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Conductive Salts of Tropylium Ions with Tetracyanoquinodimethan Anion Radical ($TCNQ^{\cdot-}$) and Bisthiadiazolotetracyanoquinodimethan Anion Radical (BTDA-$TCNQ^{\cdot-}$)

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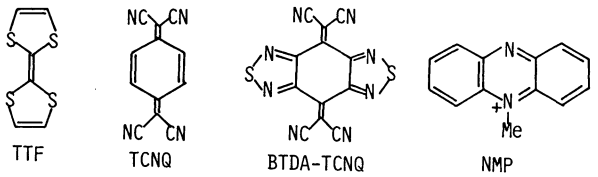
Tropylium ions have been found to be good cations for forming highly conductive salts of $TCNQ^{\cdot-}$. Tropylium ions with different reduction potentials were prepared. The first reduction potentials which are correlated with the substituent constants σ_p^+ control the formation of the salts. The cations with higher reduction potentials underwent a reaction with $TCNQ^{\cdot-}$ to give neutral TCNQ and coupling products. The molar ratios of the initially formed salts are also dependent on the reduction potentials. The simple salts are only formed when the reduction potentials are lower than −0.43 V. This fact is rationalized by the difference in the ease of electron transfer from $TCNQ^{\cdot-}$ to tropylium ions which is determined by the reduction potentials. Some simple salts show significantly low electrical resistivities compared with usual $TCNQ^{\cdot-}$ simple salts. BTDA-$TCNQ^{\cdot-}$ also gave conductive salts of tropylium ions, indicating that BTDA-TCNQ is useful for forming organic semiconductors.

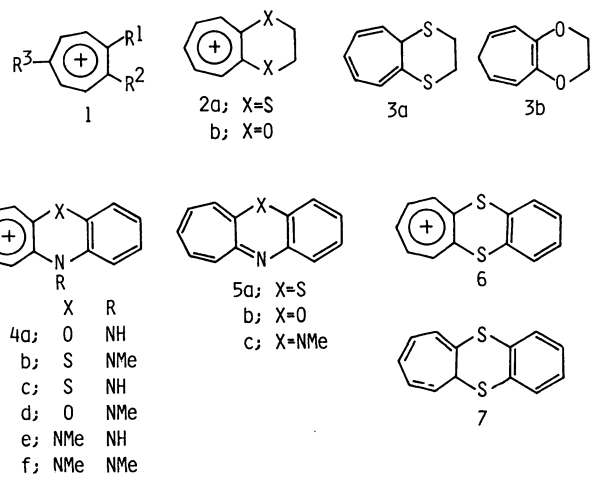
Recently much attention has been focused on organic conductors and the requirements for them have been proposed.[1] In the tetrathiafulvalene (TTF)-tetracyanoquinodimethan (TCNQ) system, the redox potentials are the most important factors to determine conductivity, where the difference between the first oxidation potentials for donors [E_1^{ox}(D)] and the first reduction potentials for acceptors [E_1^{red}(A)] is $-0.02<E_1^{ox}(D)-E_1^{red}(A)<0.34$ V for giving organic metals.[2] The difference in the redox potentials is related to the degree of charge transfer.[3] On the other hand, simple $TCNQ^{\cdot-}$ salts of cations usually exhibit low conductivity because of the complete charge transfer.[3,4] Therefore, the systematic study on the factors governing the conductivities of simple $TCNQ^{\cdot-}$ salts has not been done although the effect of the reduction potentials of cations has been pointed out by Torrance.[3] *N*-Methylphenazinium (NMP) which has a higher reduction potential compared with those for other cations is an exceptional cation whose 1:1 $TCNQ^{\cdot-}$ salt is an organic metal.[5] Tropylium ion whose reduction potential is close to that of NMP[6] has been reported to undergo a reaction with $TCNQ^{\cdot-}$ without formation of salts.[7] However, its derivatives still seemed attractive cations for preparing highly conductive salts as well as for the systematic study on the substituent effects for the following reasons. First, they are stable aromatic cations and can be easily functionalized to change electron affinity. Second, they have high polarizability which is related to the high conductivities of the complex salts of $TCNQ^{\cdot-}$ with heterocyclic cations.[8] Third, they are desirable cations for the investigation of substituent effects since substituents are directly attached to the delocalized cation ring. Finally, heteroatoms which increase intra- and interstack interactions for stabilizing the metallic state are easily introduced in the substituents. From these viewpoints, we have investigated the salt formation of tropylium ions with $TCNQ^{\cdot-}$ [9] as well as bis[1,2,5]thiadiazolotetracyanoquinodimethan anion radical (BTDA-$TCNQ^{\cdot-}$) which we prepared recently.[10]



Results and Discussion

Preparation of Tropylium Ions. Monocyclic tropylium ions **1a,b,g,j,k,o,r** are new compounds which were prepared by the following methods.[11] Reaction of 5-bromo-2-methoxytropone with trimethyloxonium tetrafluoroborate in nitromethane gave **1a** and **1b** in 12% and 61% yields, respectively. The similar reaction of 4-methoxytropone and 2-aminotropone led to the formation of **1k** and **1r** in 85% and 36% yields, respectively. Methylthio derivatives **1g,j,o** were synthesized by the reaction of the corresponding tropothiones with methyl iodide in ether in 70%, 25%, and 48% yields, respectively. Bicyclic cations **2a,b** were synthesized by deprotonation of the corresponding cycloheptatriene derivatives **3a**[12] and **3b**[13] with $NOBF_4$ in 72% and 80% yields, respectively. This method using $NOBF_4$ is useful for the deprotonation of cyclic cycloheptatrienes to give tropylium ions.[14] Tricyclic cations **4b—f** whose structures are analogous to that of NMP were prepared from the corresponding heterocycles, cyclohepta[*b*][1,4]benzothiazine (**5a**),[15] cyclohepta[*b*][1,4]benzoxazine (**5b**),[16] and *N*-methylcyclohepta[b][1,4]benzodiazine (**5c**)[17] by protonation with hydrogen chloride or methylation with methyl iodide. Cation **4a** was prepared as the BF_4^- salt according to Nozoe's method.[15b] Heterocyclic cation **6**

with two sulfur atoms were prepared as the BF_4^- salt by deprotonation of heterocycle **7**[12] in acetonitrile.



