot of log conductivity versus reciprocal temperature, all the salts exhibit semiconducting behavior in the temperature range (230-310 K) studied, as shown in Figure 1. As can be seen from the figure, all the data points fall on straight lines from which activation energies can be evaluated. The conductivities at 300 K and activation energies are also listed in Table I. It is interesting to note that the conductivity reaches a maximum value with the lowest activation energy when the γ -picolinium moieties are connected with four and five singly bonded carbon atoms.

Infrared Absorption. Introduction of neutral TCNQ molecules into TCNQ⁻ salts usually results in promotion of conductivity. This is attributed to the sharing of charges between the TCNQ molecules. IR spectroscopy is a convenient method employed for evaluation of the partial charge residing on a TCNQ molecule.^{10,11} FT-IR spectra of these TCNQ salts along with that of LiTCNQ are shown in Figure 2. The wavenumbers of the major peaks

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TABLE I: Elemental Data, Adopted Stoichiometric Values (m), Conductivities (σ) at 300 K, and Activation Energies (E_a) Measured on Compressed Pellets by the Four-Probe Method for TCNQ Salts with 1, n -Bis[1-(γ -picolinio)]alkane Homologues

formula used for calcn		C	H	N	m	σ , S cm ⁻¹	E_a , eV
C ₂ 2P3.44T	calcd	71.34	3.47	23.63	3.4	0.006	0.162
	found	71.33	3.48	23.63			
C ₃ 2P4T	calcd	72.41	3.45	24.14	4	0.0011	0.2
	found	72.41	3.56	24.08			
C ₄ 2PT4.57T	calcd	72.35	3.46	24.18	4.6	2.1	0.033
	found	72.38	3.43	24.18			
C ₅ 2P4.6T	calcd	72.53	3.58	23.91	4.6	1.6	0.064
	found	72.40	3.58	23.95			
C ₆ 2P4.5T	calcd	72.73	3.70	23.57	4.5	0.15	0.096
	found	72.75	3.79	23.40			
C ₇ 2P4.69T	calcd	72.70	3.79	23.38	4.7	0.085	0.164
	found	72.74	3.76	23.38			

TABLE II: Wavenumbers (cm⁻¹) of IR Major Peaks for the TCNQ Salts with 1, n -Bis[1-(γ -picolinio)]alkane Homologues Listed in Table I^a

C ₂		C ₃		C ₄		C ₅		C ₆		C ₇		normal mode assignnt
592	m	597	m	592	m	593	w	593	w	593	w	A _g -7
700	s	704	s	688	b, s	691	b, s	695	s	693	s	
835	s	832	s	834	m	834	m	838.6	m	836.4	m	B _u -50
954	m	957	ms	956	w	952.6	w	952.6	w	950.3	m	A _g -6
1116	s	1047	m									
1145.5	s	1160	b, s	~1080	b, s	~1100	vb, vs	~1111	vb, vs	~1111	vb, vs	A _g -5
1310.5	s	1309	s	~1293	vb, vs	~1284	vb, vs	~1326	vb, vs	~1328		A _g -4
1338	vs	1340	b, s									B _u -35
1511	w	1520	m	1525	m	1520	m	1529.3	m	1529	m	B _u -20
1563	vs	1566	vs	1557	m	1563	m	1566	m	1563	m	A _g -3
1639	m	1641	m	1664	w	1643.7	vw	1643.7	vw	1643	w	
2169	b, vs	2176.7	b, vs	~2100	vb, vs	~2100	vb, vs	2158.4	b, s	2165	b, s	B _u -19
2198.6	s	2202	s	2202	s	~2200	s	2179	b, s	2199.5	s	B _u -33
								2201	m			A _g -2

^aThe letters following the numbers stand for w = weak, m = medium, s = strong, v = very, b = broad. The normal modes are assigned after ref 12.

