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Preparation and Properties of AzaTCNQ$^-$ Anion Salts and Mixed AzaTCNQ$^-$/TCNQ$^{\cdot-}$ Salts of *N*-Alkylpyridinium and Related Cations

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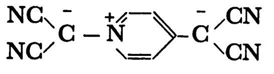
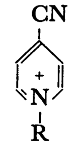
The [Cation]$^+$ATCNQ$^-$ type salts were prepared, where ATCNQ$^-$ is (4-dicyanomethyl-1-pyridinio)-dicyanomethanide anion, so-called AzaTCNQ$^-$ anion, and [Cation]$^+$ are *N*-alkylpyridinium, 4-cyano-*N*-alkylpyridinium, (4-methyl-1-pyrazinio)dicyanomethanide, *N*-alkylquinolinium (alkyl=Me and Et), *N*-methylacridinium, and *N*-methylphenazinium. Electrical resistivities of these salts as compacted samples fall in the range 10^6—10^9 Ωcm at 25 °C. The mixed ATCNQ$^-$/TCNQ$^{\cdot-}$ salts (TCNQ$^{\cdot-}$=7,7,8,8-tetracyano-*p*-quinodimethan radical anion) of *N*-alkylpyridinium and -quinolinium cations also were prepared; [Cation]$^+$(ATCNQ$^-$)$_{0.1}$(TCNQ$^{\cdot-}$)$_{0.9}$ ([Cation]$^+$=*N*-methylpyridinium, *N*-ethylpyridinium, and *N*-ethylquinolinium) and [*N*-methylquinolinium]$^+$(ATCNQ$^-$)$_{0.17}$(TCNQ$^{\cdot-}$)$_{0.83}$ whose electrical resistivities (10^4—10^6 Ωcm at 25 °C) are somewhat smaller than those of the corresponding TCNQ$^{\cdot-}$ salts. Stackings of ATCNQ$^-$ and TCNQ$^{\cdot-}$ anions are discussed on the basis of electronic reflectance and ESR spectra. The [Cation]$^+$ATCNQ$^-$ salts react with iodine in hexane to give [Cation]$^+$ATCNQ$^-$·Ix ([Cation]$^+$=*N*-methyl- and *N*-ethylpyridinium and -quinolinium; x=3.2—3.9). They exhibit electrical resistivities of 10^4—10^6 Ωcm at 25 °C, which are lower by the 10^2—10^3 order than the resistivities of the undoped [Cation]$^+$ATCNQ$^-$ salts.

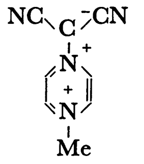
Although the ATCNQ$^-$ anion (**I**) (4-dicyanomethyl-1-pyridinio)dicyanomethanide anion; so-called Aza-TCNQ$^-$ anion) has a diamagnetic property with a $\bar{\mathrm{C}}$-$\overset{+}{\mathrm{N}}$ ylide bonding, the geometry is very similar to that of the TCNQ$^{\cdot-}$ radical anion.[1,2] It would, therefore, be of interest to compare the properties of ATCNQ$^-$ salts with those of the corresponding TCNQ$^{\cdot-}$ radical anion salts. Thus, we reported previously the preparation and electrical resistivities of [Rh(RNC)$_4$]$^+$ATCNQ$^-$, and the corresponding mixed ATCNQ$^-$/TCNQ$^{\cdot-}$ and ATCNQ$^-$/TCNQ$^{\cdot-}$/TCNQ salts (R=C$_6$H$_5$, 2,6-Me$_2$C$_6$H$_3$, and 2,4,6-Me$_3$C$_6$H$_2$) together with the crystal structure of [Rh(2,6-Me$_2$C$_6$H$_3$NC)$_4$]$^+$ATCNQ$^-$.[1] The present work was undertaken to elucidate the properties of the ATCNQ$^-$ salts with organic cations having various reduction potentials.

