Composition and Some Physical Properties of Complex TCNQ Anion Radical Salts Containing Quinolinium, *N*-Methylquinolinium, and their Isomeric Cations

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Complex TCNQ anion radical salts containing quinolinium, isoquinolinium, and their methyl derivatives were prepared. Quinolinium and cations having molecular envelopes of 2-methylnaphthalene form 1 : 2 salts, whereas isoquinolinium and cations having molecular envelopes of 1-methylnaphthalene give 2 : 3 salts. Only *N*-methylquinolinium forms salts containing the solvent of crystallization. The room temperature resistivities of the polycrystalline compactions are in the range from 0.5 to 3.9 ohm cm, and the Seebeck coefficients are in the range from −41 to −54 μV/deg for the 1 : 2 salts and in the range from −12 to −23 μV/deg for the 2 : 3 salts. The diffuse reflection spectra of all the salts are similar to each other. A splitting of the band in the 10×10^3 cm^{-1} region was observed only for the 1 : 2 salts. In the total reflectance spectra, the salts show Drude-like edges in the region from 6×10^3 to 8×10^3 cm^{-1}.

The complex anion radical salt quinolinium(TCNQ)$_2$ is one of the most highly conducting organic materials.[1,2] The resistivity value at room temperature of the pressed polycrystalline sample has been reported to be 0.25 ohm cm, and that of single crystals along the needle axis 0.01 ohm cm. The minimum resistivity has been observed for single crystals at 223 K by Walatka and Perlstein and at 240 K by Buravov *et al.*[3,4] According to the crystal structure analysis made by Kobayashi *et al.*, the cation adopts either of the alternative orientations with equal probability.[5] The composition appears to depend upon small variations introduced in the cation. The *N*-methylquinolinium cation has been shown to form a 2 : 3 salt and its isomer, the quinaldinium cation, a 1 : 2 salt.[6] Moreover, the former salt has been reported by Flandrois *et al.* to contain approximately one mole of acetonitrile per mole of the salt and by Murakami and Yoshimura two moles of the same solvent per mole of the salt.[7–9] It is of interest to examine more fully complex salts with isomeric cations. Accordingly, the authors set out to study the composition and some physical properties of the isoquinolinium salt and methyl-substituted quinolinium and isoquinolinium salts.

Experimental

Materials. Quinoline, isoquinoline, quinaldine, lepidine, and 6-methyl-, 7-methyl-, and 8-methyl-quinolines were commercially obtained, and used without further purification. The onium iodides were prepared by the usual reactions with hydroiodic acid or methyl iodide. The complex TCNQ salts were crystallized when onium iodide and TCNQ separately dissolved in hot acetonitrile were mixed. They were purified by recrystallization from the same solvent. The compositions were determined by the microanalysis of carbon, hydrogen, and nitrogen, and were checked by the ratio of the optical density at 400 nm to that at 842 nm. This quantity has been reported to be about 1.2 for the 2 : 3 salts and from 1.7 to 2.0 for the 1 : 2 salts.[10]

Measurements. The electrical resistivities and thermoelectric motive force of polycrystalline compactions were measured as a function of the temperature by methods similar to those described elsewhere.[11] The diffuse reflectance of samples diluted with sodium chloride was measured by means of a Beckman DK 2A spectroreflectometer in the range from 325 to 2500 nm. The reference was pure sodium chloride. The spectrum was then plotted using the Kubelka-Munk function. The total reflectance of the compactions was also recorded on the same instrument in the range from 700 to 2700 nm employing a polished copper plate as a reference.

