Electrical and Optical Properties of the Iodine Complexes of Phenoxazine, Phenoselenazine, and Benzophenothiazines[1]

Yoshio Matsunaga and Yukio Suzuki*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received April 26, 1972)

The electrical resistivities and Seebeck coefficients of the 2: 3 iodine complexes of phenoxazine, phenoselenazine, and benzophenothiazines were measured as a function of the temperature. They have resistivity values at 20°C ranging from 10 ohm·cm for the phenoxazine complex to 34 ohm·cm for the benzo[a]phenothiazine complex. Employing the equation of Johnson and Lark-Horowitz for the Seebeck coefficient of an intrinsic semiconductor, the ratio of the electron-to-hole mobility in the phenoselenazine complex was found to be 1.07 and the electron mobility was estimated as 0.26 cm²/V sec. By an examination of the vibrational spectra, the expected cation-radical character was confirmed for the complexes of phenoselenazine and benzophenothiazines. The presence of a broad electronic absorption band in the rock-salt region characteristic of low-resistivity organic semiconductors was noted in every case.

The phenothiazine-iodine complex, the formation of which was reported by Pummerer and Gassner as early as 1913,[2] was found to exhibit a relatively low electrical resistivity about a decade ago.[3] Further studies of the electrical resistivity of this complex have

---

* Present address: Tokyo Shibaura Electric Co., Kawasaki.

1) Presented at the 24th Annual Meeting of the Chemical Society of Japan, Suita, April 1971.

2) R. Pummerer and S. Gassner, *Ber.*, **46**, 2310 (1913).

3) Y. Matsunaga, *Helv. Phys. Acta*, **36**, 800 (1963).

been published by several workers.[4-7] More recently, measurements have been made of the Seebeck coefficient as a function of the temperature by Sano et al.[7] In addition, the electrical properties of the iodine complexes of the N-methyl and N-ethyl derivatives have been compared with those of the above-mentioned complex.[3,7,8] The electronic absorption spectrum in the visible region has been examined by Bhat and Rao, and the diffuse reflection spectrum in both the visible and near-infrared regions, by Matsunaga and Shono.[5,6] The presence of an electronic absorption maximum at 5.5 kK was shown by the latter workers. In the initial report on the resistivity, it was demonstrated that the vibrational spectrum of the phenothiazine-iodine complex is quite different from that of the parent organic compound, but practically the same as that of semiquinoid phenothiazine bromide.[3] On the basis of this observation, which was subsequently confirmed by a more detailed work,[6] it was postulated that every phenothiazine molecule in the solid complex bears an approximately unit-positive charge.

Thus, considerable interest has been shown in the phenothiazine-iodine complex; however, little work has been carried out on the complexes of structurally related compounds. One of the present authors has previously measured the electrical resistivities of the complexes of benzo[a]- and benzo[c]-phenothiazines.[3] Contrary to the introduction of the N-alkyl group, the extra ring does not appreciably affect the resistivity. No attention has been paid to their optical properties. On the other hand, nothing is known about the iodine complexes of phenoxazine and phenoselenazine. Pursuing an inquiry into the effect of the organic component on the electrical and optical properties of the iodine complexes, these four compounds have been taken up in comparison with phenothiazine.

Experimental

Materials. The phenoxazine was prepared by the condensation of o-aminophenol in the presence of iodine.[9] The crude product extracted with toluene was recrystallized from ethanol. The reaction between diphenylamine and selenium monochloride was carried out in chloroform, as has been described by Müller et al., instead of the benzene originally used by Cornelius.[10] This compound was recrystallized from ligroin. The selenium monochloride needed for the synthesis of phenoselenazine was made by the addition of concentrated sulfuric acid to a mixture of selenium, selenium dioxide, and concentrated hydrochloric acid, following the procedure of Lenher and Kao.[11] The benzo[a]- and benzo[c]-phenothiazines were obtained by the reaction of sulfur on α- and β-phenylnaphthylamines respectively, using a small amount of iodine as the catalyst.[12] Both of them were

purified by recrystallization from ligroin. The preparation of the semiquinoid bromides was carried out by the oxidation of the organic compounds with bromine, as has been reported for phenothiazine bromide by Kehrmann and Diserens.[13] The iodine complexes were precipitated when the organic component and iodine, separately dissolved in benzene, were mixed.

