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N,*N*-Disubstituted 1,3-Dithiolan-2-iminium–TCNQ$^{\overline{\cdot}}$ Salts: Effect of the Substituents on the Nitrogen Atom on the Composition and the Electrical Conductivity

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Following 10 simple and complex salts of TCNQ$^{\overline{\cdot}}$ with *N*,*N*-disubstituted 1,3-dithiolan-2-iminium cations; $(CH_2)_2\langle^{S}_{S}\rangle C{=}\overset{+}{N}R^1R^2\cdot(TCNQ)_n^{\overline{\cdot}}$ ($n=1$ when $R^1=R^2=n$-Pr, n-C_6H_{13}, n-C_8H_{17}, Ph, and $R^1=$Me and $R^2=$Ph; $n=2$ when $R^1=R^2=n$-Pr, n-Bu, Ph, and $R^1=$Me and $R^2=$Ph), and $[(CH_2)_2\langle^{S}_{S}\rangle C{=}\overset{+}{N}(n\text{-}C_{10}H_{21})_2]_2\cdot(TCNQ)_3^{2\overline{\cdot}}$ were prepared. Of these, simple salt $(CH_2)_2\langle^{S}_{S}\rangle C{=}\overset{+}{N}(n\text{-}C_8H_{17})_2\cdot TCNQ^{\overline{\cdot}}$ was obtained in two different crystalline forms; unstable violet needles and green plates. All the salts as compacted samples displayed semi-conducting behaviors in the 20—90 °C range. Electrical resistivities of the 1:2 complex salts fell in the range of 5—90 ohm cm at 25 °C, while the simple and 2:3 complex salts showed much large resistivities (the order of 10^3—10^9 ohm cm). The measurements of electronic absorption spectra and magnetic susceptibilities indicated that the simple salts in the solid state involve dimeric $(TCNQ)_2^{2-}$, except for the green salt of $(CH_2)_2\langle^{S}_{S}\rangle C{=}\overset{+}{N}(n\text{-}C_8H_{17})_2\cdot TCNQ^{\overline{\cdot}}$ which consists of the iminium cation and discrete TCNQ$^{\overline{\cdot}}$ radical anion. Electronic spectra of the 1 : 2 and 2 : 3 complex salts also are discussed in comparison with analogous TCNQ$^{\overline{\cdot}}$ salts reported so far.

In the previous paper,[1)] we reported the preparation and electrical resistivity of some simple and complex salts formed between *N*,*N*-dialkyl-1,3-dichalcogenacycloalkan-2-iminium cations and 7,7,8,8-tetracyanoquinodimethane (TCNQ) radical anion; $(CH_2)_n\langle^{Y}_{Y}\rangle C{=}\overset{+}{N}R_2\cdot TCNQ^{\overline{\cdot}}$ and $(CH_2)_n\langle^{Y}_{Y}\rangle C{=}\overset{+}{N}R_2\cdot(TCNQ)_2^{\overline{\cdot}}$ ($n=2$, 3; Y=S, Se; R=Me, Et; but not all combinations). The resistivities of the simple salts as compacted samples fell in the 10^4—10^5 ohm cm range at 25 °C with the activation energies of 0.27—0.37 eV. The complex salts (compacted samples) exhibited the resistivities of 2.4 to 4.0 ohm cm with very small activation energies (0.018—0.087 eV); there was no appreciable difference of the resistivity between the *N*,*N*-dimethyl- and *N*,*N*-diethyliminium–$(TCNQ)_2^{\overline{\cdot}}$.

The present work was undertaken to study the effect of the *N*-substituents of the iminium cations on the composition and electrical resistivity of the TCNQ$^{\overline{\cdot}}$ salts. This paper reports the preparation and electrical resistivity of a series of simple and complex salts of TCNQ$^{\overline{\cdot}}$ radical anion with *N*,*N*-disubstituted 1,3-dithiolan-2-iminium cations, $(CH_2)_2\langle^{S}_{S}\rangle C{=}\overset{+}{N}R^1R^2$ ($R^1=R^2=n$-Pr, n-Bu, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, Ph, and $R^1=$Me and $R^2=$Ph). The resistivity is discussed in terms of stacking of TCNQ$^{\overline{\cdot}}$ on the basis of electronic absorption spectra and magnetic susceptibilities in the solid state.