Results and Discussion

Composition. Six new complex TCNQ anion radical salts are listed in Table 1. The results of microanalysis are consistent with their 2 : 3 or 1 : 2 composition, but the ratio of the optical density at 400 nm to that at 842 nm tends to be larger than the above-mentioned figures. For example, Buvet *et al.* obtained 2.00, 1.20, and 1.85 for the quinolinium, *N*-methylquinolinium, and quinaldinium salts respectively.[10] The present values are respectively 2.18, 1.34, and 2.15. Especially, the values found for the 7-methyl- and 8-methylquinolinium salts are much larger than expected. Although the quinolinium cation has been known to form a 1 : 2 salt, the isomer, the isoquinolinium cation, was found to form a 2 : 3 salt. Thus, the distribution of a positive charge in the cationic nucleus appears to be the most important factor determining the composition in this pair of TCNQ salts. The methyl-substituted cations are classified into two groups on the basis of the composition of the resulting TCNQ salts. One group consists of *N*-methylquinolinium, lepidinium, and 8-methylquinolinium, which give 2 : 3 salts. The other includes quinaldinium, *N*-methylisoquinolinium, 6-methylquinolinium, and 7-methylquinolinium. They form 1 : 2 salts. This classification cannot be correlated with the position of the nitrogen atom in the nuclei, but can be correlated with the position of the methyl group. The cations in the first group have molecular envelopes of 1-methylnaphthalene, and those in the second group envelopes of 2-methylnaphthalene. This finding is in sharp contrast with the result found for quinolinium and isoquinolinium cations and also with the report on aminoquinolinium cations by Libera and Bretschneider.[12] All the TCNQ salts containing 2-amino-, 3-amino-,

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TABLE 1. COMPOSITIONS OF TCNQ ANION RADICAL SALTS

Cation		Analysis (%)			D_{400}/D_{842}
		C	H	N	
Isoquinolinium	Found	74.69	3.10	22.34	1.44
	Calcd for 2 : 3	74.47	3.01	22.52	
Lepidinium	Found	74.66	3.49	21.42	1.32
	Calcd for 2 : 3	74.65	3.58	21.77	
8-Methylquinolinium	Found	75.04	3.43	21.75	2.28
	Calcd for 2 : 3	74.65	3.58	21.77	
N-Methylisoquinolinium	Found	73.98	3.17	22.82	2.35
	Calcd for 1 : 2	73.90	3.28	22.81	
6-Methylquinolinium	Found	74.01	3.18	22.86	2.21
	Calcd for 1 : 2	73.90	3.28	22.81	
7-Methylquinolinium	Found	73.40	3.04	23.15	2.85
	Calcd for 1 : 2	73.90	3.28	22.81	

4-amino-, and 5-aminoquinolinium cations were reported to be of 1 : 2 composition. Since the amino group is a little smaller than the methyl group, the latter may be a substituent of such critical size that the molecular envelope dominates the charge distribution in the determination of the composition of complex TCNQ salts.

The *N*-methylquinolinium salt, to which a 1 : 2 composition was originally assigned by Melby *et al.* on the basis of microanalysis,[1] has been shown to be actually of 2 : 3 composition on the basis of the optical density ratio at 400 and 842 nm.[6,10] Differential-scanning calorimetric examinations indicated the presence of an endothermic change above 90 °C assignable to the loss of the solvent of crystallization reported by Flandrois *et al.* and also by Murakami and Yoshimura.[8,9] The enthalpy change observed in this work is in the range from 10 to 15 kcal/mol depending upon the preparations. These values are intermediate between those reported by the above-mentioned two groups: about 5 kcal/mol and 19.1 kcal/mol. Our preparations showed weight losses of about 8.5 percent by heating at 120 °C, indicating the presence of two moles of acetonitrile per mole of the 2 : 3 salt (calculated value: 8.35%). The results of microanalysis before and after the weight loss are in good agreement with the proposed compositions (see Table 2). It may be added that the calculated values for the 2 : 3 salt containing this amount of the solvent are very close to those for the originally assumed 1 : 2 salt, namely, C, 73.90, H, 3.28, and N, 22.81%. This conclusion agrees with that of Murakami and Yoshimura except for the ratio of the cation to the TCNQ, which they suggested to be 1 : 1.6.[9,13] The salt crystallized from acetone showed a weight loss of 9.8 percent by heating. This amount corresponds to 1.7 moles of acetone per mole of the 2 : 3 salt. Employing the less volatile ethyl methyl ketone as the solvent, the salt with a better defined composition could be isolated. The composition is consistent with a 2 : 3 salt containing one mole of the solvent. The observed weight loss by heating, about 7.7%, agrees fairly well with the calculated one, 7.41%. The microanalytical results after heating again agree with a 2 : 3 composition. Contrary to the case of acetonitrile, the loss of these ketones by heating could not be detected by differential-scanning calorimetry. However, the process is well demonstrated by a drastic change of the electrical resistivity as is described in the next section. The last salt in Table 2 was crystallized from boiling ethyl acetate and found to be free from the solvent and to be of 2 : 3 composition. Finally, it must be emphasized that in all the *N*-methylquinolinium salts prepared here the ratio of the cation to the TCNQ is stoichiometric: that is 2 : 3.