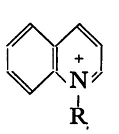

I

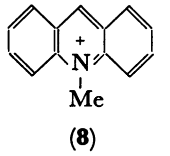
This paper reports the preparation and electrical resistivities of several ATCNQ$^-$ and mixed ATCNQ$^-$/TCNQ$^{\cdot-}$ salts with various organic cations (**1**—**9**) as well as salts obtained by the reaction of [Cation]$^+$-ATCNQ$^-$ salts with iodine. Interactions between the ATCNQ$^-$ anion and the cations and between the ATCNQ$^-$ anion and the TCNQ$^{\cdot-}$ radical anion are discussed on the basis of electronic spectra and spin concentrations.

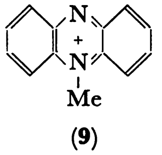

R = Me (**1**)
Et (**2**)


R = Me (**3**)
Et (**4**)


(**5**)


R = Me (**6**)
Et (**7**)


(**8**)


(**9**)

Experimental

Materials. To a nitrobenzene (55 cm^3) solution of (1-pyrazinio)dicyanomethanide[3] (0.55 g, 3.8 mmol) was added dimethyl sulfate (3.4 g, 27 mmol), and the mixture was stirred at room temperature for 4 d. The resulting precipitate was collected by filtration and recrystallized from methanol/benzene (1:1 v/v) to give orange needles of (4-methyl-1-pyrazinio)dicyanomethanide methyl sulfate in a 45% yield; mp 166—168 °C. Found: C, 39.82; H, 3.81; N, 20.13%. Calcd for C$_9$H$_{10}$N$_4$O$_4$S: C, 40.00; H, 3.73; N, 20.73%. *N*-Ethylpyridinium bromide, *N*-methylpyridinium, *N*-alkylquinolinium, and 4-cyano-*N*-alkylpyridinium iodides (alkyl=Me and Et), and *N*-methylacridinium and *N*-methylphenazinium methyl sulfates were prepared by reactions of the corresponding base with an excess amount of alkyl halides or dimethyl sulfate according to the literature.[4] *N*-Alkylpyridinium and *N*-alkylquinolinium TCNQ$^{\cdot-}$ salts (alkyl=Me and Et) were obtained by reactions of the corresponding pyridinium and quinolinium iodides with Li$^+$TCNQ$^{\cdot-}$ in methanol.[5] K$^+$ATCNQ$^-$ was prepared as described previously.[1]

Preparation of ATCNQ$^-$ Salts. All the manipulations were carried out under nitrogen atmosphere. To a boiling aqueous (30 cm^3) solution of K$^+$ATCNQ$^-$ (0.20 g, 0.82 mmol) was added *N*-methylpyridinium iodide (1.94 g, 8.8 mmol) in water (3 cm^3). The mixture was allowed to stand in a refrigerator overnight to afford microcrystals of *N*-methylpyridinium ATCNQ$^-$ salt (**1a**), which was collected by filtration and dried *in vacuo*, 52% yield. Similarly, the reactions of 4-cyano-*N*-methylpyridinium, 4-cyano-*N*-ethylpyridinium, *N*-methylquinolinium, and *N*-ethylquinolinium iodides with K$^+$ATCNQ$^-$ in water afforded the corresponding ATCNQ$^-$ salts; **3a**, **4a**, **6a**, and **7a** in 52, 69, 40, and 48% yields, respectively. (4-Methyl-1-pyrazinio)dicyanomethanide, *N*-methylacridinium, and *N*-methylphenazinium-ATCNQ$^-$ salts (**5a**, **8a**, and **9a**) were prepared in 46, 44, and 32% yields, respectively, by reactions of the corresponding pyrazinium dicyanomethylide, acridinium, and phenazinium methyl sulfates with K$^+$ATCNQ$^-$ in water.