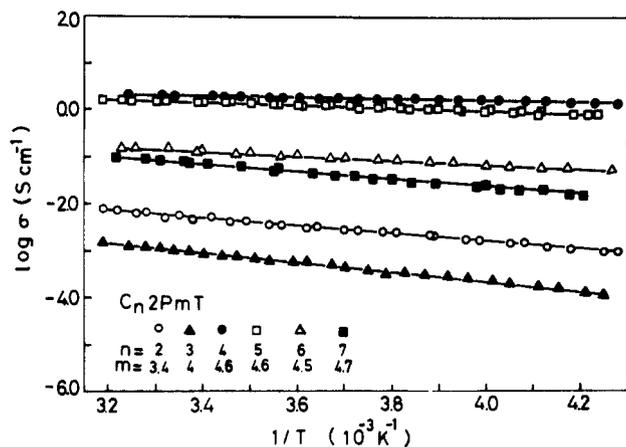


Figure 1. Logarithm of conductivity (S cm⁻¹) as a function of reciprocal temperature (kelvin) measured on compressed pellets of 1, n -bis[1-(γ -picolinio)]alkane-(TCNQ) _{m} salts.

are listed in Table II. The general features of these spectra are as follows:

(1) Within the frequency range studied, there is a very broad absorption band commencing from about 1000 cm⁻¹ and extending into the region beyond 4000 cm⁻¹ (into the near-infrared range).

(2) Superimposed on this band are the absorption peaks characteristic of TCNQ ^{q} and are down-shifted and broadened, particularly for ν_4 and ν_5 of A_g modes,¹² and that at ca. 2100 cm⁻¹ for C₄ and C₅ salts.

(3) Most of the peaks are located at about the same frequencies for these various salts, except those at 1525, 1300, and 1150 cm⁻¹.

(4) No TCNQ⁰ peaks are evident. Thus, if the peak at about 2200 cm⁻¹ is taken consistently as that of ν_2 of A_g mode as

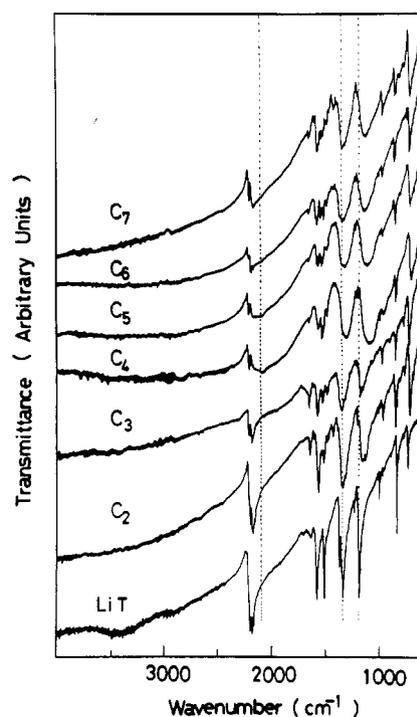


Figure 2. FT-IR spectra for 1, n -bis[1-(γ -picolinio)]alkane-(TCNQ) _{m} salts and LiTCNQ (LiT). C _{n} stands for the corresponding salts listed in Table I.

Chappell et al.¹⁰ did and a linear relationship is assumed for frequency shift versus fractional charge of TCNQ, a charge of -0.56 to -0.61 is obtained for these various salts. A similar analysis for the B_u(ν_{50}) mode, C-H out-of-plane bending,¹² with 860 and 823 cm⁻¹ for TCNQ⁰ and TCNQ⁻ respectively, as references, gives -0.6 to -0.7 charges for TCNQ molecules. However, a value of