TABLE 2. COMPOSITION OF *N*-METHYLQUINOLINIUM TCNQ SALTS

Solvent		Analysis (%)		
		C	H	N
Acetonitrile	Found	73.61	3.79	22.90
	Calcd for 2 : 3 with $2CH_3CN$	73.30	3.90	22.80
Acetonitrile[a)]	Found	75.09	3.44	21.98
	Calcd for 2 : 3	74.65	3.58	21.77
Ethyl methyl ketone	Found	73.99	4.13	19.86
	Calcd for 2 : 3 with C_4H_8O	74.05	4.14	20.15
Ethyl methyl ketone[a)]	Found	74.70	3.49	21.34
	Calcd for 2 : 3	74.65	3.58	21.77
Ethyl acetate	Found	74.62	3.57	21.22
	Calcd for 2 : 3	74.65	3.58	21.77

a) After the loss of the solvent of crystallization.

Electrical Properties. The electrical resistivities, activation energies for semiconduction, and Seebeck coefficients at 20 °C for polycrystalline compactions are listed in Table 3. The present resistivity values are in the range from 0.5 to 3.9 ohm cm and the activation energies from 0.03 to 0.09 eV. The lowest values for these two quantities were observed with the quinolinium and isoquinolinium salts. As the single crystals of the former salt are known to exhibit a resistivity minimum below room temperature, these values may be considered to arise mostly from contact between the crystals. Therefore, they may be near the limiting values obtainable with compactions of high-conductivity TCNQ salts. The Seebeck coefficients are almost constant or become slightly more negative at the higher temperatures in the measured range (see curve a in Fig. 2). Its

Table 3. Electrical properties of compactions of complex TCNQ salts

Cation	Resistivity at 20 °C (ohm cm)	Activation energy at 20 °C (eV)	Seebeck coeff. at 20 °C (μV/deg)
Quinolinium	0.5	0.03	−41
Isoquinolinium	0.5	0.03	−12
N-Methylquinolinium (with $2CH_3CN$)	3.5	0.24	−23
N-Methylquinolinium (with C_4H_8O)	3.9	0.04	−22
Lepidinium	1.7	0.05	−12
8-Methylquinolinium	1.6	0.06	−21
Quinaldinium	1.2	0.04	−45
N-Methyl-isoquinolinium	0.5	0.09	−47
6-Methylquinolinium	1.9	0.05	−54
7-Methylquinolinium	3.2	0.07	−49

magnitude appears to be largely determined by the composition, namely, the 2 : 3 salts give values from −12 to −23 μV/deg and the 1 : 2 salts values from −41 to −54 μV/deg. Similar behavior has been reported to be characteristic of high conductivity TCNQ salts.[4] Buravov *et al.* have examined the Seebeck coefficient of the quinolinium (1 : 2), acridinium (1 : 2), and 3,3′-diethylthiazolino-2,2′-carbocyaninium (1 : 2) salts and found that the values are nearly independent of temperature above 100 or 150 K and that they are practically the same for all three. The average value they obtained is −60 μV/deg. According to their theory, the coefficient is a function of the composition, however, the relation is so complicated that their equation has been solved only for the 1 : 2 salts. In the high temperature limit, the coefficient S for the 1 : 2 salts can be approximated by $S=-(k/|e|)\ln 2=-59.8$ μV/deg, which is in excellent agreement with their experimental results but not with the present values. Recently, Beni *et al.* have obtained the same theoretical value for the 1 : 2 salts employing an equation derived in connection with the strong coupling Hubbard model.[14] Their equation for the high temperature saturation thermoelectric power is