An acetonitrile (300 cm^3) solution containing K$^+$ATCNQ$^-$

(0.61 g, 2.5 mmol) and *N*-ethylpyridinium bromide (2.0 g, 11 mmol) was allowed to stand in a refrigerator overnight. A precipitate (KBr) was filtered off and the filtrate was evaporated to dryness under reduced pressure. The resulting solid was recrystallized from ethanol to afford needles of *N*-ethylpyridinium ATCNQ$^-$ salt (**2a**) in a 46% yield.

Preparation of Mixed ATCNQ$^-$/TCNQ$^{\cdot-}$ Salts. An ethanol (40 cm^3) solution containing **1a** (0.17 g, 0.55 mmol) and Li$^+$TCNQ$^{\cdot-}$ (0.12 g, 0.57 mmol) was allowed to stand in a refrigerator for one week to afford microcrystals of [*N*-methylpyridinium]$^+$(ATCNQ$^-$)$_{0.1}$ (TCNQ$^{\cdot-}$)$_{0.9}$ (**1b**), which was collected by filtration and dried *in vacuo*, 58% yield. The mole ratio of ATCNQ$^-$/TCNQ$^{\cdot-}$ in the salt was determined from the electronic absorption spectrum in acetonitrile. Analogous reactions of **2a**, **6a**, and **7a** with Li$^+$TCNQ$^{\cdot-}$ in ethanol gave [*N*-ethylpyridinium]$^+$(ATCNQ$^-$)$_{0.1}$ (TCNQ$^{\cdot-}$)$_{0.9}$ (**2b**), [*N*-methylquinolinium]$^+$(ATCNQ$^-$)$_{0.17}$ (TCNQ$^{\cdot-}$)$_{0.83}$ (**6b**), and [*N*-ethylquinolinium]$^+$(ATCNQ$^-$)$_{0.1}$ (TCNQ$^{\cdot-}$)$_{0.9}$ (**7b**) in 45, 28, and 73% yields, respectively.

Reactions of ATCNQ$^-$ Salts with Iodine. Finely powdered **1a** (0.042 g, 0.14 mmol) was suspended in a hexane (25 cm^3) solution of iodine (0.080 g, 0.28 mmol), and the mixture was stirred at room temperature under nitrogen atmosphere for 1 d. The resulting solid, [*N*-methylpyridinium]$^+$ATCNQ$^-\cdot$I$_{3.2}$ (**1c**), was collected by filtration and dried *in vacuo*. Similar reactions of **2a**, **6a**, and **7a** with iodine in hexane gave the [Cation]$^+$ATCNQ$^-\cdot$I$_x$ salts (**2c**, **6c**, and **7c**; x=3.5 or 3.9).

Properties and analyses for the ATCNQ$^-$ and the mixed ATCNQ$^-$/TCNQ$^{\cdot-}$ salts as well as the [Cation]$^+$ATCNQ$^-\cdot$I$_x$ salts are summarized in Table 1.

Physical Measurements. Electrical resistivities as compacted samples and electronic absorption spectra were measured as described previously.[6] Electronic reflectance spectra were recorded on a Hitachi 340 spectrophotometer equipped with a Hitachi NIR (near IR) or R-10A (UV and visible) integrating sphere unit. Cyclic voltammetric measurements were performed in acetonitrile using tetrabutylammonium perchlorate as a supporting electrolyte, as described elsewhere.[7] Spin concentrations of the ATCNQ$^-$, the mixed ATCNQ$^-$/TCNQ$^{\cdot-}$, and the TCNQ$^{\cdot-}$ salts as well as the ATCNQ$^-\cdot$I$_x$ salts were determined at room temperature by comparing integrated signal intensities of the samples with that of 2,2-diphenyl-1-picrylhydrazyl (DPPH).

Results and Discussion

Electrical Properties. The temperature dependence of specific resistivities indicates that all the salts behave as typical semiconductors in the temperature range measured; 0—85 °C for [Cation]$^+$ATCNQ$^-$, 15—50 °C for the mixed ATCNQ$^-$/TCNQ$^{\cdot-}$ salts, and 0—20 °C for [Cation]$^+$ATCNQ$^-\cdot$I$_x$(x=3.2—3.9).