Measurements. The electrical resistivities and Seebeck coefficients were recorded as a function of the temperature by the methods described in the paper by Kan and Matsunaga.[8] Measurements of the vibrational and electronic spectra were made as have been reported elsewhere.[6]

Results and Discussion

The iodine contents presented in Table 1 indicate that all the complexes consist of two molecules of the organic component and three of iodine. They are all black polycrystalline powder except for the phenoxazine complex, which is in the form of needles with metallic luster.

TABLE 1. COMPOSITION OF THE IODINE COMPLEXES

Organic component	Iodine content (%)	
	Calcd for 2:3	Found
Phenoxazine	67.6	67.7
Phenothiazine	65.7	65.6
Phenoselenazine	60.7	60.9
Benzo[a]phenothiazine	60.5	61.4
Benzo[c]phenothiazine	60.5	61.3

Electrical Properties. The resistivity of the complexes under study shows a temperature dependence which follows the typical semiconductor behavior:
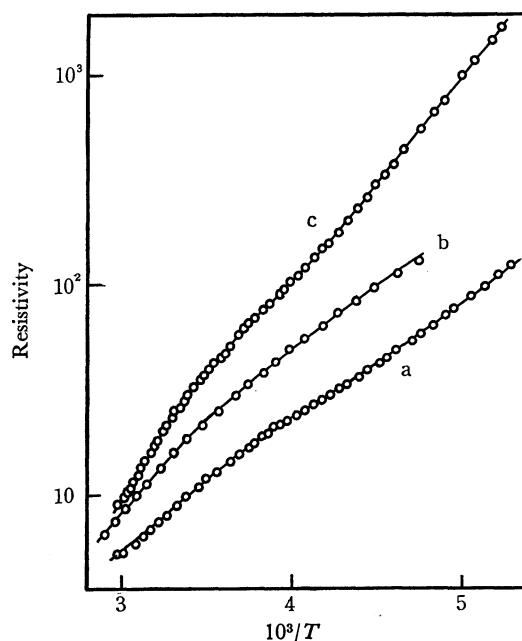
$$\rho = \rho_0 \exp (E/kT) \tag{1}$$

Fig. 1. Electrical resistivities of the iodine complexes of a) phenoxazine, b) phenothiazine, and c) phenoselenazine.

4) F. Gutmann and H. Keyzer, *J. Chem. Phys.*, **46**, 1969 (1967).

5) S. N. Bhat and C. N. R. Rao, *Can. J. Chem.*, **47**, 3899 (1969).

6) Y. Matsunaga and K. Shono, This Bulletin, **43**, 2007 (1970).

7) M. Sano, K. Ohno, and H. Akamatu, *ibid.*, **44**, 3269 (1971).

8) K. Kan and Y. Matsunaga, *ibid.*, **45**, 2096 (1972).

9) P. Müller, N. P. Buu-Hoï, and R. Rips, *J. Org. Chem.*, **24**, 37 (1959).

10) W. Cornelius, *J. Prakt. Chem.*, (2), **88**, 407 (1913).

11) V. Lenher and C. H. Kao, *J. Amer. Chem. Soc.*, **47**, 772 (1925).

12) E. Knoevenagel, *J. Prakt. Chem.*, (2), **89**, 1 (1914).

13) F. Kehrmann and L. Diserens, *Ber.*, **48**, 318 (1915).

TABLE 2. ELECTRICAL PROPERTIES OF THE IODINE COMPLEXES
IN THE HIGHER TEMPERATURE REGION

Organic component	ρ at 20°C (ohm cm)	E (eV)	μ_e/μ_h	m_e/m_h	Ref.
Phenoxazine	10	0.14	2.11	1/40	This work
Phenothiazine	20	0.17	—	—	3
Phenothiazine	13	0.19	—	—	6
Phenothiazine	17	0.164	$ca.$ 0.7	—	7
Phenothiazine	19	0.19	<1	—	This work
Phenoselenazine	32	0.28	1.07	1/2	This work
Benzo[a]phenothiazine	20	0.19	—	—	3
Benzo[a]phenothiazine	34	0.16	>1	—	This work
Benzo[c]phenothiazine	20	0.20	—	—	3
Benzo[c]phenothiazine	18	0.14	>1	—	This work