$$S = -\frac{k}{|e|}\ln 2(1-\rho)/\rho,$$

where ρ is the carrier concentration defined by the ratio of the number of carriers to the number of sites. If we take $\rho=1/2$, the equation yields $S=-59.8$ μV/deg. Conversely, ρ may be estimated to be 0.52—0.55 assuming tentatively the room temperature values as the saturation values and employing the above equation as novel way of determining the amount of charge following a proposal made by Beni *et al.* Similarly, values from 0.60 to 0.62 may be obtained for the 2 : 3 salt. On the other hand, the equation yields $S=0$ for $\rho=2/3$.

The *N*-methylquinolinium salt crystallized from acetonitrile has been reported to show a large irreversible increase in the resistivity by the loss of the solvent of crystallization.[13] In our measurements, the activation energy for semiconduction was temperature-dependent and was about 0.24 eV at 20 °C. The resistivity remained at about 3 ohm cm between 30 and 50 °C, then increased gradually above 50 °C and sharply above 55 °C. The value at 103 °C was about 4300 ohm cm. After this heating process, the room temperature resistivity became about 8000 ohm cm. On the other hand, compaction made after the loss of the solvent of crystallization showed a resistivity of about 2600 ohm cm and an activation energy of 0.25 eV at 20 °C. These values are close to those reported by Murakami and Yoshimura, about 2000 ohm cm and 0.3 eV, and are essentially the same as those given by the solvent-free salt crystallized from ethyl acetate (see curve c in Fig. 1).

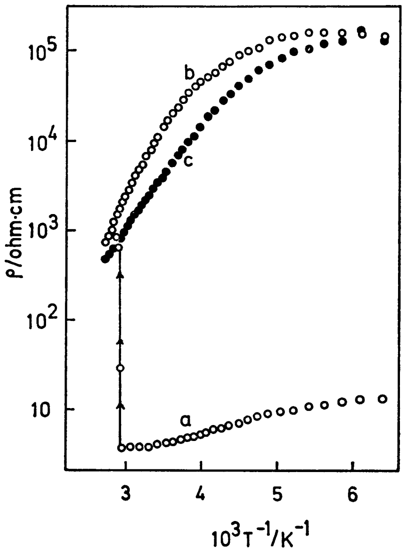

Fig. 1. Electrical resistivities of *N*-methyl quinolinium-TCNQ (2 : 3) salts, (a) with ethyl methyl ketone of crystallization, (b) after the loss of ethyl methyl ketone, and (c) the solvent-free salt crystallized from ethyl acetate.

The results of measurements made on the salt crystallized from ethyl methyl ketone are shown in Fig. 1. The resistivity change occurred over a rather narrow temperature range. The irreversible increase began at 63 °C and ended at 84 °C. The resistivity value at the latter temperature was about 1000 ohm cm and that at room temperature after the loss of the solvent about 10000 ohm cm. Thus, curve b and the corresponding curve observed with the salt crystallized from acetonitrile are in close resemblance with each other. The behavior of the salt crystallized from acetone was very similar to that mentioned above. However, an abrupt increase in the resistivity was observed in a slightly lower temperature range. The increase began at 50 °C and ended at 65 °C, reflecting the volatility of the solvent.