Experimental

Materials. Bis(*N*,*N*-disubstituted 1,3-dithiolan-2-iminium) tetrabromodimethylstannate(IV), $[(CH_2)_2\langle^{S}_{S}\rangle C{=}\overset{+}{N}R_2]_2\cdot[SnBr_4Me_2]^{2-}$, was synthesized by reaction of bis(*N*,*N*-disubstituted dithiocarbamato)dimethyltin(IV), $Me_2Sn(S_2CNR_2)_2$, with 1,2-dibromoethane by a manner similar to the *N*,*N*-dimethyliminium analog.[2)] R=n-Pr, mp 143.5—145.5 °C. Found: C, 27.28; H, 4.73; N, 3.32%. Calcd for $C_{20}H_{42}N_2S_4Br_4Sn$: C, 27.38; H, 4.84; N, 3.19%. R=n-Bu, mp 121—122.5 °C. Found: C, 30.74; H, 5.38; N, 3.02%. Calcd for $C_{24}H_{50}N_2S_4Br_4Sn$: C, 30.88; H, 5.41; N, 3.00%. R=n-C_6H_{13}, mp 86—87 °C. Found: C, 36.54; H, 6.28; N, 2.78%. Calcd for $C_{32}H_{66}N_2S_4Br_4Sn$: C, 36.76; H, 6.38; N, 2.68%. R=n-C_8H_{17}, mp 86—88 °C. Found: C, 41.31; H, 7.10; N, 2.48%. Calcd for $C_{40}H_{82}N_2S_4Br_4Sn$: C, 41.49; H, 7.15; N, 2.42%. R=n-$C_{10}H_{21}$, mp 88—91 °C. Found: C, 45.07; H, 7.79; N, 2.24%. Calcd for $C_{48}H_{98}N_2S_4Br_4Sn$: C, 45.39; H, 7.79; N, 2.21%. R=Ph, mp 153—157 °C. Found: C, 37.47; H, 3.37; N, 2.74%. Calcd for $C_{32}H_{34}N_2S_4Br_4Sn$: C, 37.93; H, 3.39; N, 2.77%.

N-Methyl-*N*-phenyl-1,3-dithiolan-2-iminium trichlorodimethyl-stannate(IV), $(CH_2)_2\langle^{S}_{S}\rangle C{=}\overset{+}{N}MePh\cdot[SnCl_3Me_2]^-$,[2)] was prepared as described in the literature.

N,N-*Disubstituted 1,3-Dithiolan-2-iminium-TCNQ Simple Salts,* $(CH_2)_2\langle^{S}_{S}\rangle C{=}\overset{+}{N}R^1R^2\cdot TCNQ^{\overline{\cdot}}$ *(*$R^1=R^2=$n-*Pr (1),* n-C_6H_{13} *(2),* n-C_8H_{17} *(3), Ph (4), and* $R^1=$*Me and* $R^2=$*Ph (5).)* To a solution of $Li^+TCNQ^{\overline{\cdot}}$ (2.4 mmol) in hot ethanol was added a hot ethanol solution of $[(CH_2)_2\langle^{S}_{S}\rangle C{=}\overset{+}{N}(n\text{-}Pr)_2]_2\cdot[SnBr_4Me_2]^{2-}$ (1.2 mmol). The mixture was filtered. The filtrate was allowed to stand in a refrigerator overnight to afford **1**, which was recrystallized from acetonitrile, 71% yield. Other four simple salts were similarly prepared by reaction of TCNQ$^{\overline{\cdot}}$ with the appropriate iminium cation in ethanol, 70—83% yields. Of these salts, **3** was obtained as a mixture of violet crystals (**3a**) and green ones (**3b**). These were separated by fractional crystallization from ethanol.