For example, the logarithm of the resistivity of the complexes of phenoxazine, phenothiazine, and phenoselenazine is plotted against the reciprocal temperature in Fig. 1. The presence of a break near or a little below room temperature is noted in these three cases. The values of the resistivity (ρ) at 20°C and the activation energy (E) in the higher temperature region are summarized in Table 2, where literature values are also included for the sake of comparison. Except for the case of the benzo[a]phenothiazine complex, the present results are in fair agreement with the available data. Both the resistivity and activation energy increase in this order of organic components: phenoxazine<phenothiazine<phenoselenazine.

The plot for the benzophenothiazine complexes does not show a break in the temperature range measured. We confirmed the earlier observation that the presence of an extra benzene nucleus —in other words, a more widespread electron delocalization in the organic component— modifies only a little the electrical properties of the iodine complex. This conclusion is in marked contrast with the appreciable effect of the size of an alkyl group on the nitrogen atom of phenothiazine on the electrical resistivity of the iodine complex.[8]

Single crystals of the low-resistivity tetracyanoquinodimethane (TCNQ) anion-radical salts have been known to be highly anisotropic.[14-16] The resistivity value observed along the long-needle axis of crystal of the simple N-methylphenazinium salt, 0.007 ohm·cm, is the lowest ever recorded for any organic compound. This value is much lower than the resistivity determined on the polycrystalline compaction of the same salt, 0.5 ohm·cm.[16] Similar results have been reported for the complex N-methylquinolinium salt, 0.01 ohm·cm in the long axis direction and 0.5 ohm·cm with a compacted sample. In addition, the activation energy measured with the single crystal is known also to be lower than that obtained with a compaction: <0.01 eV vs. 0.07 eV.[15] As was mentioned above, the phenoxazine-iodine complex is obtainable in the form of needles. Therefore, it seemed worthwhile to attempt

measurements of the resistivity along the long needle axis of this iodine complex as a function of the temperature. Surprisingly, the resistivity at 20°C was found to be 8 ohm·cm, which must be considered in good agreement with the value observed with a compaction if one takes into consideration the errors involved in the geometrical measurements of small crystals. Moreover, the activation energy estimated by the measurements in the range from −65 to 20°C is 0.14 eV. Here again, the agreement with the value given in Table 2 is excellent.
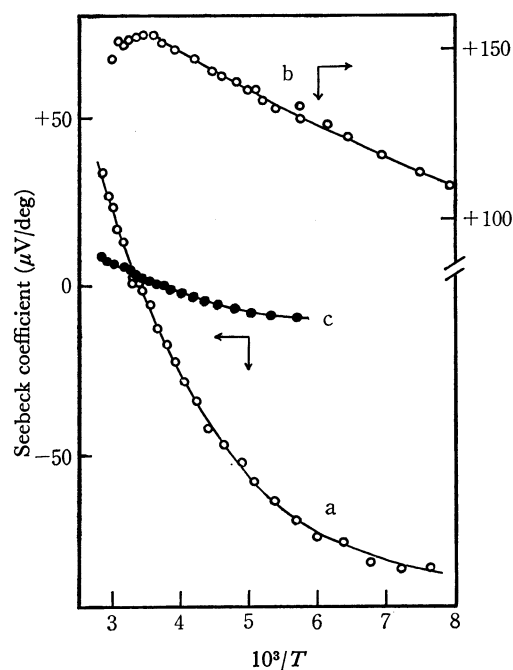

Fig. 2. Seebeck coefficients of the iodine complexes of a) phenoxazine, b) phenothiazine, and c) phenoselenazine.

The temperature dependence of the Seebeck coefficient (Q) is shown in Fig. 2 for the iodine complexes of phenoxazine, phenothiazine, and phenoselenazine. At 20°C, the values are as follows: $+5$ μV/deg for the oxazine complex, $+153$ μV/deg for the thiazine complex, and $+4$ μV/deg for the selenazine complex. Our value for the second complex agrees well with that reported by Sano et al.[7] Although a tendency for the better conducting materials to have smaller Seebeck

14) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).

15) W. J. Siemons, P. E. Bierstedt, and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963).