The drastic change in the Seebeck coefficient by the loss of the solvent of crystallization is illustrated in Fig. 2 for the salt crystallized from acetonitrile. The coefficient becomes more negative and markedly temperature dependent by the loss of acetonitrile (see curve b). A minimum value of −0.4 mV/deg is located near 240 K. Above this temperature, the slope defined by $dS/d(1/T)$ is as large as −0.26 V. The same slope

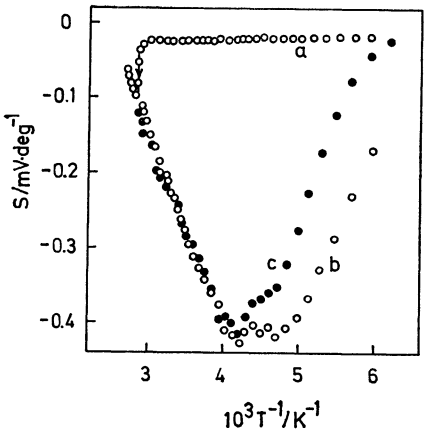

Fig. 2. Seebeck coefficients of *N*-methylquinolinium-TCNQ (2 : 3) salts, (a) with acetonitrile of crystallization, (b) after the loss of acetonitrile, and (c) the solvent-free salt crystallized from ethyl acetate.

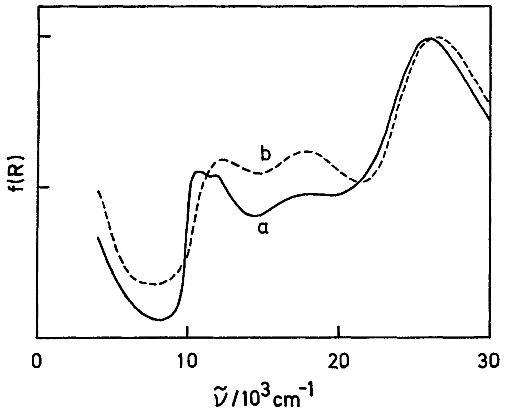

Fig. 3. Diffuse reflection spectra, (a) quinolinium-TCNQ (1 : 2) salt and (b) isoquinolinium-TCNQ (2 : 3) salt.

could be observed with the solvent-free salt crystallized from boiling ethyl acetate (see curve c). However, the agreement between these two below 240 K is merely qualitative.

Optical Properties. The visible and near infrared absorption spectra of complex TCNQ anion radical salts both of intermediate- and high-conductivity are known to resemble each other and to consist of four bands, the maxima of which are approximately located at $<4\times10^3$, 10×10^3, 17×10^3, and $27\times10^3\ \mathrm{cm}^{-1}$.[15–17] On the basis of polarized normal-incidence reflection of the methyltriphenylphosphonium salt, the assignment of these bands has been made by Oohashi and Sakata. The band in the near infrared region arises from the charge-transfer interaction between the TCNQ$^-$ anion radical and the neutral molecule and the second one from the charge-transfer interaction between the anions. The latter two bands have been attributed to locally-excited transitions in the anion radical and/or the neutral molecule. Among the TCNQ salts studied here, the following five were examined for diffuse reflection spectra by Iida some years ago: the quinolinium, *N*-methylquinolinium, *N*-methylisoquinolinium, quinaldinium, and lepidinium salts. A splitting of the band around $10\times10^3\ \mathrm{cm}^{-1}$ was noted in the case of *N*-methylquinolinium and *N*-methylisoquinolinium salts. Assuming a 1 : 2 composition for these five, Iida has noted that the splitting becomes appreciable with an increase of the electrical resistivity. As a matter of fact, such splitting has been commonly observed in the intermediate- and high-conductivity 1 : 2 salts.[15,16] However, the present work clarifies that the five salts studied by Iida are not of the same composition. The measurements on the present five 1 : 2 and four 2 : 3 salts revealed that the spectral pattern is essentially determined by the composition. The difference caused by the composition may be best exemplified by a comparison of the spectrum of the quinolinium salt with that of the isoquinolinium salt exhibiting almost the same electrical resistivity. As is shown in Fig. 3, the quinolinium salt shows a doublet in the $10\times10^3\ \mathrm{cm}^{-1}$ region. The maxima of the sharp peaks are located at 10.5×10^3 and $11.0\times10^3\ \mathrm{cm}^{-1}$. Both previous workers noted only one maximum for this 1 : 2 salt. The location of the former peak agrees well with that recorded by Iida and that of the latter with the value reported by Oohashi and Sakata. On the other hand, a broad single band appears at $12.3\times10^3\ \mathrm{cm}^{-1}$ in the isoquinolinium salt. The spectra of the complex salts containing methylated cations are presented in Fig. 4. Again, the 1 : 2 salts are generally distinct from the 2 : 3 salts. A splitting of the band in the $10\times10^3\ \mathrm{cm}^{-1}$ region can be clearly observed in all the 1 : 2 salts but not in the 2 : 3 salts. It must be noted, however, a shoulder around $10\times10^3\ \mathrm{cm}^{-1}$ is present in the spectrum of the solvent-free *N*-methylquinolinium salt, the only intermediate-conductivity salt examined in the present