N,N-*Disubstituted 1,3-Dithiolan-2-iminium-TCNQ Complex Salts,* $(CH_2)_2\langle^{S}_{S}\rangle C{=}\overset{+}{N}R^1R^2\cdot(TCNQ)_2^{\overline{\cdot}}$ *(*$R^1=R^2=$n-*Pr (6), Ph (8), and* $R^1=$*Me and* $R^2=$*Ph (9)).* To a hot acetonitrile solution of **1** obtained as above (1.5 mmol) was added neutral TCNQ (1.5 mmol) in hot acetonitrile. After filtration, the mixture was allowed to stand in a refrigerator overnight to afford **6**, 73% yield. Complex salts **8** and **9** were similarly prepared by reaction of **4** or **5** with TCNQ at the mole ratio of 1:1 in acetonitrile, 75 and 78% yields respectively.

TABLE 1. PROPERTIES AND ANALYTICAL DATA OF THE $\mathrm{TCNQ}^{\cdot-}$ SALTS

No.	Compound		Mp (dec) °C	%C Found (Calcd)	%H Found (Calcd)	%N Found (Calcd)
1	$\Big[{}^{\mathrm{S}}_{\mathrm{S}}\!>\mathrm{C{=}\overset{+}{N}}(n\text{-Pr})_2\cdot\mathrm{TCNQ}^{\cdot-}$	Purple needles	131—133	61.32 (61.73)	5.29 (5.44)	17.06 (17.14)
2	$\Big[{}^{\mathrm{S}}_{\mathrm{S}}\!>\mathrm{C{=}\overset{+}{N}}(n\text{-C}_6\mathrm{H}_{13})_2\cdot\mathrm{TCNQ}^{\cdot-}$	Purple needles	>110	65.41 (65.80)	6.80 (6.97)	14.52 (14.22)
3a	$\Big[{}^{\mathrm{S}}_{\mathrm{S}}\!>\mathrm{C{=}\overset{+}{N}}(n\text{-C}_8\mathrm{H}_{17})_2\cdot\mathrm{TCNQ}^{\cdot-}$	Violet needles	97— 98	67.98 (67.83)	7.59 (7.73)	12.90 (12.76)
3b	$\Big[{}^{\mathrm{S}}_{\mathrm{S}}\!>\mathrm{C{=}\overset{+}{N}}(n\text{-C}_8\mathrm{H}_{17})_2\cdot\mathrm{TCNQ}^{\cdot-}$	Green plates	97— 98	68.01 (67.83)	7.64 (7.73)	12.87 (12.76)
4	$\Big[{}^{\mathrm{S}}_{\mathrm{S}}\!>\mathrm{C{=}\overset{+}{N}Ph_2}\cdot\mathrm{TCNQ}^{\cdot-}$	Dark-purple needles	>140	67.18 (68.04)	3.63 (3.81)	14.84 (14.70)
5	$\Big[{}^{\mathrm{S}}_{\mathrm{S}}\!>\mathrm{C{=}\overset{+}{N}MePh}\cdot\mathrm{TCNQ}^{\cdot-}$	Purple needles	>170	63.23 (63.74)	3.67 (3.90)	16.92 (16.90)
6	$\Big[{}^{\mathrm{S}}_{\mathrm{S}}\!>\mathrm{C{=}\overset{+}{N}}(n\text{-Pr})_2\cdot(\mathrm{TCNQ})_2^{\cdot-}$	Black needles	>212	64.58 (64.68)	4.04 (4.29)	20.85 (20.58)
7	$\Big[{}^{\mathrm{S}}_{\mathrm{S}}\!>\mathrm{C{=}\overset{+}{N}}(n\text{-Bu})_2\cdot(\mathrm{TCNQ})_2^{\cdot-}$	Black plates	>196	65.83 (65.59)	4.28 (4.73)	20.42 (19.68)
8	$\Big[{}^{\mathrm{S}}_{\mathrm{S}}\!>\mathrm{C{=}\overset{+}{N}Ph_2}\cdot(\mathrm{TCNQ})_2^{\cdot-}$	Black plates	>195	68.59 (68.80)	2.91 (3.26)	18.23 (18.52)
9	$\Big[{}^{\mathrm{S}}_{\mathrm{S}}\!>\mathrm{C{=}\overset{+}{N}MePh}\cdot(\mathrm{TCNQ})_2^{\cdot-}$	Black needles	>222	65.87 (65.99)	3.02 (3.26)	20.38 (20.38)
10	$\Big[\Big[{}^{\mathrm{S}}_{\mathrm{S}}\!>\mathrm{C{=}\overset{+}{N}}(n\text{-C}_{10}\mathrm{H}_{21})_2\Big]_2\cdot(\mathrm{TCNQ})_3^{2\cdot-}$	Dark-purple needles	88— 90	69.65 (69.64)	7.44 (7.43)	13.61 (13.87)