TABLE 1. PROPERTIES AND ANALYSES OF THE ATCNQ$^-$ SALTS

No.	Salt	Color[a)]	Mp (dec.) θ_m/°C	Found (Calcd)[b)] %C	%H	%N
1a	[C$_5$H$_5$N-Me]$^+$ATCNQ$^-$	brown (m)	234—237	67.50 (67.99)	4.01 (4.03)	28.02 (27.98)
2a	[C$_5$H$_5$N-Et]$^+$ATCNQ$^-$	light brown (n)	151—152	68.48 (68.78)	4.47 (4.49)	26.73 (26.73)
3a	[4-CN-C$_5$H$_4$N-Me]$^+$ATCNQ$^-$-$\cdot$0.5H$_2$O	purple (f)	167—170	64.77 (64.66)	3.54 (3.62)	29.47 (29.33)
4a	[4-CN-C$_5$H$_4$N-Et]$^+$ATCNQ$^-$	purple (m)	179—181	66.32 (67.25)	3.74 (3.86)	28.62 (28.89)
5a	[4-C(CN)$_2$-C$_4$H$_4$N$_2$-Me]$^+$ATCNQ$^-$	dark brown (m)	162	61.49 (62.46)	3.13 (3.03)	34.29 (34.50)
6a	[C$_9$H$_7$N-Me]$^+$ATCNQ$^-$	dark brown (m)	216—217	71.65 (71.99)	4.06 (4.03)	23.43 (23.99)
7a	[C$_9$H$_7$N-Et]$^+$ATCNQ$^-$	dark brown (m)	166—167	72.41 (72.51)	4.43 (4.43)	22.57 (23.06)
8a	[C$_{13}$H$_9$N-Me]$^+$ATCNQ$^-$	dark brown (m)	172—174	74.32 (74.99)	4.05 (4.03)	20.45 (20.99)
9a	[C$_{12}$H$_8$N$_2$-Me]$^+$ATCNQ$^-$	dark brown (m)	147—149	71.02 (71.82)	3.82 (3.77)	24.17 (24.42)
1b	[C$_5$H$_5$N-Me]$^+$(ATCNQ$^-$)$_{0.1}$-(TCNQ$^{\cdot-}$)$_{0.9}$	black (m)	202—204	71.79 (72.02)	4.04 (4.05)	23.67 (23.93)
2b	[C$_5$H$_5$N-Et]$^+$(ATCNQ$^-$)$_{0.1}$-(TCNQ$^{\cdot-}$)$_{0.9}$	black (m)	156—159	72.49 (72.63)	4.35 (4.04)	22.66 (23.67)
6b	[C$_9$H$_7$N-Me]$^+$(ATCNQ$^-$)$_{0.17}$-(TCNQ$^{\cdot-}$)$_{0.83}$	purple (m)	208—210	74.30 (75.20)	3.83 (4.05)	20.66 (20.75)
7b	[C$_9$H$_7$N-Et]$^+$(ATCNQ$^-$)$_{0.1}$-(TCNQ$^{\cdot-}$)$_{0.9}$	purple (m)	158—160	74.79 (75.85)	4.41 (4.45)	19.58 (19.70)
1c	[C$_5$H$_5$N-Me]$^+$ATCNQ$^-\cdot$I$_{3.2}$	dark brown (p)	c	28.94 (28.90)	1.89 (1.71)	11.77 (11.90)
2c	[C$_5$H$_5$N-Et]$^+$ATCNQ$^-\cdot$I$_{3.5}$	dark brown (p)	c	28.19 (28.50)	2.01 (1.86)	11.09 (11.08)
6c	[C$_9$H$_7$N-Me]$^+$ATCNQ$^-\cdot$I$_{3.5}$	dark brown (p)	c	31.92 (31.74)	1.93 (1.76)	10.25 (10.58)
7c	[C$_9$H$_7$N-Et]$^+$ATCNQ$^-\cdot$I$_{3.9}$	dark brown (p)	c	30.42 (30.75)	1.95 (1.88)	9.45 (9.78)

a) Crystal forms in parentheses; m: microcrystals, n: needles, f: flakes, p: powder. b) %I. **1c**: 57.62(57.46), **2c**: 58.34(58.56), **6c**: 55.57(55.92), **7c**: 57.47(57.59). c) Not measured.