16) L. R. Melby, *Can. J. Chem.*, **43**, 1448 (1965).

coefficients, and *vice versa*, has often been noted,[17] the present complexes do not follow it. The higher-temperature region of the curve is nearly straight in the cases of the first and third complexes. To this region, one may apply the expression for the thermo-electric motive force of an intrinsic semiconductor:[18,19]

$$Q = -\frac{k}{e}\left[\frac{b-1}{b+1}\left(\frac{E_G}{2kT}+2\right)+\frac{3}{4}\ln\frac{m_e}{m_h}\right] \qquad (2)$$

where b is the ratio of the electron-to-hole mobility, μ_e/μ_h, E_G is the width of the forbidden band, and m_e and m_h are the effective masses of the electron and the hole respectively. On the assumption that E_G is twice the activation energy given in Table 2, b is evaluated as 2.11 for the oxazine complex and as 1.07 for the selenazine complex. With the values of temperature where the sign of the coefficient changes, the ratio of the effective masses was estimated to be as is shown in the table. The Seebeck coefficients of the benzo[a]- and benzo[c]-phenothiazine complexes are −47 and −57 μV/deg respectively at 20°C. The curves are nearly parallel to that for the selenazine complex; however, the linear parts are too short to fit Eq. (2).

The conductivity (σ) is given by:

$$\sigma = \frac{1}{\rho} = e\mu_e\left(\frac{b+1}{b}\right)N\exp\left(-E/kT\right) \qquad (3)$$

On the basis of the density determined from the compactions, N is estimated to be 2.54×10^{22} phenoxazine molecules or 2.50×10^{22} phenoselenazine molecules per cm^3 of the complex. Employing the resistivity and activation energy listed in Table 2, the electron mobility in the selenazine complex is calculated to be 0.26 cm^2/V sec. This value is close to that estimated for the electron in the N-methylphenothiazine-iodine complex by the same method,[8] and is of the same order as the only known Hall mobility observed with iodine complexes.[20] On the other hand, the electron mobility estimated for the oxazine complex, 0.004 cm^2/V sec, rules out the application of a band model to this iodine complex. The present organic components are structurally related, and the electrical resistivities of the iodine complexes are of the same order as each other. Nevertheless, the results indicate that the conduction mechanism in the complexes is very sensitive to a minor modification of the component molecule.

An alternative explanation for the behavior shown in Fig. 2 may be proposed on the basis of a hopping model. The Seebeck coefficient for hopping electrons is given by:

$$Q = -\frac{k}{e}\left[(1-2\beta)\frac{E}{kT}+\ln\frac{c_0-c}{c}\right] \qquad (4)$$

where c is the charge carrier concentration and where c_0 is the total concentration of accessible sites.[21,22] It

may be supposed that the site initially containing the electron requires a fraction, β, of the activation energy. By comparison with the terms in Eq. (2), β is estimated as 0.41 for the oxazine complex and as 0.49 for the selenazine complex; that is, the motional energy is divided into a ratio of about 2:3 between the two sites in the former complex and nearly equally between the two in the latter. The c/c_0 ratios are approximately 0.9 and 0.6 respectively; however, their meaning in the present complexes is still unknown.
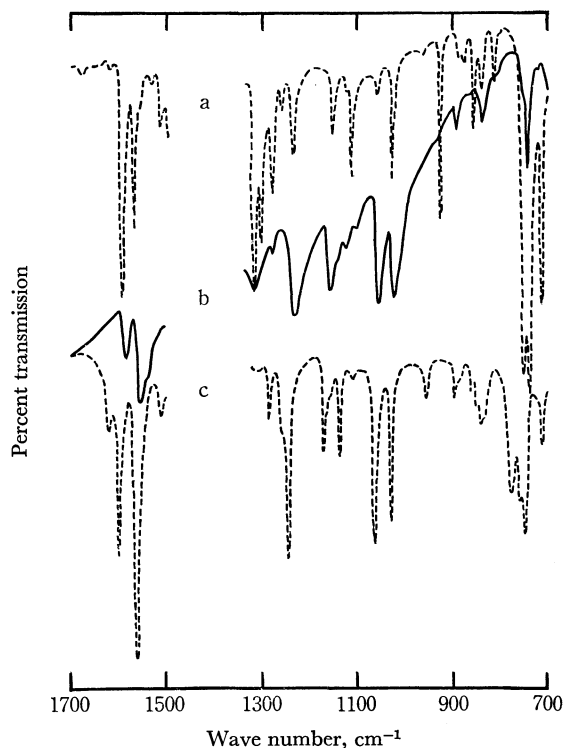

Fig. 3. Vibrational spectra of a) phenoselenazine, b) the iodine complex, and c) the semiquinoid bromide.

