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Synthesis and Electrical Resistivity of TCNQ Radical Anion Salts with 4,5-Disubstituted *N*,*N*-Dimethyl-1,3-dithiolan-2-iminium Cations

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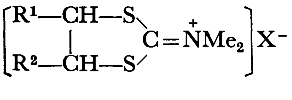
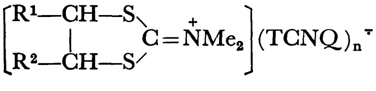
Synopsis. The title salts with the formula $[\overline{\text{S-CHR}^1\text{-CHR}^2\text{-S-C}}\text{=}\overset{+}{\text{N}}\text{Me}_2](\text{TCNQ})_n^{\dot{-}}$ (R^1,R^2=Me, H; Et, H; Ph, H; Me, Me; and Me, Br; $n=1$ and 2) were prepared. Electrical resistivities, electronic spectra, and magnetic susceptibilities of these salts in the solid state are reported.

Recently, one of the authors reported the preparation of a series of 7,7,8,8-tetracyanoquinodimethane (TCNQ) radical anion salts with *N*,*N*-dialkyl-1,3-dithiolan-2-iminium cations, $[\overline{\text{S(CH}_2)_2\text{SC}}\text{=}\overset{+}{\text{N}}\text{R}_2](\text{TCNQ})_n^{\dot{-}}$ (R= Me, Et, *n*-Pr, *n*-Bu, *n*-C_6H_{13}, and *n*-C_8H_{17}; $n=1$ and 2, but not all combinations),[1,2] whose electrical resistivities increase with the bulkiness of substituents on the iminium nitrogen atom for each series of $n=1$ and 2, respectively.[2] The present work was undertaken to examine the effect of substituents on the dithiolane ring on the resistivity of TCNQ$^{\dot{-}}$ radical anion salts. This note reports the preparation and the electrical resistivities of some simple and complex salts of TCNQ$^{\dot{-}}$ radical anion with 4,5-disubstituted *N*,*N*-dimethyl-1,3-dithiolan-2-iminium cations, $[\overline{\text{S-CHR}^1\text{-CHR}^2\text{-S-C}}\text{=}\overset{+}{\text{N}}\text{Me}_2](\text{TCNQ})_n^{\dot{-}}$ (R^1,R^2=Me,H; Et,H; Ph,H; Me,Me; and Me,Br; $n=1$ and 2). Electronic spectra and magnetic susceptibilities of these salts are described in terms of the modes of stacking of TCNQ in the solid state. For the sake of abbreviation, the following numbers are used for compounds appeared in this note.

Compound	Number	R¹	R²	X
	**1a**	Me	H	Br
	1b	Et	H	Br
	1c	Ph	H	Br
	1d	Me	Me	PF_6
	1e	Me	Br	Br
Compound	**Number**	**R¹**	**R²**	***n***
	**2a**	Me	H	1
	2b	Et	H	1
	2c	Ph	H	1
	2d	Me	Me	1
	2e	Me	Br	1
	3a	Me	H	2
	3b	Et	H	2
	3c	Ph	H	2
	3d	Me	Me	2
	3e	Me	Br	2

Experimental

Materials. Compounds **1a**—**c** were prepared by the reactions of sodium dimethyldithiocarbamate, $Na(S_2CNMe_2)$, with 1,2-dibromopropane, 1,2-dibromobutane, and 1-phenyl-1,2-dibromoethane, respectively, in refluxing acetone by the procedure described elsewhere.[3] The reaction of $Na(S_2CNMe_2)$ with 2,3-dibromobutane in refluxing acetone yielded an oily product, which was dissolved in ethanol, followed by the addition of an equimolar ethanol solution of $NaPF_6$ to give white microcrystals of **1d**. Recrystallization was carried out from dichloromethane–petroleum ether (1 : 1). Compound **1e** was obtained according to the literature method.[4]

Preparation of Simple Salts 2a—e. To a filtered solution of Li$^+$TCNQ$^{\dot{-}}$ (0.74 g, 3.5 mmol) in boiling ethanol (40 cm^3) was added a hot ethanol (20 cm^3) solution of **1a** (0.85 g, 3.5 mmol). The mixture was allowed to stand in a refrigerator overnight. The resulting precipitate was collected by filtration and recrystallized from ethanol to afford purple plates of **2a** in 85% yield. Similarly, purple needles or plates of **2b**—**e** were prepared in 60—80% yields by the equimolar reactions of Li$^+$TCNQ$^{\dot{-}}$ with **1b**—**e**, respectively, in ethanol.

Preparation of Complex Salts 3a—e. To a hot acetonitrile (30 cm^3) solution of **2a** (0.52 g, 1.4 mmol) was added a solution of neutral TCNQ (0.29 g, 1.4 mmol) in boiling acetonitrile (30 cm^3). The mixture was allowed to stand in a refrigerator overnight, giving black microcrystals of **3a**, which was recrystallized from acetonitrile, 68% yield. Dark violet or black crystals of **3b**—**e** were obtained similarly in 45—76% yields by the reaction of neutral TCNQ with the appropriate simple salts in acetonitrile.