N,N-Dibutyl- and N,N-Didecyl-1,3-dithiolan-2-iminium-TCNQ Complex Salts, $(\mathrm{CH_2})_2\!<{}^{S}_{S}\!>\mathrm{C{=}\overset{+}{N}}(n\text{-Bu})_2\cdot(\mathrm{TCNQ})_2^{\cdot-}$ *(7) and* $[(\mathrm{CH_2})_2\!<{}^{S}_{S}\!>\mathrm{C{=}\overset{+}{N}}(n\text{-C}_{10}\mathrm{H}_{21})_2]_2\cdot(\mathrm{TCNQ})_3^{2\cdot-}$ *(10).* The reaction of $\mathrm{Li^+TCNQ^{\cdot-}}$ (2.4 mmol) with $[(\mathrm{CH_2})_2\!<{}^{S}_{S}\!>\mathrm{C{=}\overset{+}{N}}(n\text{-Bu})_2]_2\cdot[\mathrm{SnBr_4Me_2}]^{2-}$ (1.2 mmol) in hot ethanol was carried out as described in **1**, giving **7**, which was recrystallized from acetonitrile, 65% yield based on $\mathrm{Li^+TCNQ^{\cdot-}}$. Similarly, $\mathrm{Li^+TCNQ^{\cdot-}}$ reacted with $[(\mathrm{CH_2})_2\!<{}^{S}_{S}\!>\mathrm{C{=}\overset{+}{N}}(n\text{-C}_{10}\mathrm{H}_{21})_2]_2\cdot[\mathrm{SnBr_4Me_2}]^{2-}$ at the mole ratio of 2:1 in ethanol to afford **10**, 63% yield based on $\mathrm{Li^+TCNQ^{\cdot-}}$.

Elemental analyses and properties of the simple and complex salts obtained are listed in Table 1.

Physical Measurements. Electrical resistivities, electronic absorption and infrared spectra, and magnetic susceptibilities were measured as described previously.[1]

Results and Discussion

Synthesis and Electrical Properties. The reaction of *N,N*-dibutyl- and *N,N*-didecyl-1,3-dithiolan-2-iminium cations with $\mathrm{TCNQ}^{\cdot-}$ radical anion gave the 1 : 2 and 2 : 3 complex salts, **7** and **10**, respectively, irrespective of the mole ratio of the reactants. These results are analogous to the reaction of the *N,N*-diethyliminium cation with $\mathrm{TCNQ}^{\cdot-}$.[1] There are two possible oxidizing agents in the reaction mixture. One is the iminium cation, because the cation easily undergoes a nucleophilic attack on the carbon atom at the 2, 4, or 5 position.[3] The other is the $[\mathrm{SnBr_4Me_2}]^{2-}$ anion which may be reduced to give any Sn(II) species. However, no reduced product has been obtained in the present study. On the other hand, the other iminium cations used here reacted with $\mathrm{TCNQ}^{\cdot-}$ to give simple salts **1**—**5**, of which **3** was obtained in two crystalline forms with different colors; violet needles (**3a**) and green plates (**3b**). Crystals **3a** slowly changed in color to green at room temperature irreversibly, suggesting that **3a** is in a metastable state. This color change occurred instantly on heating **3a** at 70 °C. Simple salts **1**, **4**, and **5** further reacted with an equimolar amount of neutral TCNQ to yield complex salts **6**, **8**, and **9**, respec-