TABLE 2. SPECIFIC RESISTIVITIES AS COMPACTED SAMPLES (ρ) AND ACTIVATION ENERGIES (E_a) OF THE $ATCNQ^-$- AND RELATED SALTS

Salt	$\rho_{25\,°C}$	E_a	Spin concentration
	Ω cm	eV	%
1a	3.1×10^8	1.1	0
2a	1.1×10^6	0.39	0
3a	5.2×10^8	0.72	0
4a	5.1×10^8	1.2	0
5a	4.1×10^8	0.66	0.30
6a	4.7×10^9	0.53	0
7a	7.7×10^9	0.77	0
8a	7.1×10^8	0.89	0.032
9a	2.3×10^8	0.92	7.5
1b	9.7×10^4	0.40	6.2
2b	4.2×10^5	0.44	6.2
6b	4.3×10^6	0.40	12
7b	1.4×10^6	0.36	5.2
1c	1.5×10^5	0.88	0.91
2c	9.1×10^4	0.47	0.85
6c	3.5×10^6	1.3	0.89
7c	1.2×10^6	1.8	0.50
$[C_5H_5N\text{-}Me]^+TCNQ^{\overline{\cdot}}$ (**1d**)	2.3×10^5	0.50	0.25
$[C_5H_5N\text{-}Et]^+TCNQ^{\overline{\cdot}}$ (**2d**)	7.5×10^4	0.50	0.11
$[C_9H_7N\text{-}Me]^+TCNQ^{\overline{\cdot}}$ (**6d**)	1.0×10^7	0.58	0.083
$[C_9H_7N\text{-}Et]^+TCNQ^{\overline{\cdot}}$ (**7d**)	1.4×10^8	0.69	0.43
A mixture of **1a/1d**[a)]	5.6×10^5	b	b
2a/2d[a)]	9.0×10^5	b	b
6a/6d[a)]	1.1×10^7	b	b
7a/7d[a)]	3.3×10^8	b	b

a) The mole ratios of **1a/1d**, **2a/2d**, **6a/6d**, and **7a/7d** are the same as those of **1b**, **2b**, **6b**, and **7b**. b) Not measured.

Specific resistivities at 25 °C ($\rho_{25\,°C}$) and the activation energies (E_a) calculated from the equation $\rho=\rho_0\exp(E_a/kT)$ are listed in Table 2, which involves also the $\rho_{25\,°C}$ and E_a values of the $[Cation]^+TCNQ^{\overline{\cdot}}$ salts and their mixtures with $[Cation]^+ATCNQ^-$, as well as spin concentrations of the salts obtained from ESR spectra. Salts of the $[Cation]^+ATCNQ^-$ type (**1a**—**9a**) exhibit fairly large $\rho_{25\,°C}$ values, which may be suggestive of an alternative $ATCNQ^-/[Cation]^+$ stack in the solid state.