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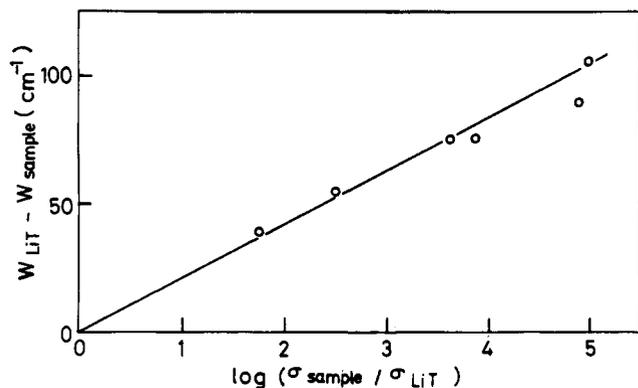


Figure 3. Frequency shift for ν_s of the A_g mode for $\text{TCNQ}^{\cdot-}$ versus logarithm of conductivity for 1,*n*-bis[1-(γ -picolinio)]alkane-(TCNQ)_{*m*} salts with those of LiTCNQ (LiT) as references.

-0.44 should be obtained, if the charges, -2, are uniformly distributed among the TCNQ molecules (assuming a stoichiometry of 4.5).

The very broad absorption band in the IR and near-IR (see electronic absorption below) and the broadened $\text{TCNQ}^{\cdot-}$ characteristic peaks are results of strong electron-phonon coupling¹¹ and the highly delocalized conduction electrons. This is also supported by the relatively high electrical conductivity of these salts. Of particular interests are peaks at 2100, 1300, and 1100 cm^{-1} of salts with carbon number varying from 4 to 7, and especially for C_4 and C_5 salts, which are the most conducting salts. Therefore, it is interesting to see if the conductivity can be directly correlated to the frequency shift. Taking 1185 cm^{-1} and 2×10^{-5} S cm^{-1} of LiTCNQ as references, a plot of $\Delta w = w_{\text{LiTCNQ}} - w_{\text{sample}}$ versus logarithm ($\sigma_{\text{sample}}/\sigma_{\text{LiTCNQ}}$) is shown in Figure 3. Considering the uncertainty in obtaining the band center of a broad peak, the linear relationship is rather acceptable. However, it should be noted that this is the only system that exhibits such a linear relationship.

As shown in Figure 2, all these salts exhibit a broad absorption band in the high-energy portion of their spectra. It appears that for salts of C_2 , C_3 , and C_7 the absorption maximum is located in the region beyond the IR range. Whereas for those of C_4 , C_5 , and C_6 the broad absorption maximum is located in the IR range ($\sim 3000 \text{ cm}^{-1}$); this is particularly clear for the C_4 salts. This property is consistent with that observed in the low-energy portion of the electronic absorption spectra.

Electronic Absorption. The electronic absorption spectra of these salts are very similar, and typical examples are shown in Figure 4. For C_4 2P2T salt, the absorption curve resembles those of LiTCNQ and KTCNQ and displays the characteristic features of a TCNQ anion radical dimer in a solid phase. The peaks located at 365 and 620 nm are due to the local excitations (LE_1 and LE_2 , respectively) of a TCNQ radical anion in a solid, and the peak at 1200 nm is due to charge transfer of the dimer (CT_1 band).¹²⁻¹⁴ After the neutral TCNQ molecules are incorporated (C_4 2P4.6T and C_3 2P4T), the intensities of the local excitations decrease (particularly that of the LE_2 band) due to the decrease of the dimer number. Meanwhile, a peak appears at 870 nm, which is due to the TCNQ radical anion monomer. The LE_1 intensity does not change much because of the neutral TCNQ absorption at 390 nm. A slight blue shift of LE_2 is observed. The band located at 1000 nm is attributed to the blue-shifted CT_1 band. This pair of peaks (870 and 1000 nm) has been observed for many TCNQ salts with medium to high electrical conductivities and has been considered as a slightly mixed LE_2 and CT_1 band.¹⁴

Another important feature occurs in the low-energy region. For C_4 2P2T and LiTCNQ, the absorbance is nearly zero. However, for C_4 2P4.6T and C_3 2P4T, it is very clear that there exists an absorption band. The wavelength of the absorption maximum