TABLE 2. ELECTRICAL RESISTIVITY (ρ) AND ACTIVATION ENERGY (E_a) OF THE $\mathrm{TCNQ}^{\cdot-}$ SALTS

Compound	$\rho_{25\,^\circ\mathrm{C}}$[a] / ohm cm	E_a / eV
Simple salt		
1	2.2×10^5	0.20
2	1.3×10^7	0.54
3b	1.9×10^9	1.3
4	4.4×10^3 (5.0×10^3)	0.16
5	8.2×10^5	0.29
Complex salt		
6	6.9×10	0.061
7	9.0×10	0.099
8	3.4×10 (3.3×10)	0.12
9	5.4	0.059
10	6.3×10^6	0.53

a) The values in parentheses were obtained by the four-probe method.

tively. On the other hand, **2** and **3** were only recovered in their reactions with neutral TCNQ in acetonitrile.

The electrical resistivities (ρ) of simple and complex salts at 25 °C and the activation energies (E_a) calculated from the equation $\rho=\rho_0\exp(E_a/kT)$ are listed in Table 2. The resistivity of **3a** has not been measured for its thermal instability as described above. All the simple and complex salts show typical semi-conducting behavior in the temperature range measured. The resistivity of **9** is low in the same degree as those of the corresponding *N*,*N*-dimethyl- and *N*,*N*-diethyliminium salts, $(CH_2)_2\langle^{S}_{S}\rangle C{=}\overset{+}{N}R_2\cdot(TCNQ)_2^{\overline{\cdot}}$ (3.8 and 3.3 ohm cm for R=Me and Et, respectively).1) Other 1 : 2 complex salts obtained here showed about 10 times higher resistivities than **9** as well as the *N*,*N*-dimethyl- and *N*,*N*-diethyliminium analogs. This result seems to indicate that the electrical resistivity of the 1 : 2 complex salts increases by introducing bulky substituents on the iminium nitrogen.

Electronic Spectra and Magnetic Susceptibilities. Figure 1 shows the electronic absorption spectra of **1** and **2** in the solid state. These spectral patterns closely resemble those of analogous simple salts, $(CH_2)_n\langle^{S}_{S}\rangle C{=}\overset{+}{N}Me_2\cdot TCNQ^{\overline{\cdot}}$ (n=2 or 3) and $(CH_2)_2\langle^{Se}_{Se}\rangle C{=}\overset{+}{N}Me_2\cdot TCNQ^{\overline{\cdot}}$, which have been reported to involve dimeric $(TCNQ)_2{}^{2-}$.1) The existence of the $(TCNQ)_2{}^{2-}$ dimer in **1** and **2** is also suggested from their diamagnetic properties in the solid state ($\chi_M=-3.4\times10^{-4}$ and -4.5×10^{-4} emu mol^{-1}, respectively). Many TCNQ$^{\overline{\cdot}}$ simple salts reported so far exhibit a band in the 8000—10000 cm^{-1} region, which has been assigned to the charge-transfer (CT) transition between TCNQ$^{\overline{\cdot}}$ radical anions.1,4,5) It is noted that the CT band of **2** was fairly blue-shifted compared with **1**. This fact may be correlated with the higher electrical resistivity and the larger activation energy of **2** than **1**. Simple salts **4** and **5** in the solid state exhibited electronic absorption spectra similar to that of **1**, as shown in Table 3. They also showed diamagnetic properties at room temperature. These facts confirm that dimeric $(TCNQ)_2{}^{2-}$ also exists in solid **4** and **5**.