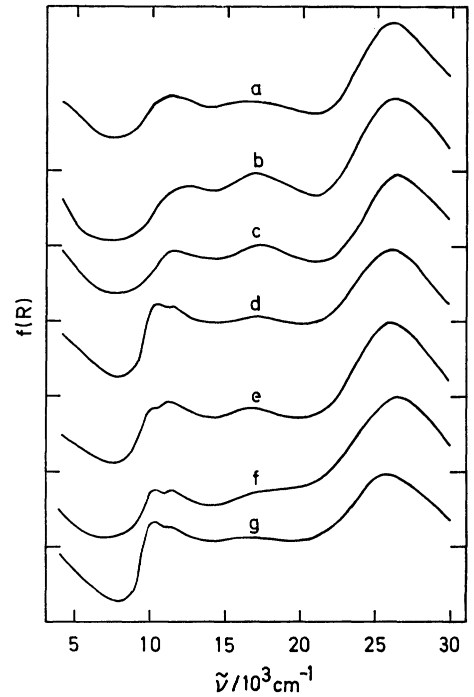

Fig. 4. Diffuse reflection spectra of the complex TCNQ anion radical salts containing (a) *N*-methylquinolinium (solvent-free), (b) lepidinium, (c) 8-methylquinolinium, (d) quinaldinium, (e) 6-methylquinolinium, (f) 7-methylquinolinium, and (g) *N*-methylisoquinolinium.

work.

Polarized reflectance spectra have been measured on single crystals of $Cs_2(TCNQ)_3$ by Vlasova and Gutman.[18] This complex salt has a resistivity of the order of 10^4 ohm cm at room temperature and has been classified into intermediate-conductivity salts by Siemons *et al.*[2] The reflectance for light polarized parallel to the needle axis rises from a minimum of about 2 percent at $14.5\times10^3\,\mathrm{cm}^{-1}$ to a value of about 17 percent at $10\times10^3\,\mathrm{cm}^{-1}$. They have considered such a rapid decrease of the reflectance to such a low value to be typical of the plasma edge observed with metals and semiconductors and have estimated the plasma frequency for this salt to be $2.8\times10^{15}\,\mathrm{s}^{-1}$. The spectral behavior of an organic metal, tetrathiofulvalene–tetracyanoquinodimethane (TTF–TCNQ), with a resistivity of the order of 10^{-3} ohm cm along the needle axis has been examined similarly by Bright *et al.* and also by Grant *et al.*[19–21] The change in the reflectance for light polarized parallel to the conducting axis is much more pronounced than that reported for $Cs_2(TCNQ)_3$, less than 1 percent at $7\times10^3\,\mathrm{cm}^{-1}$ and 34 percent at $5\times10^3\,\mathrm{cm}^{-1}$ according to the former group. The plasma frequency has been estimated to be 1.80×10^{15} and $2.1\times10^{15}\,\mathrm{s}^{-1}$ and the electronic relaxation time, 2.83×10^{-15} and 2.3×10^{-15} s by Bright *et al.* and by Grant *et al.*, respectively. The conductivity calculated on the basis of these optical data is in good agreement with the measured d.c. conductivity. Bright *et al.* have extended their measurements to $0.8\times10^3\,\mathrm{cm}^{-1}$ employing a polycrystalline compaction. In this case, the measured reflectance is an average over all crystalline orientations in the solid. Therefore, the component parallel to the conducting axis must be extracted by subtracting the reflectance due to the transverse directions and by correcting the resultant value for $\overline{\cos^2\theta}$. The perpendicular reflectance was assumed constant in the infrared region and equal to the minimum value at the plasma edge. Although, among the salts studied above, only the quinolinium salt is known to show metallic behavior at room temperature, the authors included the measurements of the total reflectance spectra of polycrystalline compactions to find out what kind of optical data one can obtain for these complex TCNQ salts and whether metallic salts can be distinguished from nonmetallic ones by such data.