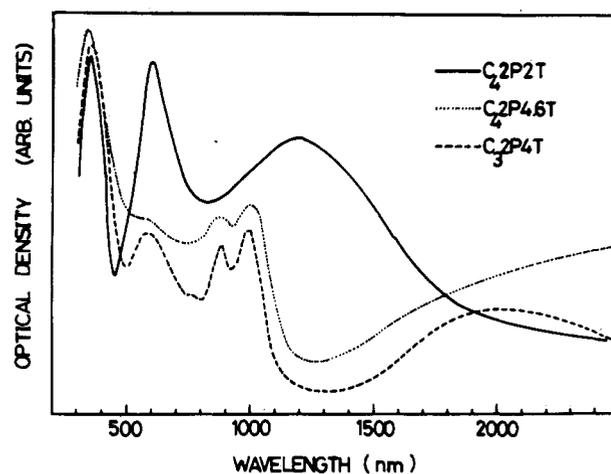


Figure 4. Electronic spectra of 1,*n*-bis[1-(γ -picolinio)]alkane-(TCNQ)_{*m*} salts. For abbreviations, see text and Table I.

is about 2000 nm for the C_3 salt, but it extends into the IR region for the C_4 salt. These behaviors correlate well with the results of the IR spectra. The occurrence of this absorption band (CT_2 band) is attributed to the charge transfer from a radical to a neighboring neutral molecule.^{13,14} The energy required is apparently less than that for a CT_1 band.

These electronic absorption properties have been observed and discussed separately by Torrance et al.¹³ and Tanaka et al.¹⁴ for many different single-crystal TCNQ conducting salts. While the bands of LE_1 and LE_2 are due to intramolecular excitations, those of CT_1 and CT_2 are due to intermolecular excitations. We are unable to measure the polarization ratio at the present time since the crystals obtained are too small. However, the existence of a CT_2 band (at ~ 2000 nm) in the present salts clearly indicates that there is a transfer of charge from one TCNQ to the neighboring neutral TCNQ. This is clear evidence that the introduced neutral TCNQ molecules are mixed into the stacked TCNQ column. This is also supported from the FT-IR and conductivity observations.

The Dications. Thus far no role played by the dication is evident. FT-IR spectra of C_n 2P2T salts (not shown) display complicated peaks that are actually comparable to a combination spectra composed of C_n 2P2⁺ and $\text{TCNQ}^{\cdot-}$, being dominated by $\text{TCNQ}^{\cdot-}$. However, this complexity is greatly reduced when extra neutral TCNQ molecules are introduced. Even the very strong peaks characteristic of the dication are not observed in the spectra (Figure 2). Therefore, the coupling between the dications and TCNQ columns is rather strong, although the dications probably do not take part in the conduction mechanism.

From the structural similarity of the present dications and those reported by Ashwell^{5,7} and Ashwell et al.,⁶ the comparable conductivities observed, and the optical properties presented here, we anticipate that the crystal structures of the present salts are similar to those reported in ref 5-7. That is, the TCNQ molecules are stacked in columns, and the dications are arranged in ordered or disordered arrays with molecular long axes penetrating through the channels in the direction of TCNQ columns. In such a lattice, the conduction electrons are propagating in the TCNQ columns and experiencing the electric potential exerted from the positive charges of the dications. The periodicity of this potential is regulated by the number of carbon-carbon single bonds. Therefore, the dications are of primary importance in that they provide a framework in space into which the TCNQ molecules are arranged. Similar structural factors are observed in many organic metals.¹⁵

Conclusion

The relatively high conductivity is associated with highly delocalized charge carriers in the conduction chains. The broad

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peaks and large frequency shift observed in the FT-IR spectra along with the occurrence of low-energy absorption bands (CT_2 band) in the electronic absorption spectra (extending into IR region) indicate that these charge carriers are migrating along the TCNQ molecules. Thus, the TCNQ molecules are stacked in columns.