Reduction Potentials for Tropylium Ions. The first reduction potentials (E_1^{red}) for tropylium ions were measured by cyclic voltammetry. The data for monocyclic tropylium ions summarized in Table 1 show that electron-donating substituents lower the first reduction potentials. The values are linearly correlated with the sum of the substituent constants σ_p^+ as shown in Fig. 1.[18] This linear relationship means the presence of the additive properties of substituent effects on the reduction potentials. Introduction of an SMe group decreases the reduction potentials by −0.10—−0.15 V, while introduction of an OMe group decreases them by −0.20—−0.26 V.[19] The reduction potentials for bicyclic cations **2a,b** are also shown in Table 1. Their higher reduction potentials compared with those for the corresponding monocyclic cations

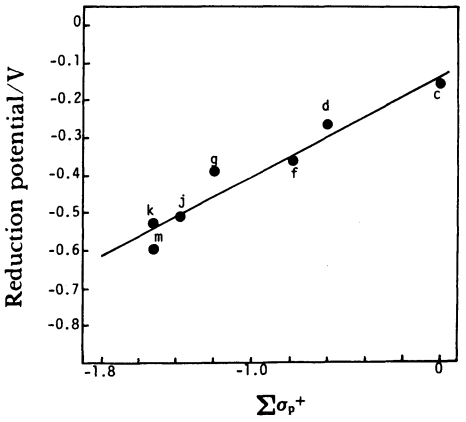


Fig. 1. Plots of first reduction potentials vs. the sum of the substituent constants σ_p^+.
$E_1^{red}=-0.14+0.27\ \Sigma\sigma_p^+$ $r=0.944$.

Table 2. Redox Potentials of Tricyclic Cations **4** and **6**[a]

Cation	E_1^{ox}/V vs. SCE[b]	E_1^{red}/V vs. SCE[c]
4a-BF_4^-	1.44	−0.43
4b-BF_4^-	1.54	−0.45
4c-BF_4^-	1.41	−0.47
4d-I^-	1.65	−0.55
4e-BF_4^-	1.10	−0.58
4f-BF_4^-	1.15	−0.85
6-BF_4^-	1.86	−0.13

a) 0.1 M Et_4NClO_4 in MeCN, Pt electrode, 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.

Table 1. Reduction Potentials of Tropylium Ions **1** and **2**[a]

Cation	R^1	R^2	R^3	Counter Ion	E_1^{red}/V vs. SCE[b]
1a	OMe	OH	Br	BF_4^-	−0.06
1b	OMe	OMe	Br	BF_4^-	−0.13
1c	H	H	H	BF_4^-	−0.16
1d	SMe	H	H	ClO_4^-	−0.26
1e	OMe	OH	H	Cl^-	−0.33
1f	OMe	H	H	ClO_4^-	−0.36
1g	SMe	SMe	H	ClO_4^-	−0.38
1h	*p*-$NMe_2C_6H_4$	H	H	ClO_4^-	−0.40
1i	1,3,5-Trimethyl			BF_4^-	−0.42
1j	OMe	SMe	H	I^-	−0.51
1k	OMe	H	OMe	BF_4^-	−0.53
1l	1,2,4,5-Tetramethyl			BF_4^-	−0.55
1m	OMe	OMe	H	BF_4^-	−0.55
1n	NHMe	H	H	BF_4^-	−0.64
1o	NH_2	SMe	H	I^-	−0.64
1p	-NMePh	H	H	ClO_4^-	−0.73
1q	NMe_2	H	H	BF_4^-	−0.80
1r	NHMe	OMe	H	BF_4^-	−0.90
2a	$-SCH_2CH_2S-$		H	BF_4^-	−0.29
2b	$-OCH_2CH_2O-$		H	BF_4^-	−0.51

a) 0.1 M Et_4NClO_4 (1 M=1 mol dm^{-3}) in MeCN, Pt electrode, scan rate 100 mV s^{-1}. b) These peaks are all irreversible. Calculated as E_{pc} (cathodic peak potential)+0.03.

1g,m by 0.09 V may be attributed to the nonplanar structures of **2a,b**. The redox potentials for the tricyclic cations **4** are shown in Table 2. The values are higher than those for the corresponding monocyclic or bicyclic cations and even oxidation potentials are observed. These results show that tropylium ions with different reduction potentials can be readily prepared.

Reaction of Tropylium Ions with $TCNQ^{\cdot-}$. When a boiling ethanol or acetonitrile solution of the salts of monocyclic tropylium ions **1** was treated with $TCNQ^{\cdot-}$ lithium salt in boiling ethanol, **1j,k,l,m,n,q** gave simple salts and **1d,f,g,h,p** gave complex salts. The molar ratios are shown in Table 3. Cation **1g** which formed a complex salt by direct mixing gave a simple salt when the metathesis was carried out in the presence of lithium iodide. Treatment of the simple salts with TCNQ in boiling acetonitrile gave their complex salts. These salts are the first $TCNQ^{\cdot-}$ salts of tropylium ion species.