The spectra for light polarized parallel to the conducting axis were derived from the data on polycrystalline compactions following the procedure proposed by Bright *et al.* In Fig. 5, the Drude-like edges observed with the quinolinium and isoquinolinium salts are presented. The reflectance of the former salt shows a minimum centered at $6.8\times10^3\,\mathrm{cm}^{-1}$ and rises to a value of 13 percent at $5\times10^3\,\mathrm{cm}^{-1}$. There are weak peaks located at 9.9×10^3 and $11.3\times10^3\,\mathrm{cm}^{-1}$ which may correspond to the absorption bands around $10\times10^3\,\mathrm{cm}^{-1}$ (see Fig. 3). The curve of the latter salt is shifted slightly to the high-energy side. The minimum is located at $7.5\times10^3\,\mathrm{cm}^{-1}$ and the value at $5\times10^3\,\mathrm{cm}^{-1}$ is about 27 percent. In the $10\times10^3\,\mathrm{cm}^{-1}$ region, a broad band centered at $10.6\times10^3\,\mathrm{cm}^{-1}$ appears with a shoulder around $9\times10^3\,\mathrm{cm}^{-1}$. One assumes that the dielectric constant ε is a function of frequency ω and is given by

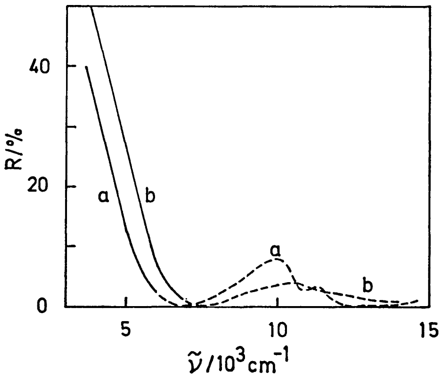

Fig. 5. Reflectance spectra for light polarized parallel to the conducting axis derived from polycrystalline measurements, (a) quinolinium-TCNQ (1 : 2) salt and (b) isoquinolinium-TCNQ (2 : 3) salt.

$$\varepsilon=\varepsilon_0-\frac{\omega_p{}^2}{\omega^2+i\omega/\tau}$$

where ε_0 is the frequency-independent background dielectric constant, ω_p is the plasma frequency, and τ is the electronic relaxation time. The reflectance R is given in terms of the real and imaginary parts of the dielectric constant $\varepsilon=n^2(1-i\kappa)^2$ by the well-known Drude formula

$$R=\frac{n^2(1+\kappa^2)+1-2n}{n^2(1+\kappa^2)+1+2n}$$

The best fit was obtained with $\varepsilon_0=2.18$, $\omega_p=2.31\times10^{15}\,\mathrm{s}^{-1}$, and $\tau=1.73\times10^{-15}$ s for the quinolinium salt and with $\varepsilon_0=2.36$, $\omega_p=2.62\times10^{15}\,\mathrm{s}^{-1}$, and $\tau=1.91\times10^{-15}$ s for the isoquinolinium salt. The solid curves in Fig. 5 are parts of the reflectance fitted to the above expression. In the vicinity of the minimum, the fits cannot be good because of the approximations employed. If the conventional expression relating the plasma frequency and the d.c. conductivity for metals, $\sigma=\omega_p{}^2\tau/4\pi$, is assumed using the above values for ω_p and τ, one obtains an estimate of 817 $\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$, which markedly higher than the experimental value