Optical Properties. As the phenoxazine complex is difficult to be pulverized, only a spectrum with a very poor resolution could be recorded. Therefore, the vibrational spectra of the other three iodine complexes will be considered in this paper. In Fig. 3 the spectrum of the phenoselenazine-iodine complex in the region from 700 to 1700 cm^{-1} is compared with those of the parent compound and the semiquinoid bromide. Of course, iodine is not active in this spectral region. Each spectrum bears a resemblance to that of the corresponding phenothiazine compound reported earlier.[6] The relative intensity and location of the two bands in the iodine complex appearing in the region from 1550 to 1600 cm^{-1} resemble those of the two in the bromide, but not those in the selenazine itself. Furthermore, the strong bands located at 1025, 1055, and 1235 cm^{-1} can be well compared with the three in the bromide located at 1030, 1060, and 1345 cm^{-1}. Thus, the main feature in the above-mentioned region seems to agree with that of the cation-radical. However, the following differences must be noted. The band to be compared with the one at 1330 cm^{-1} in the iodine complex can be found only in the parent

17) E. A. Perez-Albuerne, H. Johnson, Jr., and D. J. Trevoy, *J. Chem. Phys.*, **55**, 1547 (1971).

18) V. A. Johnson and K. Lark-Horowitz, *Phys. Rev.*, **92**, 226 (1953).

19) J. Tauc, *ibid.*, **95**, 1394 (1954).

20) A. M. Hermann and A. Rembaum, *J. Appl. Phys.*, **37**, 3642 (1966).

21) I. G. Austin and N. F. Mott, *Advan. Phys.*, **18**, 41 (1969).

22) I. Bransky, N. M. Tallan, and A. Z. Hed, *J. Appl. Phys.*, **41**, 1787 (1970).

compound. Neither the selenazine nor the bromide shows the band corresponding to that 1160 cm^{-1} in the iodine complex. It must be added that a strong band appearing at 925 cm^{-1} in the selenazine is not observed in the spectrum of the complex. On the basis of these observations, it is very likely that the positive charge on the selenazine molecule in the complex is fairly large, if not a unit.
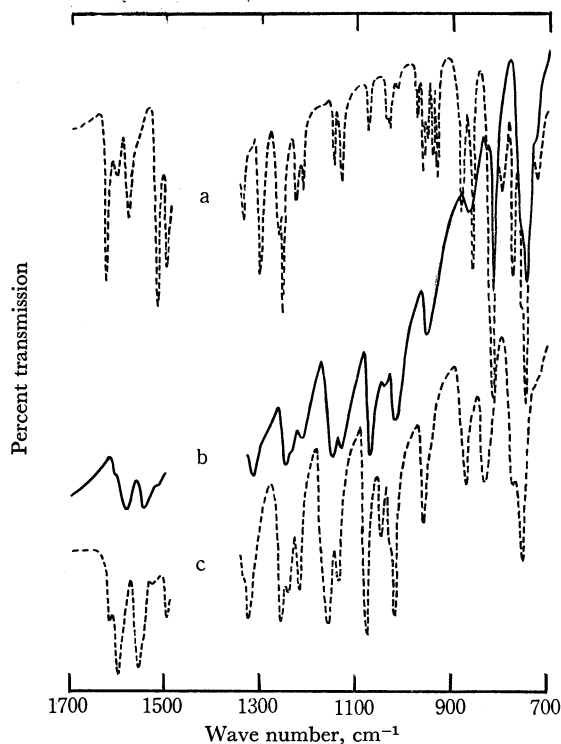

Fig. 4. Vibrational spectra of a) benzo[c]phenothiazine, b) the iodine complex, and c) the semiquinoid bromide.

