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NOVEL TETRACYANOQUINODIMETHAN ANION RADICAL SALTS OF HETEROCYCLIC CATIONS CONTAINING A TROPYLIUM ION SKELETON

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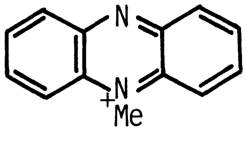
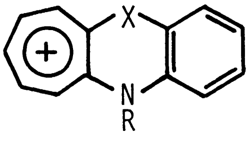
Heterocyclic cations containing a tropylium ion skeleton form 1:1 simple salts with tetracyanoquinodimethan anion radical, which show good conductivities and novel values of nitrile stretching frequencies. The reduction potentials of cations are related to the reactivities of the salt formation as well as the conductivities of the salts.

Tetracyanoquinodimethan anion radical ($\mathrm{TCNQ}^{\overline{\cdot}}$) forms organic semiconductors with a large number of cations.1) However, 1:1 $\mathrm{TCNQ}^{\overline{\cdot}}$ salts of heterocyclic cations except N-methylphenazinium (NMP)2) exhibit low conductivities.1) We report here a new type of conducting 1:1 $\mathrm{TCNQ}^{\overline{\cdot}}$ salts of heterocyclic cations **1** containing a tropylium ion and a heterocyclic ring related to NMP.

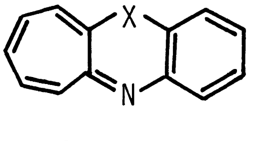
Heterocyclic cations **1a**-**1e** were prepared from the corresponding heterocycles, N-methylcyclohepta[b][1,4]benzodiazine (**2a**),3) cyclohepta[b][1,4]benzoxazine (**2b**),4) and cyclohepta[b][1,4]benzothiazine (**2c**),5,6) by protonation with hydrogen chloride or methylation with methyl iodide.7) Cation **1f** was prepared as the $\mathrm{BF_4}^-$ salt by Nozoe's method.6) When each boiling ethanol solution of the salts of **1a**-**1e** and $\mathrm{TCNQ}^{\overline{\cdot}}$ lithium salt were mixed, 1:1 salts (**1**-$\mathrm{TCNQ}^{\overline{\cdot}}$) precipitated. In the case of **1f**, acetone was used as a solvent instead of ethanol due to insolubility of the $\mathrm{BF_4}^-$ salt. In that case, only a 1:2 salt [**1f**-$(\mathrm{TCNQ})_2^{\overline{\cdot}}$] was obtained.



NMP

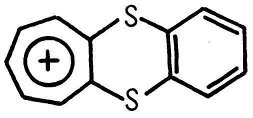


	X	R
1a;	NMe	H
1b;	NMe	Me
1c;	O	H
1d;	O	Me
1e;	S	H
1f;	S	Me



2a; X=NMe
2b; X=O
2c; X=S

The 1:2 salts of cations **1b**-**1e** were prepared by treating the 1:1 salts with another equivalent of TCNQ in boiling acetonitrile although that of **1a** could not be purely obtained. The molar ratios were determined based on the elemental analyses.[8) These salts obtained here are the first TCNQ salts of tropylium ion species. The electrical resistivities of the salts measured as compressed pellets at room temperature are shown in Table 1 together with the decomposition points (decomp.) and nitrile stretching frequencies of the salts. It should be noted here that the 1:1 TCNQ$^{\bar{\cdot}}$ salts of **1c**, **1d**, and **1e** exhibit good conductivities. These values are significantly high in the TCNQ$^{\bar{\cdot}}$ simple salts.[1,9) The 1:2 salts are more conductive than the corresponding 1:1 salts as found in a lot of TCNQ$^{\bar{\cdot}}$ salts with heterocyclic cations.[1)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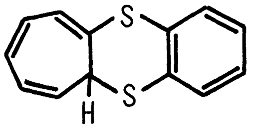
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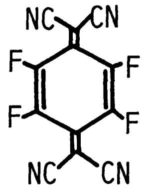
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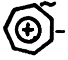
In contrast, heterocyclic cation **3** with two sulfur atoms which were prepared as the BF_4^- salt by deprotonation of heterocycle **4**[10) with $NOBF_4$ in acetonitrile[11) underwent a chemical reaction with TCNQ$^{\bar{\cdot}}$ lithium salt to give neutral TCNQ and a heterocyclic compound derived from **3**[12) without the formation of any salts. The difference in the reactivities may be rationalized in terms of the redox potentials of the cations shown in Table 2, since the reduction potential of **3** is higher than that of **1** and almost the same as that of tropylium fluoroborate which also undergoes a reaction with TCNQ$^{\bar{\cdot}}$ to give neutral TCNQ and a coupling product without the salt formation.[13) This fact seems to indicate that tropylium ions with lower reduction potentials due to the interaction with electron donating substituents can form novel TCNQ$^{\bar{\cdot}}$ salts, whereas tropylium ions with higher reduction potentials undergo reactions with TCNQ$^{\bar{\cdot}}$. In addition, the fact that the cations **1a** and **1b** containing a NMe group in the bridge X and having lower reduction potentials form lower conductive salts may indicate that there is a low limit of the reduction potentials of the cations to show good conductivities as pointed out by Torrance.[1) This is supported by the finding that the anion radical of $TCNQF_4$ (**5**) which is a stronger acceptor than TCNQ forms a low conductive 1:1 salt with **3d** (ρ; 1.8×10^5 Ω cm).