Table 1. Melting point and analytical data of the TCNQ$^{\dot{-}}$ salts

Salt	Mp(dec) / °C	%C Found (Calcd)	%H Found (Calcd)	%N Found (Calcd)
2a	174—177	59.06 (58.99)	4.20 (4.40)	19.36 (19.11)
2b	139—141	59.75 (59.98)	4.57 (4.77)	18.18 (18.41)
2c	166—168	64.51 (64.46)	4.13 (4.23)	16.45 (16.34)
2d	166—168	59.78 (59.98)	4.60 (4.77)	18.43 (18.41)
2e	174—176	48.40 (48.54)	3.22 (3.39)	15.63 (15.72)
3a	231—233	62.84 (63.14)	3.45 (3.53)	22.02 (22.09)
3b	218—221	63.64 (63.68)	3.48 (3.79)	21.38 (21.56)
3c	211—214	66.27 (66.44)	3.38 (3.50)	19.83 (19.92)
3d	238—240	63.82 (63.68)	3.48 (3.79)	21.82 (21.56)
3e	185—186	55.43 (55.47)	2.75 (2.95)	19.45 (19.41)

Physical Measurements. Electrical resistivities, electronic and infrared absorption spectra, and magnetic susceptibilities were measured as described previously.[2]

Results and Discussion

All the simple and complex salts obtained are stable

Table 2. Electrical resistivity(ρ), activation energy (E_a), magnetic susceptibility(χ_M), and absorption maxima (λ_{max}) of the $\text{TCNQ}^{\overline{\cdot}}$ salts

Salt	$\rho_{25°C}$ / Ω cm	E_a[a)] / eV	χ_M[b)] / 10^{-4}emu mol^{-1}	λ_{max}[c)] / 10^3cm^{-1}			
2a	2.1×10^8	0.77	−1.9	8.3		14.7	23.8
2b	1.2×10^8	0.80	−1.9	11.1		14.1	25.0
2c	1.3×10^7	0.46	−2.0	11.1		14.2	25.4
2d	2.2×10^6	0.42	−1.5	8.5		14.2	24.3
2e	8.8×10^5	0.44	−1.8	8.9		15.2	24.4
3a	36	0.068	+3.8	10.0	11.1	15.4	24.6
3b	10	0.038	+4.3	10.0	11.4	16.0	25.3
3c	5.1	0.046	+1.7	10.0	11.5	(18.2)	25.6
3d	3.8	0.11	+4.9	9.9	10.8	16.0	25.4
3e	520	0.13	+7.8	10.3	11.9	15.4	25.6

a) Calculated from the expression $\rho=\rho_0\exp(E_a/kT)$. b) Measured at room temperature. c) Measured in Nujol mulls, and shoulder in parenthesis.

to air. Plots of log ρ (ρ: electrical resistivities as compacted sample) *vs.* the reciprocal temperature ($1/T$) for each salt show a good linear relation in the 20—90 °C range, indicating that all the salts are typical semiconductors in the temperature range measured. The ρ values of simple salts **2a**—**e** and complex salts **3a**—**e** at 25 °C (Table 2) are the same order of magnitude as or larger by one or two orders of magnitude than those of the iminium salts without substituents on the 1,3-dithiolane ring, $[\overline{\text{S(CH}_2)_2\text{SC}}{=}\overset{+}{\text{N}}\text{Me}_2](\text{TCNQ})_n^{\overline{\cdot}}$ (8.7×10^5 Ω cm for $n=1$ and 3.8 Ω cm for $n=2$),[1)] respectively. In view of these results, there may be a trend that the introduction of substituents on the 1,3-dithilane ring results in occasional increases of the resistivity of the $\text{TCNQ}^{\overline{\cdot}}$ radical anion salts depending on the nature of substituents, although no detail of the trend is evident in this study.

The electronic absorption spectra of simple salt **2a** and complex salt **3a** in the solid state (Fig. 1) resemble well those of the iminium salts without substituents on the 1,3-dithiolane ring, as one may expect. The spectral patterns similar to **2a** and **3a** were obtained for simple salts **2b**—**e** and complex salts **3b**—**e**, respectively, except that the lowest frequency bands of **2b** and **2c**, assignable to charge-transfer (CT) transitions between the $\text{TCNQ}^{\overline{\cdot}}$ radical anions,[5)] are shifted to higher frequencies than that of **2a** (Table 2). In addition, all the complex salts exhibited a broad absorption band in the 4000—2500 cm^{-1} range, which is due to the CT transition between the $\text{TCNQ}^{\overline{\cdot}}$ radical anion and neutral TCNQ.[5)] These results can be subjected to the same discussion as that given previously,[1)] which leads us to the conclusion that simple salts **2a**—**e** involve the $(\text{TCNQ})_2^{2-}$ dimer, whereas complex salts **3a**—**e** contain monomeric $\text{TCNQ}^{\overline{\cdot}}$ radical anions in their columnar structure in the solid state. This is consistent with the facts that simple and complex salts show diamagnetic and paramagnetic properties, respectively, at room temperature (Table 2).

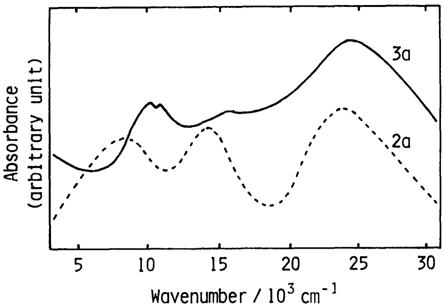


Fig. 1. Absorption spectra of **2a** and **3a** in Nujol mulls.

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