The vibrational spectra of benzo[c]phenothiazine, the iodine complex, and the semiquinoid bromide are presented in Fig. 4. The pattern shown by the complex is in essential agreement with that of the bromide, confirming the expected ion-radical character of the iodine complex. The similarity of the iodine complex and the bromide of benzo[a]phenothiazine is also found in the vibrational pattern.
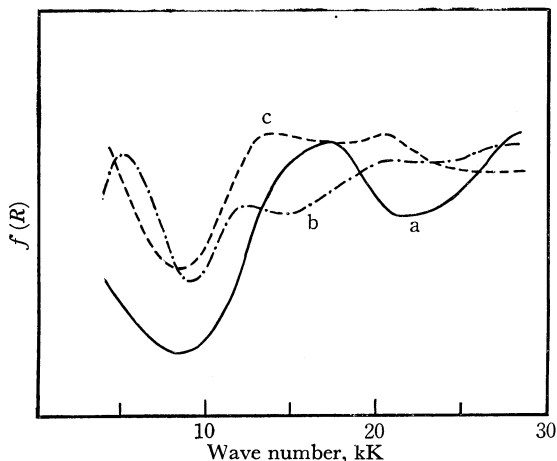

Fig. 5. Diffuse reflection spectra of the iodine complexes of a) phenoxazine, b) phenothiazine, and c) phenoselenazine.

In Fig. 5 the electronic spectra, as measured by the diffuse reflectance method, are shown for the iodine complexes of phenoxazine, phenothiazine, and phenoselenazine. The maximum of the low-energy band in the thiazine complex is found at 5.2 kK, while it was found at 5.5 kK in our previous work.[6] On the other hand, those of the other two complexes are expected to be below 4 kK, the limit of the spectrophotometer employed. This is the reason why a strong back-ground absorption is seen in the vibrational spectrum of the selenazine complex presented in Fig. 3. The appearance of a low-energy absorption band attributable to an electronic transition is common to low-resistivity organic semiconductors, e.g., the TCNQ anion-radical salts and some ionic molecular complexes.[14,17,23-25] However, the location of its maximum is not necessarily correlated with the resistivity, as has been pointed out in our paper on the TCDQ and TBDQ anion-radical salts.[26] In the present complexes, it may be noted that the location of the maximum cannot be correlated with the magnitude of the activation energy (see Table 2).
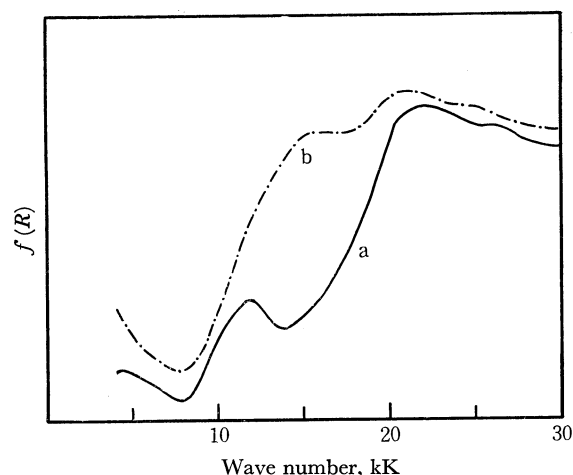

Fig. 6. Diffuse reflection spectra of the iodine complexes of a) benzo[a]phenothiazine and b) benzo[c]phenothiazine.

The reflection spectra of the benzophenothiazine complexes are given in Fig. 6. In contrast with the complexes in Fig. 5, the low-energy bands are appreciably weaker than those in the visible region. Nevertheless, these two complexes are as conductive as the other three. The maximum is located at 4.4 kK in the case of the benzo[a]phenothiazine complex, but below 4 kK in the other. This difference can be noted in the vibrational spectra, too. The recording of the spectrum of the former complex is much easier than that of the latter because of the absence of a strong back-ground absorption, which tends to produce distortions and a lack of resolution in the vibrational spectrum.

23) Y. Matsunaga, J. Chem. Phys., 42, 1982 (1965).
24) Y. Matsunaga, ibid., 42, 2248 (1965).
25) Y. Matsunaga, Nippon Kagaku Zasshi, 89, 905 (1968).
26) Y. Matsunaga and Y. Narita, This Bulletin, 45, 408 (1972).