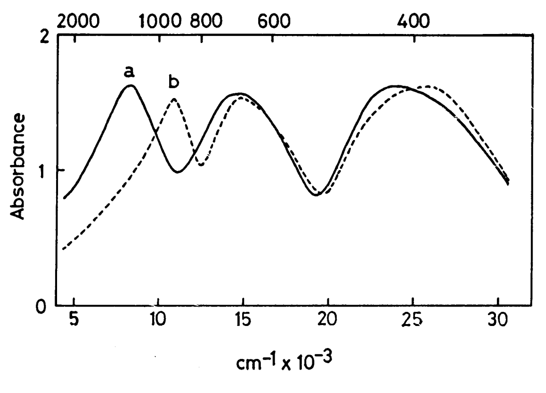

Fig. 1. Absorption spectra of **1** (a) and **2** (b) in Nujol mulls.

Table 3. Absorption maxima of the electronic spectra of the TCNQ$^{\overline{\cdot}}$ salts in Nujol mulls

Compound	cm^{-1}×10^{-3} a)						
1		8.4			14.7	23.8	
2		10.9			14.9	26.0	
3a		9.1			14.9	24.1	
3b			11.2	13.0		22.2—25.6	
4		8.6			14.5	23.8	
5		8.8			14.9	23.8	
6			10.4	11.6	(17)	25.3	
7			9.8	11.1	(17)	25.0	
8			9.6	11.0	(17)	24.4	
9			10.0	11.4	(17)	26.3	
10	5.3	11.2			17.7	24.4	26.3

a) Shoulders in parentheses.

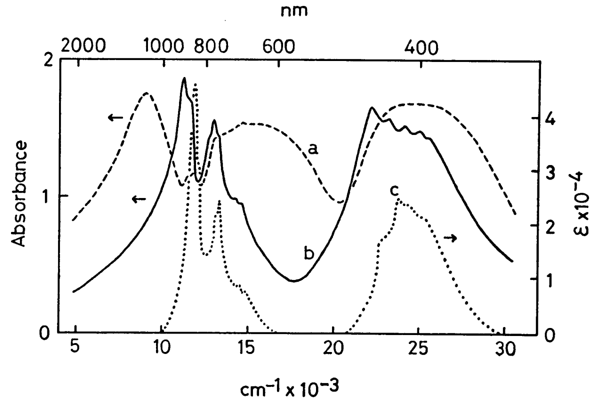

Fig. 2. Absorption spectra of **3a** (a) **3b** (b) in Nujol mulls, and of **3a** or **3b** in acetonitrile (c).

Figure 2 illustrates the electronic absorption spectra of **3a** and **3b** in the solid state and in acetonitrile. Solid **3a** exhibited three absorptions, and the spectral pattern resembles that of **1** shown in Fig. 1, suggesting that the stacking of TCNQ$^{\overline{\cdot}}$ in **3a** can be described in terms of a dimeric pair. On the other hand, solid **3b** displayed a quite different spectrum from those of other simple salts; the spectrum of **3b** is rather similar in appearance to that of **3a** or **3b** in acetonitrile, where the salt is expected to dissociate into the iminium cation and TCNQ$^{\overline{\cdot}}$ radical anion.1) This observation shows that solid **3b** essentially consists of the iminium cation and the discrete TCNQ$^{\overline{\cdot}}$ radical anion. This is also supported from the observation that **3b** exhibited a large paramagentic susceptibility ($\chi_M=1.2\times10^{-3}$ emu mol^{-1}) in the solid state at room temperature, while **3a** showed a diamagentic property ($\chi_M=-5.7\times10^{-4}$ emu mol^{-1}). This result is consistent with high electrical resistivity and large activation energy of **3b** compared with other simple salts (Table 2).