In contrast, nonsubstituted one **1c** underwent a reaction with $TCNQ^{\cdot-}$ to give **8** (R=H) and neutral TCNQ without the formation of salts as reported by Melby.[7] Tropylium ions **1b,i** underwent the same type of reaction to give **8** and neutral TCNQ. The bicyclic cations **2a** also underwent the same type of reaction, while **2b** gave a complex salt. In the case of tricyclic cations, **4a,c—f** gave simple salts and **4b** gave a 1:2 salt by metathesis, while **6** underwent the reaction with $TCNQ^{\cdot-}$. It should be noted that the cations **1b,c,i,2a** and **6** which underwent the reaction have higher reduction potentials. This fact shows that the reduction potentials strongly affect the formation of salts. The molar ratios of the initially formed salts are also related to the reduction potentials. Figure 2 clearly shows the effects of the reduction potentials. The tropylium ions in region I ($E_1^{red}>-0.2$ V) underwent the reaction. The ions in region II (-0.43 V$<E_1^{red}<-0.2$ V) formed complex salts, while the ions in region III ($E_1^{red}<-0.43$ V) formed simple salts. There are some exceptions, indicating that the salt formation is also affected by other factors. For example, the bicyclic cation **2a** in region II underwent the reaction and **2b** in region III formed a complex salt. This can be attributed to the nonplanar structures which make it difficult to form salts. The reason for the formation of the complex salt of **1p** which is in region III may be attributed to the large size of **1p**. Decrease in the Coulomb force due to the low electron affinity of **1r** may be the reason for the formation of the complex salt of **1r**.

These findings suggest the reaction mechanism shown in Scheme 1. When the salt formation takes place faster than the coupling reaction or electron transfer, simple salts are formed. When electron transfer competes with the salt formation, complex salts are formed since electron transfer leads to the formation of neutral TCNQ which reacts with simple salts to give complex salts. The effect of lithium

Table 3. Properties of $TCNQ^{\cdot-}$ Salts

Cation	Molar ratio	ν/cm^{-1}	ρ/Ω cm[a]
1d	1:2	2187	9.4
1f	2:3	2184	3.7×10
1g	1:1[b]	2184	1.3×10^2
	2:3	2183	1.6×10
1h	1:2:$(H_2O)_{0.5}$	2188	9.6
1j	1:1	2187	5.2×10^2
	1:1:H_2O	2188	3.8×10^2
1k	1:1	2173	2.7×10^7
	1:2[c]	2194	9.2×10^3
1l	1:1	2167	1.1×10^6
	1:2[c]	—[d]	1.1×10^2
1m	1:1	2182	5.8×10
	1:2[c]	2187	2.9×10
1n	1:1:H_2O	2189	3.3×10^2
	2:3[c]	2188	7.4
1p	1:2	2189	4.8×10
1q	1:1	2160	5.1×10^6
	1:2[c]	2188	2.4
1r	1:2:$(H_2O)_2$	2188	9.1
2b	2:3	2184	2.8×10^4
4a	1:1	2170	1.9×10^3
	1:2[c]	2190	4.0
4b	1:2	2190	1.3×10
4c	1:1	2178	2.8×10
	1:2[c]	2188	4.3
4d	1:1	2178	1.4×10^3
	1:2[c]	2192	5.2
4e	1:1	2173	7.1×10^7
4f	1:1	2167	7.4×10^7
	1:2[c]	2193	9.0

a) Measured at room temperature as compressed pellets by two probe technique. The electrical resistivity of the TTF-TCNQ complex measured by this method was 0.37. b) In the presence of LiI. c) Obtained by reaction of 1:1 salts with TCNQ. d) No measurement.

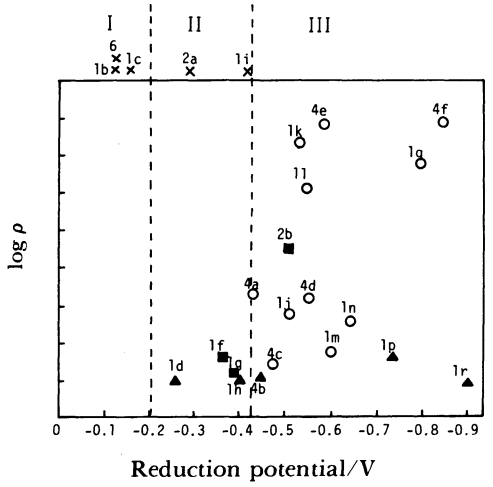
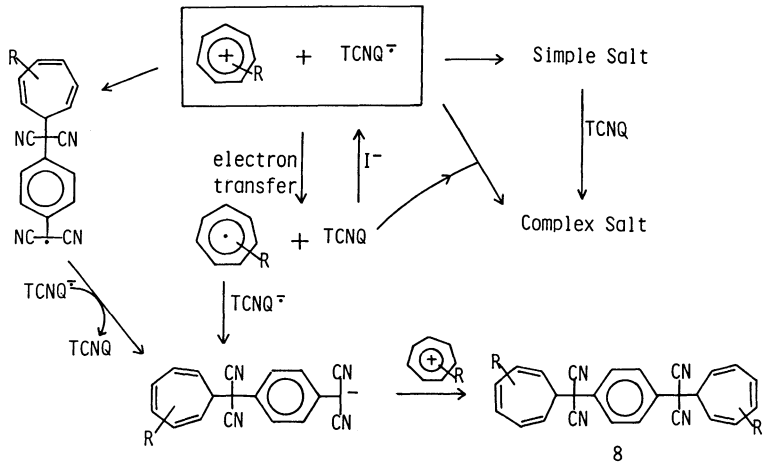


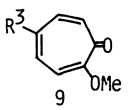
Fig. 2. Relationship between reduction potentials of cations and electrical resistivities (ρ) and molar ratios of the initially for med salts. 1: salt (○); 1:2 salt (▲); 2:3 salt (■); reaction (×).