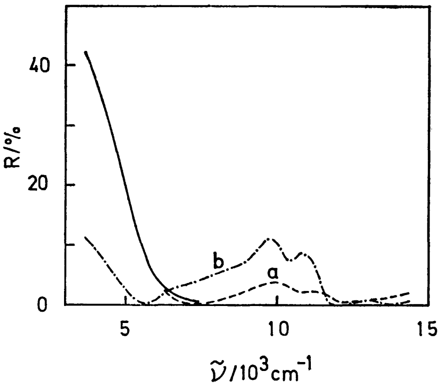

Fig. 6. Reflectance spectra for light polarized parallel to the conducting axis derived from polycrystalline measurements, (a) *N*-methylquinolinium-TCNQ salt with acetonitrile of crystallization and (b) the same salt after the loss of the solvent.

Table 4. Optical data for TCNQ anion radical salts

Cation (Composition)	ε_0	ω_p (10^{15} s^{-1})	τ (10^{-15} s)	σ (ohm^{-1} cm^{-1})
Quinolinium (1 : 2)	2.18	2.31	1.73	817
Isoquinolinium (2 : 3)	2.36	2.62	1.91	1160
N-Methylquinolinium (2 : 3) with $2CH_3CN$	1.89	2.27	1.68	766
Lepidinium (2 : 3)	2.45	2.66	1.53	958
8-Methylquinolinium (2 : 3)	1.78	1.98	1.39	482
Quinaldinium (1 : 2)	1.75	1.87	1.41	436
N-Methylisoquinolinium (1 : 2)	2.05	2.09	1.69	653
6-Methylquinolinium (1 : 2)	1.77	1.75	1.72	466
7-Methylquinolinium (1 : 2)	1.74	1.79	1.38	391
N-Methylphenazinium (1 : 1)	1.51	1.99	0.96	336
Acridinium (1 : 2)	1.85	1.93	1.55	511

reported by Walatka and Perlstein of 100 ohm^{-1} cm^{-1}.3)

The change in the spectrum of the *N*-methylquinolinium salt with the loss of the acetonitrile of crystallization is sharp as is shown in Fig. 6. The reflectance at 5×10^3 cm^{-1} decreases from 20 percent to 2.5 percent and the minimum shifts from 7.5×10^3 cm^{-1} to 5.2×10^3 cm^{-1}. The latter change is in the direction opposite to that one might expect from a comparison between $Cs_2(TCNQ)_3$ and TTF–TCNQ. Furthermore, the peaks around 10×10^3 cm^{-1} are intensified by a factor of three, and additional peaks appear in the range from 6×10^3 to 9×10^3 cm^{-1}. Thus, an increase by a factor of one thousand in the electrical resistivity is reflected by a significant change in the spectrum. Therefore, it is rather surprising to see in the other high-conductivity salts that the reflectance in the near-infrared region varies considerably by from 4 percent in the 7-methylquinolinium salt to 22 percent in the lepidinium salt at 5×10^3 cm^{-1}. The minima are scattered in the range from 6×10^3 to 8×10^3 cm^{-1}. The estimates of the background dielectric constant, plasma frequency, relaxation time, and conductivity are listed in Table 4. The *N*-methylphenazinium and acridinium salts included in the table are known to be as conducting as the quinolinium salt and to show resistivity minima below room temperature.4,22) It may be noted that the estimated d.c. conductivity for the former salt is in good agreement with the value observed by Coleman *et al.*, 380 ohm^{-1} cm^{-1}.22) Such an agreement is probably fortuitous. The experimental conductivity may depend considerably upon the crystals. The value reported by Coleman *et al.* is more than twice that obtained by Shchegolev *et al.*23) The latter group has reported a conductivity of about 70 ohm^{-1} cm^{-1} along the direction of the TCNQ column of the acridinium salt.4) Therefore, it appears to be difficult to judge whether the conductivity estimated from the optical data is in agreement with the experimental value or not. The remarkable feature of the data in Table 4 is the relative insensitivity of the estimated conductivity to the materials. Moreover, there appears to be no correlation with the resistivity observed for polycrystalline compactions. As has been pointed out by Grant *et al.*, the observed Drude-like edge may be of other than simple metallic origin.20)

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