Figure 3 shows the electronic absorption spectra of complex salts **8** and **10** in the solid state. The spectrum of **8** resembles not only those of the *N*,*N*-dimethyl- and *N*,*N*-diethyliminium analogs1) but also the reflectance spectra of several TCNQ$^{\overline{\cdot}}$ complex salts such as with $MePh_3P^+$ and *N*-propylquinolinium$^+$.4) Similar spectra were observed in other 1:2 complex salts, **6**, **7**, and

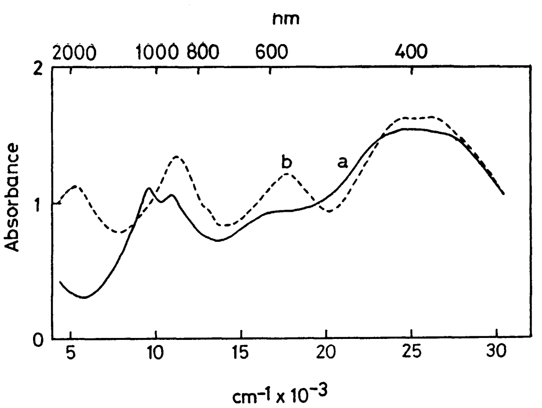

Fig. 3. Absorption spectra of **8** (a) and **10** (b) in Nujol mulls.

9 (Table 3). Furthermore, complex salts **6**—**9** exhibited the CT band between $\mathrm{TCNQ}^{\cdot-}$ and TCNQ in the 3400—2700 cm^{-1} range in the infrared spectra, as the *N*,*N*-dimethyl- and *N*,*N*-diethyliminium analogs[1] and $\mathrm{MePh_3P^+(TCNQ)_2^{\cdot-}}$[4] did.

The spectrum of 2:3 complex salt **10** in the solid state showed four absorption bands (Table 3). Except for the lowest energy band at 5300 cm^{-1}, the appearance of the spectrum roughly resembles those of the simple salts except for **3b**, suggesting the existence of dimeric $\mathrm{(TCNQ)_2^{2\cdot-}}$. This is compatible with the diamagnetism of **10** ($\chi_{\mathrm{M}} = -5.2\times10^{-4}$ emu mol^{-1}). The lowest energy band may tentatively be assigned to the CT transition between $\mathrm{TCNQ}^{\cdot-}$ and TCNQ. The spectral features of **10** are nearly coincident with those of the reflectance spectra of $\mathrm{(Cs^+)_2(TCNQ)_3^{2\cdot-}}$ and (morpholinium$^+$)$_2$$\mathrm{(TCNQ)_3^{2\cdot-}}$.[4] Complex salt **10** is therefore suggested to have a stacking of TCNQ moiety similar to the Cs$^+$ and morpholinium$^+$ salts, whose X-ray structure analyses revealed that interplanar separations of the TCNQ moieties are short enough to cause a CT interaction, while there exists the unit consisting of two $\mathrm{TCNQ}^{\cdot-}$ radical anions and one neutral TCNQ.[6,7]

References

1) S. Araki, H. Ishida, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **51**, 407 (1978).

2) T. Tanaka and T. Abe, *Inorg. Nucl. Chem. Lett.*, **4**, 569 (1968); T. Tanaka, K. Tanaka, and T. Yoshimitsu, *Bull. Chem. Soc. Jpn.*, **44**, 112 (1971).

3) T. Nakai and M. Okawara, *Tetrahedron Lett.*, **1967**, 3835.

4) Y. Iida, *Bull. Chem. Soc. Jpn.*, **42**, 71, 637 (1969).

5) J. Tanaka, M. Tanaka, T. Kawai, T. Takabe, and O. Maki, *Bull. Chem. Soc. Jpn.*, **49**, 2358 (1976).

6) C. J. Fritchie, Jr. and P. Arthur, Jr., *Acta. Crystallogr.*, **21**, 139 (1966).

7) T. Sundaresan and S. C. Wallwork, *Acta Crystallogr., B*, **28**, 491 (1972).