Scheme 1.

iodide can be explained by considering that neutral TCNQ which was formed by the electron transfer reaction was reduced by I^- to give $TCNQ^{\cdot-}$. On the other hand, highly reactive tropylium ions undergo the reaction to give the adducts **8** by the mechanism shown in Scheme **1** instead of the salt formation. The reduction potentials for the cations play an important role in determining the reactivities, since the reduction potentials of tropylium ions are related to their pK_R^+ values and electron affinities.[19]

This mechanism is supported by the following results. When each ethanol solution of cations and $Li^+TCNQ^{\cdot-}$ (1 equiv) at low concentration (ca. 10^{-4} M) were mixed, the green color due to $TCNQ^{\cdot-}$ immediately disappeared in the case of cations which belong to region I and II, while in the case of cations which belong to region III the green color remained. The molar ratios of the cations to TCNQ can be determined by measuring the intensity ratios of the absorbance at 400 nm to that at 842 nm in the absorption spectra in which those for the simple salts are shown to be 0.5.[5,20] In fact, ratios in the above green solutions were about 0.5. The ratios for the **1p,r** which belong to region III but form complex salts were 0.50 and 0.54, respectively, indicating that the cations **1p,r** as well as other cations which belong to region III are stable under these conditions. These findings suggest that the reactivity of cations to $TCNQ^{\cdot-}$ is determined by the reduction potentials, but the salt formation is also affected by the factors other than the reactivity of cations.



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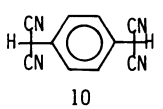

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On the other hand, hydroxy derivatives **1a,e** underwent a proton transfer to give tropone derivatives **9** and dihydrodihydroxy-TCNQ **10**, indicating that hydroxy derivatives cannot be used for the formation of salts.

The properties of $TCNQ^{\cdot-}$ salts are summarized in Table 3. Electrical resistivities are relatively low, indicating that tropylium ions are good cations for forming highly conductive $TCNQ^{\cdot-}$ salts. It is interesting that even alkyl derivative **11** forms conductive $TCNQ^{\cdot-}$ salts. The 1:2 salts are more conductive than the corresponding 1:1 salts as found in usual $TCNQ^{\cdot-}$ salts.[3,4] It should be noted here that the simple salts of **1m** and **4c** show significantly low resistivities compared with those for $TCNQ^{\cdot-}$ simple salts of other cations except NMP.[3,4] Resistivities of the simple salts seem to be related to the structures of cations as well as the reduction potentials as shown in Fig. 2. For example, the resistivity of 1,4-dimethoxy derivative **1k** is higher than that of 1,2-dimethoxy derivative **1m**. This can be accounted for by the nonplanar structure of **1k** which is deduced from the higher reduction potential compared with that for **1m**. The high resistivity of the $TCNQ^{\cdot-}$ simple salt of tetramethyl derivative **11** may also be explained in terms of the steric factor. In addition, the fact that the cations **1q** and **4f** having lower reduction potentials form lower conductive salts indicates that there is a lower limit of the reduction potentials for the cations to show good conductivities. In the salts of cations having lower reduction potentials, the ions seem to be completely charged due to the poor electron affinity of the cations. This is supported by the finding that the anion radical of $TCNQF_4$ which is a strong electron acceptor than TCNQ forms a low conductive simple salt with tricyclic cation **4c** (ρ; $1.8\times10^5\ \Omega$ cm).

Another interesting feature is that the nitrile stretching frequencies for 1:1 salts are lower than those for the metal salts[21] even if the salts show high conductivities. Nitrile stretching frequencies for TCNQ complexes or salts are reported to be linearly correlated with the degree of charge transfer[22] and are

conventionally used for determining it. It has recently been reported that when a salt or a complex takes a mixed stack, there is no linear correlation between them.[23] Our result shows that even in the case of good conductive salts which are considered to form segregated stacks, nitrile stretching frequencies are not always linearly correlated with the degree of charge transfer.

BTDA-TCNQ$^-$ Salts of Tropylium Ions. Bis-[1,2,5]thiadiazolotetracyanoquinodimethan (BTDA-TCNQ) has been found to afford highly conductive charge transfer (CT) complexes with some donors.[10,24] BTDA-TCNQ which forms a two dimensional network by a strong S···N≡C interaction[25] is expected to give two- or three-dimensional CT complexes or anion radical salts. The first reduction potential of BTDA-TCNQ (−0.02 V vs. SCE) is a little lower than that of TCNQ (+0.18 V vs. SCE), indicating that the electron transfer from BTDA-TCNQ$^-$ to cations more easily takes place than that from TCNQ$^-$. On the other hand, the nucleophilicity of BTDA-TCNQ$^-$ is considered to be weaker than that of TCNQ$^-$ since negative charge is delocalized in the thiadiazole rings.[26]

When a boiling ethanol or acetonitrile solution of monocyclic tropylium ions was treated with Li$^+$ BTDA-TCNQ$^-$ in boiling ethanol, salts whose molar ratios are shown in Table 4 precipitated. Most of salts contain water, indicating that BTDA-TCNQ$^-$ tends to uptake water. It should be noted that the cations **1b** and **1i** which underwent the coupling reaction with TCNQ$^-$ gave salts with BTDA-TCNQ$^-$. Bicyclic cation **2a** which underwent the coupling reaction with TCNQ$^-$ also formed a salt with BTDA-TCNQ$^-$. These facts can be explained in terms of the low nucleophilicity of BTDA-TCNQ$^-$ which reduces the reactivity for the coupling reaction. The electrical resistivities of the BTDA-TCNQ$^-$ salts summarized in Table 4 show that these salts are conductive, indicating the usefulness of BTDA-TCNQ$^-$ for forming organic semiconductors with cations. The nitrile stretching frequencies are lower than those for the metal salts.[27] This may be accounted for by the strong S···N≡C interaction.