Another interesting feature is that nitrile stretching frequencies of 1:1 salts are different from those of 1:2 salts, being lower than those of the metal salts of TCNQ$^{\bar{\cdot}}$.[14) This property is unusual since nitrile stretching frequencies of TCNQ complexes or salts are reported to be linearly correlated with the degree of charge transfer and are located between that of neutral TCNQ and those of the metal salts due to the partial electron transfer.[15) What makes this characteristic is still ambiguous. Further studies are in progress to investigate more

Table 1. Decomposition points, CN stretching frequencies, and electrical resistivities of $TCNQ^{\cdot-}$ salts of cations **1**

Compd	Decomp./°C	ν/cm^{-1}	ρ/Ω cm
1a-$TCNQ^{\cdot-}$	157-160	2173	7.1×10^7
1b-$TCNQ^{\cdot-}$	226-227	2167	7.4×10^7
1c-$TCNQ^{\cdot-}$	195-200	2170	1.9×10^3
1d-$TCNQ^{\cdot-}$	208-210	2173	1.4×10^3
1e-$TCNQ^{\cdot-}$	198-200	2178	2.8×10
1b-$(TCNQ)_2^{\cdot-}$	264-266	2193	9.0
1c-$(TCNQ)_2^{\cdot-}$	>350	2190	4.0
1d-$(TCNQ)_2^{\cdot-}$	251-255	2192	5.2
1e-$(TCNQ)_2^{\cdot-}$	>350	2188	4.3
1f-$(TCNQ)_2^{\cdot-}$	229-231	2190	1.3×10

Table 2. Redox potentials of cations **1**, **3**, and tropylium ion

Compd	$E_{1/2}^{ox}$ /V vs. SCE[a)]	$E_{1/2}^{red}$ /V vs. SCE[a)]
1a-Cl^-	1.10[b)]	-0.58[c)]
1b-BF_4^-	1.15[b)]	-0.85[c)]
1c-Cl^-	1.44[b)]	-0.43[c)]
1d-I^-	1.65[b)]	-0.55[c)]
1e-Cl^-	1.41[b)]	-0.47[c)]
1f-BF_4^-	1.54[b)]	-0.45[c)]
3-BF_4^-	1.86[b)]	-0.13[c)]
-BF_4^-	—	-0.16[c)]

a) Measured at a platinum electrode in acetonitrile with 0.1 mol dm^{-3} tetraethylammonium perchlorate as a supporting electrolyte; scan rate 100 mV s^{-1}. b) Irreversible. Calculated as E_{pa} (anodic peak potential) -0.03. c) Irreversible. Calculated as E_{pc} (cathodic peak potential) + 0.03.

detailed properties of these novel $\text{TCNQ}^{\bar{\cdot}}$ salts as well as to prepare $\text{TCNQ}^{\bar{\cdot}}$ salts of other tropylium ions.

References

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7) **1a**-Cl; decomp. 260 °C, **1b**-I; decomp. 267-268 °C, **1c**-Cl; decomp. 132-134 °C, **1d**-I; decomp. 196-198 °C, **1e**-Cl; decomp. 145-146 °C.
8) Satisfactory elemental analyses were obtained for all of the salts.
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11) Other methods of the deprotonation failed to give **3**. **3**-BF_4^-; decomp. 96 °C. This method using $NOBF_4$ seems to be useful for the deprotonation of cycloheptatrienes to produce tropylium ions.
12) The heterocyclic compound is a neutral molecule and easily forms a molecular complex with TCNQ. The structure is under study.
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14) The IR spectra of the $\text{TCNQ}^{\bar{\cdot}}$ salts of **1** were measured in KBr disks with a Shimadzu IR-435 spectrometer and a Shimadzu DR-1 data recorder. For comparisons, the nitrile stretching frequencies of $\text{TCNQ}^{\bar{\cdot}}$-Li, $\text{TCNQ}^{\bar{\cdot}}$-Na, and $\text{TCNQ}^{\bar{\cdot}}$-K were measured to be 2197, 2185, and 2188 cm^{-1}, respectively, which are almost identical with the reported values.15)
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