This stacking is affected by the surrounding dications via the structural configuration and periodicity of the electric potential. The stoichiometry of TCNQ evaluated from the results of elemental analysis is, in most of the cases, close to 4.5. This number becomes smaller for shorter dications. It is known that in TCNQ salts, TCNQ molecules are sometimes arranged in tetrads or pentads in the TCNQ columns.^{5-7,14} Hence, it is reasonable to expect that there are two tetrads sharing an extra TCNQ molecule in the crystal lattice of these salts. Assuming a uniform distribution of charges among these TCNQ molecules, a value of -0.44 fractional charges is obtained. However, the fractional charge is evaluated to be -0.56 to -0.7 on the basis of the frequency shift of infrared peaks. Thus, neutral TCNQ molecules very likely exist

in the stacks. Migration of charge from charged to neutral TCNQ molecules is indeed observed in the electronic absorption spectra (CT_2 band). The difference in conductivity by 3 orders of magnitude for C_3 and C_4 salts could be due to the larger separation between the tetrads (CT_2 bands located at ~ 2000 and >2500 nm, respectively).

It would be very helpful to have single crystals of these salts to study their properties. More efforts are currently underway to obtain these and also for elucidation of the conduction mechanism. More affirmative evidence is needed to show if the length made by four or five singly bonded carbon atoms is the best match for giving high conductivities. This could be important in future design of polymeric conductors.

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Registry No. $C_2P3.44T$, 114957-95-8; C_3P4T , 114958-01-9; $C_4P4.57T$, 114957-97-0; $C_5P4.6T$, 114957-99-2; $C_6P4.5T$, 114958-07-5; $C_7P4.69T$, 114958-04-2.

Permeability-Controllable Membranes. 7.¹ Electrochemical Responsive Gate Membranes of a Multibilayer Film Containing a Viologen Group as Redox Sites²

Yoshio Okahata* and Gen-ichiro En-na

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan
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The polyion complex-type bilayer-immobilized film was prepared from viologen-containing dialkyl amphiphiles and poly(styrenesulfonate) ($2C_{16}V^{2+}/PSS^-$) or from anionic bilayer-forming amphiphiles and viologen ionene polymers ($2C_{12}SO_3^-/polyV^{2+}$). Permeability of water-soluble nonionic fluorescent probes could be reversibly controlled through the $2C_{16}V^{2+}/PSS^-$ film cast on a Pt minigrid sheet by electrochemical redox reactions of viologen units in bilayers depending on temperatures. These reversible permeation changes of the film were attributed to the fluidity change of the bilayer matrix because the phase-transition temperature (T_c) of lipid bilayers is changed from 24 °C ($2C_{16}V^{2+}$ bilayers) to 38 °C ($2C_{16}V^{++}$ bilayers) by the electrochemical reduction. The permeability of the $2C_{12}SO_3^-/polyV^{2+}$ film was not affected by the redox reaction because the viologen site is located in the hydrophilic polymer chains.

Introduction

Recently, various types of permeability-controllable synthetic membranes have been developed in connection with studies of the transport mechanism in biological membranes. In these membranes, lipid monolayers,^{3,4} built-up multilayers,⁵⁻⁷ liquid crystals,⁸⁻¹² grafted polymers,¹³⁻¹⁶ and polypeptides^{17,18} are immobilized

on a support membrane. We have reported that the bilayer-corked capsule membrane showed a reversible permeation control responding to various outside effects such as temperature change, pH change, photoirradiation, and interaction with Ca^{2+} ions.^{19,20} We have observed that the permeability through the Langmuir-Blodgett monolayer-immobilized porous glass plate can be reversibly controlled by the phase transition from solid to liquid crystal of the monolayer.³ These permeation changes could be explained by changes of the physical state of corking bilayers or

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