Table 4. Properties of TCNQ$^-$ Salts

Cation	Molar ratio	ν/cm^{-1}	ρ/Ω cm[a]
1b	3:4	2173	3.7×10^2
1d	1:1	2172	2.5×10^3
1f	1:3:H_2O	2177	9.7×10^3
1g	1:1:H_2O	2172	7.6×10^2
1h	1:1.5:H_2O	2170	1.4×10
1i	2:3:H_2O	2167	4.5×10
1j	1:1:$(H_2O)_{1.5}$	2170	9.4×10
1l	1:2:H_2O	2173	8.5×10
1m	2:3	2174	4.0×10
1n	1:1:$(H_2O)_2$	2166	2.9×10^2
1p	3:4	2177	3.0×10
1q	1:1:H_2O	2167	4.4×10^3
1r	2:3:$(H_2O)_3$	2167	3.0×10^3

a) Measured under the same conditions as those of TCNQ$^-$ Salts

Conclusion

Tropylium ions with different reduction potentials were prepared. The first reduction potentials are correlated with the substituent constants σ_p^+ and the substituent effects are additive. The tropylium ions were found to form conductive salts with TCNQ$^-$. The reduction potentials for cations affect the salt formation. The tropylium ions with higher reduction potentials (E_1^{red}>−0.2 V) undergo the reaction with TCNQ$^-$. When the reduction potentials are between −0.2 V and −0.43 V, complex salts are formed. When they are lower than −0.43 V, simple salts are formed. Electrical resistivities of the salts are relatively low and particularly, those of the simple salts of **1m** and **4c** are much lower than those of usual TCNQ$^-$ simple salts. The nitrile stretching frequencies for the salts are not linearly correlated with the degree of charge transfer. BTDA-TCNQ$^-$ also gave conductive salts of tropylium ions. Due to the low nucleophilicity, BTDA-TCNQ$^-$ formed salts with even tropylium ions which have high reduction potentials and underwent the reaction with TCNQ$^-$.

Experimental

General Methods. IR spectra were taken on a Shimadzu IR-27G spectrometer or a Shimadzu IR-435 spectrometer equipped with a Shimadzu DR-1 data recorder. UV spectra were measured with a Hitachi 340 spectrophotometer and mass spectra with a Hitachi M-52 mass spectrometer. ^{1}H NMR spectra were obtained at 60 MHz on a Varian EM-360, at 90 MHz on a Varian EM-390, at 200 MHz on a Varian XL-200 spectrometer. Redox potentials were measured on a Yanako Voltammetric Analyzer p-1000. All reaction solvents were distilled prior to use. Melting points were measured on a Laboratory Devices MEL-TEMP apparatus and are uncorrected.

Preparation of 5-Bromo-1-hydroxy-2-methoxytropylium Tetrafluoroborate and 5-Bromo-1,2-dimethoxytropylium Tetrafluoroborate. A solution of 900 mg (4.19 mmol) of 5-bromo-2-methoxytropone and 743 mg (7.03 mmol) of trimethyloxonium tetrafluoroborate in 5 ml of anhydrous nitromethane was stirred under nitrogen for 58 h at room temperature. After 1 ml of methanol was added to quench the excess of the methylating reagent, addition of 15 ml of absolute ether precipitated pale yellow crystals which were collected by filtration followed by washing with absolute ether to give 810 mg (61% yield) of the BF_4^- salt of **1b**. From the filtrate, pale yellow crystals were precipitated on cooling. Filtration followed by washing with absolute ether gave 150 mg (12% yield) of the BF_4^- salt of **1a**. **1a**-BF_4^-: mp 155—158 °C; IR (KBr) 3400—3300, 3100—3000, 1592, 1570, 1500, 1450, 1350, 1275, 1150—980, 830, 530 cm^{-1}; ^{1}H NMR (CD_3CN, 90 MHz) δ=4.05 (s, 3H), 5.75—5.95 (brs, 1H), 7.31 (d, 1H, J=12 Hz), 7.41 (d, 1H, J=12 Hz), 8.10 (d, 2H,

J=12 Hz). **1b**-BF_4^-: mp 157—159 °C; IR (KBr) 3100, 1530, 1475, 1445, 1280, 1150-950, 923, 840, 700 cm^{-1}; MS m/z 316 (M^+); ^1H NMR (CD_3CN, 90 MHz) δ=4.28 (s, 6H), 8.07 (d, 2H, J=12 Hz), 8.73 (d, 2H, J=12 Hz).

Preparation of 1,4-Dimethoxytropylium Tetrafluoroborate. A solution of 80 mg (0.588 mmol) of 4-methoxytropone and 100 mg (0.647 mmol) of trimethyloxonium tetrafluoroborate in 3 ml of dichloromethane was stirred under nitrogen for 12 h. Addition of 50 ml of absolute ether precipitated 80 mg (85% yield) of **1k**-BF_4^- as colorless crystals which were used for the salt formation without further purification due to the deliquescent property. **1k**-BF_4^-: mp 93—95 °C; IR (KBr) 3100—2950, 1570, 1490, 1431, 1305, 1205, 1150—950, 862, 682 cm^{-1}; MS m/z 150 (M^+-BF_4); ^1H NMR (CD_3CN, 90 MHz) δ=4.12 (s, 6H), 7.95 (d, 2H, J=11 Hz), 8.11 (s, 2H), 8.70 (t, 1H, J=11 Hz).