The mixed $ATCNQ^-/TCNQ^{\overline{\cdot}}$ salts **1b**, **6b**, and **7b** except for **2b** display somewhat smaller $\rho_{25\,°C}$ and E_a values than the corresponding $TCNQ^{\overline{\cdot}}$ salts in which the $TCNQ^{\overline{\cdot}}$ radical anion assumes a columnar structure.[8)] In addition, all the mixed salts are more conductive than the mixtures of the $ATCNQ^-$ and $TCNQ^{\overline{\cdot}}$ salts with the same $ATCNQ^-/TCNQ^{\overline{\cdot}}$ mole ratios as those in the respective mixed $ATCNQ^-/TCNQ^{\overline{\cdot}}$ salts. These results suggest the incorporation of the $ATCNQ^-$ anion into the $TCNQ^{\overline{\cdot}}$ radical anion column. Such an incorporation may bring about a disorder in the $TCNQ^{\overline{\cdot}}$ column, which may be responsible for rather lower E_a Values of the mixed $ATCNQ^-/TCNQ^{\overline{\cdot}}$ salts than those of the $TCNQ^{\overline{\cdot}}$ salts, as reported for $(TMTTF)_x(TMTSF)_{1-x}(TCNQ)$ ($x=0.005$ and 0.03; TMTTF=tetramethyltetrathiafulvalene and TMTSF=tetramethyltetraselenafulvalene),[9)] $(TTF)_x(TSF)_{1-x}(TCNQ)$ ($x=0$—1; TTF=tetrathiafulvalene and TSF=tetraselenafulvalene),[10)] $(TMTSF)_2(ClO_4)_{0.95}(IO_4)_{0.05}$,[9)] and $(TSF)(MTCNQ)_{0.1}(TCNQ)_{0.9}$(MTCNQ=methyltetracyanoquinodimethan).[11)]

The temperature dependence of specific resistivities of the $[Cation]^+ATCNQ^-\cdot I_x$ salts is illustrated in Fig. 1. Although the plots of $\log\rho$ *vs.* $1/T$ give a linear relationship below 30 or 20 °C, they deviate from the straight lines above this temperature. The $\log\rho-1/T$ relations of **1c**, **6c**, and **7c**, however, had a reproducible nature in the range of 20—35 °C, while all the $[Cation]^+ATCNQ^-\cdot I_x$ salts decomposed above 35 °C.

Electronic Spectra and Magnetic Properties. Figure 2 shows the electronic reflectance spectra of K^+ATCNQ^- and **7a**—**7c**. The shoulder-like band around 23000 cm^{-1} observed for K^+ATCNQ^- (dotted line in Fig. 2), which corresponds to the absorption band at 22000 cm^{-1} in acetonitrile, is due to the intramolecular charge transfer (CT) transition arising from the $\overset{-}{C}\text{-}\overset{+}{N}$ ylide bond.[1)] Salt **7a** also exhibits this band around 23000 cm^{-1} (solid line in Fig. 2). Other several strong absorptions in the frequency region higher than 20000 cm^{-1} observed for **7a** are ascribed to transitions within the $ATCNQ^-$ anion or the cation. It should be noted that **7a** displays a band at 17500 cm^{-1}, which may be due to an electronic interaction between the $ATCNQ^-$ anion and the cation, since both K^+ATCNQ^- and *N*-ethylquinolinium perchlorate show no band in this region. Such a new band was observed also in the reflectance spectra of the other $[Cation]^+ATCNQ^-$ salts. The frequency of the band maxima (ν_{max}) newly appeared in the $[Cation]^+ATCNQ^-$ salts are listed in Table 3, together with cathode

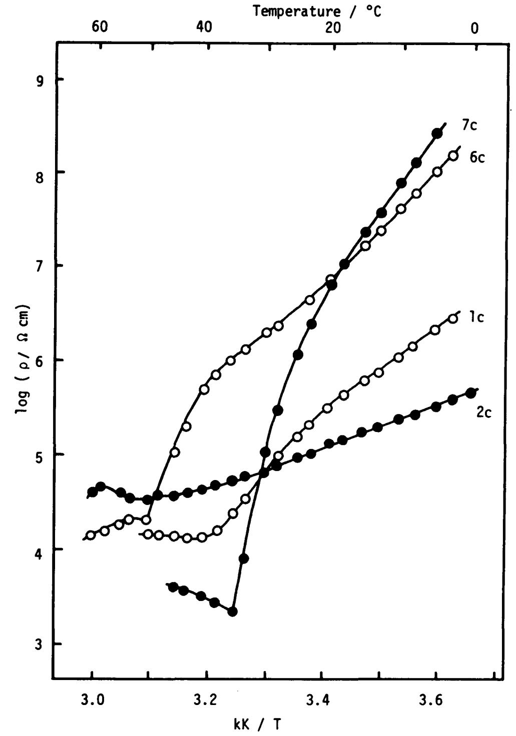


Fig. 1. Temperature dependence of the specific resistivities of the [Cation]$^+$ATCNQ$^-$·I$_x$ salts.