Preparation of 1-Methylamino-2-methoxytropylium Tetrafluoroborate. 300 mg (2.83 mmol) of 2-aminotropone and 460 mg (3.11 mmol) of trimethyloxonium tetrafluoroborate in 5 ml of anhydrous nitromethane was stirred at room temperature for 82 h. After methanol was added to quench the excess of trimethyloxonium salt, addition of 30 ml of absolute ether precipitated yellow crystals. Filtration followed by washing with absolute ether gave 225 mg (36% yield) of **1r**-BF_4^- which was used without further purification due to the strongly deliquescent property. **1r**-BF_4^-: mp 93—98 °C, IR (KBr) 3200—2900, 1640, 1590, 1500, 1440, 1275, 1218, 1150—950, 940, 745 cm^{-1}; MS m/z 150 (M^+-BF_4); ^1H NMR (CD_3CN, 90 MHz) δ=4.19 (s, 3H), 4.73 (s, 3H), 7.40—7.95 (m, 5H).

Preparation of Methylthio Derivatives 1g,j,o. These tropylium ions were prepared by the reaction of corresponding tropothiones with methyl iodide. 2-Methyltropothione[28] and 2-aminotropothione[29] were prepared according to Nozoe's method. 2-Methoxytropothione was synthesized by the following method. To a suspension of 1.63 g (7.35 mmol) of phosphorus pentasulfide and 0.800 g (8.09 mmol) of triethylamine in 50 ml of carbon disulfide, a solution of 1.00 g (7.35 mmol) of 2-methoxytropone in 50 ml of carbon disulfide was added and stirred under nitrogen for 12 h at room temperature. The precipitated deep orange crystals were separated by decantation and washed with 10 ml of carbon disulfide 3 times. The combined carbon disulfide solution was evaporated under reduced pressure below 20 °C to give 670 mg (60% yield) of 2-methoxytropothione which was used without further purification. The structure of 2-methoxytropothione was confirmed by the ^1H NMR spectrum. ($CDCl_3$, 60 MHz) δ=3.90 (s, 3H), 6.5—7.0 (m, 4H), 8.15 (d, 1H, J=12 Hz).

When a solution of tropothiones and methyl iodide (10—30 equiv) in absolute ether was stirred under nitrogen for 12—15 h at room temperature, red solids deposited. Filtration followed by washing with absolute ether gave the iodides of tropylium ions **1g,j,o** in 70%, 25%, and 48% yields, respectively. **1g**: mp 178—180 °C; IR (KBr) 3100—2900, 1490, 1472, 1400, 1389, 1320, 1278, 1240, 1090, 1045, 735, 550 cm^{-1}; MS m/z 183 (M^+-I); ^1H NMR (CD_3CN, 90 MHz) δ=2.92 (s, 6H), 8.13—8.47 (m, 5H). **1j**: mp 93—95 °C; IR (KBr) 3000—2950, 1510, 1488, 1450, 1420, 1280, 1220, 1020, 938, 750, 560 cm^{-1}; ^1H NMR (CD_3CN, 90 MHz) δ=2.79 (s, 3H), 4.40 (s, 3H), 8.2—8.5 (m, 5H). **1o**: mp 130 °C (decomp); ^1H NMR (CD_3CN, 90 MHz) δ=2.78 (s, 3H), 7.6—8.1 (m, 5H).

Since the solubility of the iodide of **1g** in ethanol or acetonitrile was too low to be used for the salt formation, the counter anion was substituted for BF_4^-. To a solution of 200 mg of the iodide in 5 ml of absolute acetonitrile, 126 mg (0.645 mmol) of $AgBF_4$ was added. After the solution was stirred at room temperature for 1 h, the deposited AgI was filtered off and washed with absolute acetonitrile. The combined acetonitrile solution was evaporated to give 147 mg (84% yield) of the BF_4^- salt: mp 205—210 °C (decomp).

Preparation of Bicyclic Tropylium Ions 2. These ions were prepared by the deprotonation of the corresponding cycloheptatrienes **3a**[12] and **3b**.[13] To a solution of 200 mg (0.338 mmol) of bicyclic cycloheptatriene **3a** in 10 ml of anhydrous acetonitrile, 236 mg (2.02 mmol) of $NOBF_4$ in 5 ml of anhydrous acetonitrile was added with nitrogen bubbling. After the solution was stirred at room temperature for 15 min, addition of 50 ml of absolute ether precipitated yellow crystals. Filtration followed by washing with absolute ether gave 65 mg of **2a**-BF_4^-. The residue which was obtained by evaporation of the filtrate was treated with absolute ethanol. From the soluble part in ethanol, 130 mg of **2a**-BF_4^- was obtained by removal of the solvent. The total yield was 72%. **2a**-BF_4^-: mp 138—140 °C, IR (KBr) 3050—2950, 1500, 1470, 1425, 1285, 1150—950, 730 cm^{-1}; ^1H NMR (CD_3CN, 90 MHz) δ=3.61 (s, 4H), 8.02 (d, 2H, J=11 Hz), 8.10 (t, 1H, J=11 Hz), 8.45 (dd, 2H, J=11, 11 Hz).

Similarly, the reaction of 150 mg (1 mmol) of bicyclic cycloheptatriene **3b** with $NOBF_4$ (2 equiv) gave 189 mg (80% yield) of ethylenedioxytropylium ion **2b**: mp 128—130 °C; IR (KBr) 3100—3000, 1480, 1468, 1284, 1185, 1150—950, 750, 700 cm^{-1}; ^1H NMR (CD_3CN, 90 MHz) δ=4.70 (s, 4H), 8.40 (s, 5H).

Preparation of 5-Methyl-5*H*-cyclohepta[*b*]quinoxaline. A solution of 4.69 g (33.4 mmol) of 2-chlorotropone and 4.50 g (36.9 mmol) of *N*-methyl-1,2-phenylenediamine[30] in 60 ml of absolute ethanol was refluxed under nitrogen for 48 h. Removal of the solvent gave black tarry matter to which 2 M hydrochloric acid was added. The solution was washed with benzene to remove the recovered 2-chlorotropone, made basic with 2 M sodium hydroxide, and extracted with 100 ml of benzene 3 times. The extract was washed with sat. aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent followed by column chromatography on alumina (2:1 ether-hexane) gave 2.38 g of dark green crystals which were recrystallized from pentane-hexane to give 1.80 g (26% yield) of **5c** as dark green needles: mp 92—93 °C; IR (KBr) 3050, 2900, 1620, 1570, 1480, 1330, 720 cm^{-1}; MS (25 ev)(relative intensity) 208 (M^+, 92), 193 (M^+,$-CH_3$); ^1H NMR ($CDCl_3$, 200 MHz) δ=2.74 (s, 3H), 4.42 (ddd, 1H, J=9.5, 2.0, 0.8 Hz), 5.29 (dddd, 1H, J=11.0, 8.0, 2.9, 2.0 Hz), 5.57 (ddd, 1H, J=12.0, 2.9, 1.0 Hz), 5.85 (dddd, 1H, J=12.0, 8.0, 1.2, 0.8 Hz), 5.86 (dddd, 1H, J=11.0, 9.5, 1.2, 1.0 Hz), 6.19 (dd, 1H, J=8.0, 1.2 Hz), 6.63 (ddd, 1H, J=10.0, 7.0, 1.2 Hz), 6.66 (dd, 1H, J=10.0, 2.3 Hz), 6.73 (ddd, 1H, J=8.0, 7.0, 2.3 Hz). Found: C, 80.74; H, 5.81; N, 13.45%. Calcd for $C_{14}H_{12}N_2$: C, 80.46; H, 5.81; N, 13.51%.

Preparation of Tricyclic Cation 4b,d,f by Methylation of the Corresponding Heterocycles 5. Methylation of **5a** using methyl iodide or dimethyl sulfate gave a complex mixture of products. However, reaction of **5a** with trimethyloxonium tetrafluoroborate gave the methylated

Table 5. Decomposition Points, Crystal Forms, and Analytical Data of $TCNQ^{-}$ Salts

Cation	Decomp °C	Crystal form	Molar ratio	Anal. Calcd / Found C/%	H/%	N/%
1d	208—210	Black needles	1:2	70.43 70.14	3.14 2.88	20.54 20.00
1f	185—188	Violet needles	2:3	73.06 73.15	3.54 3.32	19.00 19.55
1g	206—208	Black needles	1:1	65.09 64.95	3.90 3.86	14.46 15.02
	202—205	Black needles	2:3	66.23 65.38	3.50 3.47	17.17 17.15
1h	205—210	Black powder	$1:2:(H_2O)_{0.5}$	74.63 74.90	3.85 3.80	20.08 19.75
1j	203—205	Black needles	1:1	67.91 67.58	4.08 3.92	15.08 15.79
	203—205	Black needles	$1:1:H_2O$	64.76 65.09	4.40 4.27	14.39 14.25
1k	205—208	Black needles	1:1	70.98 70.66	4.25 4.72	15.77 15.88
	208—210	Black needles	1:2	70.83 70.84	3.42 3.48	20.03 19.55
1l	>120	Green powder	1:1	78.83 78.99	5.18 5.38	15.99 15.87
	158—160	Black needles	1:2	75.80 75.76	4.00 4.05	20.20 20.05
1m	172—174	Violet needles	1:1	70.98 70.71	4.25 4.83	15.77 15.18
	210—213	Black powder	1:2	70.83 71.07	3.42 3.29	20.03 20.59
1n	135—140	Blue-violet powder	$1:1:H_2O$	70.58 70.40	4.15 4.15	20.58 19.93
	180—185	Black needles	2:3	73.23 73.00	3.78 3.45	22.99 23.24
1p	210—220	Violet powder	1:2	75.48 75.13	3.67 3.30	20.86 20.03
1q	204—206	Violet needles	1:1	74.54 74.29	4.77 4.56	20.70 20.48
	>350	Black needles	1:2	73.05 73.41	3.92 3.49	23.23 23.03
1r	>350	Violet needles	$1:2:(H_2O)_2$	66.66 67.16	4.07 3.55	21.20 20.57
2b	>350	Black needles	2:3	71.20 70.79	3.32 3.30	18.45 18.04
4a	195—200	Violet needles	1:1	74.99 75.19	3.52 3.42	17.49 17.14
	>350	Violet needles	1:2	73.50 72.66	3.00 2.91	20.85 21.29
4b	229—231	Violet needles	1:2	71.91 71.42	3.18 3.02	19.86 19.16
4c	198—200	Blue-violet needles	1:1	72.10 71.39	3.39 3.29	16.82 16.47
	>350	Violet plates	1:2	71.60 70.65	2.92 2.94	20.31 19.69
4d	208—210	Red-violet needles	1:1	75.35 74.70	3.89 3.56	16.90 17.13
	251—255	Violet needles	1:2	73.28 72.95	3.26 3.12	20.38 20.62
4e	157—160	Green columns	1:1	75.53 74.94	4.14 3.87	20.33 20.22
4f	226—227	Blue-violet needles	1:1	75.86 76.18	4.48 4.34	19.66 19.41
	264—266	Blue-violet needles	1:1	74.16 74.11	3.67 3.43	22.17 22.19