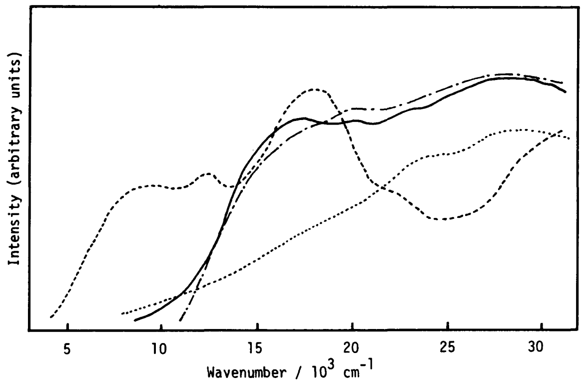


Fig. 2. Powder reflectance spectra of K$^+$ATCNQ$^-$ (·······), [C$_9$H$_7$N-Et]$^+$ATCNQ$^-$ (7a, ——), [C$_9$H$_7$N-Et]$^+$(ATCNQ$^-$)$_{0.1}$(TCNQ$^{\cdot-}$)$_{0.9}$ (7b, ------), and [C$_9$H$_7$N-Et]$^+$ATCNQ$^-$·I$_{3.9}$ (7c, –·–·–).

peak potentials (E_{cp}) of the counter cations determined from cyclic voltammetry. There can be seen an approximate linear relation between ν_{max} and E_{cp} as shown in Fig. 3; ν_{max} decreases with the positive shift of E_{cp}, suggesting that the band is due to an intermolecular CT transition from the ATCNQ$^-$ anion to the counter cations. The smaller difference between the anode peak potential of ATCNQ$^-$ (0.54 V *vs.* SCE in acetonitrile)[1] and the E_{cp} value of a counter cation is expected to cause more effective CT. Although there has been observed no signal in the ESR spectra of **1a**—**4a**, **6a**, and **7a**, salts **5a**, **8a**, and **9a** displayed a weak ESR signal in the solid state, whose g values were essentially the same as that of DPPH (g=2.0037). Based on the signal intensities in comparing with that of DPPH, spin concentrations of **9a**, **5a**, and **8a** at room temperature were estimated 7.5, 0.3, and 0.032%, respectively,

TABLE 3. CT BAND MAXIMA (ν_{max}) OF THE ATCNQ$^-$ SALTS AND CATHODE PEAK POTENTIALS (E_{cp}) OF THE COUNTER CATIONS

Salt	ν_{max} cm^{-1}	E_{cp} V *vs.* SCE
2a	21000	−1.36
1a	20500	−1.28
7a	17500	−0.92
6a	19500	−0.86
3a	19200	−0.76
4a	17900	−0.70
8a	15300	−0.41
5a	14700	−0.25
9a	10000	−0.11