Table 6. Decomposition Points, Color, and Analytical Data of BTDA-TCNA$^-$ Salts

Cation	Decomp °C	Color	Molar ratio	Anal. Calcd / Found C/%	H/%	N/%
1b	310—315	Blue-black	3:4	45.69	1.53	22.73
				46.15	1.71	22.53
1d	265—270	Violet	1:1	52.04	2.84	24.28
				51.15	1.76	24.68
1f	230—260	Black	1:3:H_2O	48.04	1.01	30.56
				47.38	0.78	30.49
1g	265—270	Black	1:1:H_2O	48.35	2.41	21.48
				48.22	1.98	21.48
1h	219—224	Black	1:1.5:H_2O	55.92	2.56	25.69
				56.33	2.11	24.95
1i	155—158	Black	2:3:H_2O	53.23	1.57	26.60
				53.79	2.34	26.63
1j	252—255	Black	1:1:$(H_2O)_{1.5}$	49.02	2.74	21.78
				48.62	1.98	22.32
1l	204—205	Violet	1:2:H_2O	54.11	2.35	26.11
				53.42	2.40	25.54
1m	295—310	Violet	2:3	50.62	1.88	26.24
				51.16	1.86	25.78
1n	238—240	Violet	1:1:$(H_2O)_2$	50.47	2.96	26.45
				50.57	2.78	26.49
1p	215—218	Violet	3:4	57.80	2.26	26.21
				57.63	2.35	26.16
1q	250—252	Violet	1:1:H_2O	53.38	2.99	26.68
				53.55	2.49	26.24
1r	238—240	Violet	2:3:$(H_2O)_3$	49.30	2.29	27.68
				49.26	1.96	26.71
2a	277—280	Brown	—[a]	—	—	—
				48.88	2.40	16.28

a) The molar ratio could not be determined on the basis of the analytical data.

compound **4b**. 99 mg (0.711 mmol) of trimethyloxonium tetrafluoroborate was added under nitrogen to a solution of 150 mg (0.711 mmol) of **5a** in 5 ml of dichloromethane. Stirring at room temperature for 24 h gave 180 mg (80% yield) of **4b**-BF_4^-: mp 158—160 °C (decomp); ^{1}H NMR (CD_3CN, 60 MHz) δ=3.67 (s, 3H), 6.97—7.67 (m, 9H).

Methylation of **5b** with methyl iodide in absolute ether readily gave **4d**-I^-: mp 196—198 °C (decomp); ^{1}H NMR (CD_3CN, 90 MHz) δ=3.33 (s, 3H), 6.67—9.96 (m, 9H).

Methylation of **5c** with methyl iodide in absolute ether gave deep green crystals which were recrystallized from ethanol to give **4f**-I^- in 75% yield as deep green plates: mp 267—268 °C (decomp); ^{1}H NMR (DMSO-d_6, 90 MHz) δ=3.13 (s, 6H), 6.46 (m, 2H), 6.55 (m, 1H), 6.67—7.10 (m, 4H), 7.30 (m, 2H). Found: C, 51.26; H, 4.36; N, 7.94%. Calcd for $C_{15}H_{15}N_2I$: C, 51.45; H, 4.32; N, 8.00%.

Preparation of Heterocyclic Cation 6. In a similar manner as the preparation of bicyclic cations **2a,b**, heterocyclic cation **6** was prepared by the dehydrogenation of heterocycle **7**[12] with $NOBF_4$. The reaction of 100 mg (0.434 mmol) of **7** with 51 mg (0.434 mg) of $NOBF_4$ in anhydrous acetonitrile gave 51 mg (37% yield) of **6**-BF_4^-: mp 40—42 °C; IR (KBr) 3020, 1604, 1510, 1457, 1440, 1270, 1100—980, 755, 730, 560 cm^{-1}; MS *m/z* 230 (M^+-BF_4) ^{1}H NMR (CD_3CN, 90 MHz) δ=7.4—7.9 (m, 4H), 8.3—8.7 (m, 5H). Found: C, 47.40; H, 3.48; S, 19.82%. Calcd for $C_{13}H_{10}S_2BF_4(H_2O)_{0.5}$: C, 48.02; H, 3.10; S, 19.72%.

Preparation of TCNQ$^-$ salts. The following is a general procedure to prepare salts. A boiling saturated absolute ethanol or acetonitrile solution of cations and a boiling saturated absolute ethanol solution of Li^+TCNQ^- were mixed. The solution was allowed to stand at room temperature until crystals precipitated. Filtration followed by washing with a small amount of absolute ethanol and then absolute ether gave salts. The reaction of 1:1 salts with another equivalent of TCNQ in boiling acetonitrile gave their complex salts. Melting points, forms of crystals, and analytical data of salts are shown in Table 5.

Preparation of BTDA-TCNQ$^-$ Salts. BTDA-$TCNQ^-$ of tropylium ions were prepared by metathesis of tropylium ions and Li^+BTDA-$TCNQ^-$ in a similar manner as $TCNQ^-$ salts. The properties along with analytical data are shown in Table 6.

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