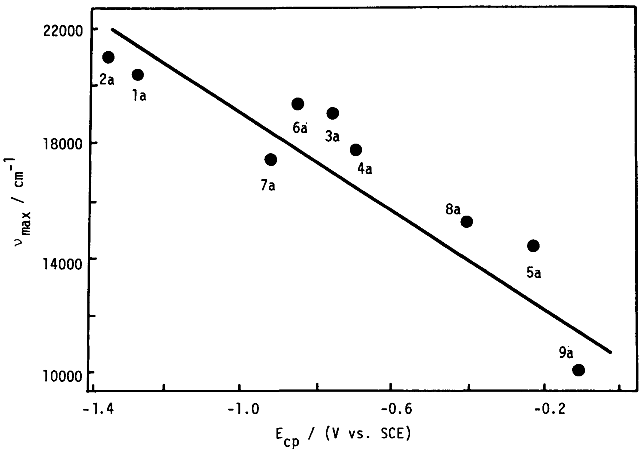


Fig. 3. Plots of CT band maxima (ν_{max}) of the ATCNQ$^-$ salts *vs.* cathode peak potentials (E_{cp}) of the counter cations.

which indicates a radical formation caused by a stronger CT in these salts.

The reflectance spectrum of **7b** shows a band around 9500 cm^{-1} (broken line in Fig. 2), which can be assigned to the CT transition between TCNQ$^{\cdot-}$ radical anions as observed for simple salts such as Na$^+$TCNQ$^{\cdot-}$, Rb$^+$TCNQ$^{\cdot-}$ and [morpholinium]$^+$TCNQ$^{\cdot-}$.[8] In accordance with this, a strong band appears around 18000 cm^{-1}, which is the blueshifted LE$_1$ band characteristic of the dimeric interaction of the TCNQ$^{\cdot-}$ radical anions. On the other hand, a weak band observed at 12000 cm^{-1} is ascribed to the TCNQ$^{\cdot-}$ radical anion monomer.[8] Salts **1b**, **2b**, and **6b** gave essentially the same spectra as **7b**. Thus, these mixed ATCNQ$^-$/TCNQ$^{\cdot-}$ salts are suggested to contain predominantly TCNQ$^{\cdot-}$ radical anions with the dimeric interaction and small amounts of the ATCNQ$^-$ anion seem to prevent the TCNQ$^{\cdot-}$/TCNQ$^{\cdot-}$ interaction, resulting in the formation of a part of monomeric TCNQ$^{\cdot-}$. Although the TCNQ$^{\cdot-}$ simple salts (**1d**, **2d**, **6d**, and **7d**) in which the TCNQ$^{\cdot-}$ radical anion may have the dimeric interactionon[8] exhibited very weak signals, the mixed ATCNQ$^-$/TCNQ$^{\cdot-}$ salts displayed a sharp ESR signal (g=2.0037) with moderate intensities, resulting in much larger spin concentrations in the mixed ATCNQ$^-$/TCNQ$^{\cdot-}$ salts than in the TCNQ$^{\cdot-}$ salts (Table 2). This is consistent with the assumption that the ATCNQ$^-$ anions may prevent the dimeric interaction between the TCNQ$^{\overline{\cdot}}$ radical anions in the mixed ATCNQ$^-$/TCNQ$^{\overline{\cdot}}$ salts.

The iodine-doped salts, **1c**, **2c**, **6c**, and **7c**, exhibited essentially the same IR absorption spectra as those of the undoped salts, **1a**, **2a**, **6a**, and **7a**, respectively, suggesting that the dopant has little effect on the skeletons of either cationic or anionic moieties. In the electronic reflectance spectra, however, the band due to the CT transition between ATCNQ$^-$ and the cation ($\approx$17000 cm^{-1}) is weakened (dot-dash line in Fig. 2). Thus, the introduction of iodine to the ATCNQ$^-$ salts seems to reduce the CT interaction between ATCNQ$^-$ and the cation. It is noted that the spin concentrations of **1c**, **2c**, **6c**, and **7c** obtained from ESR signal intensities are small (Table 2). Only a small portion of the ATCNQ$^-$ anion may, therefore, be oxidized by iodine; most of iodine as a dopant would remain as I_2 in the crystals. Small amounts of the oxidized ATCNQ$^{\cdot}$ radical may contribute to the conductivities of **1c**, **2c**, **6c**, and **7c**, which are 10^2—10^3 greater than those of **1a**, **2a**, **6a**, and **7a**, respectively.

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