March, 1973] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 719—722 (1973) 719

The Cation-radical Salts Derived from Benzo- and Dibenzo-phenothiazines

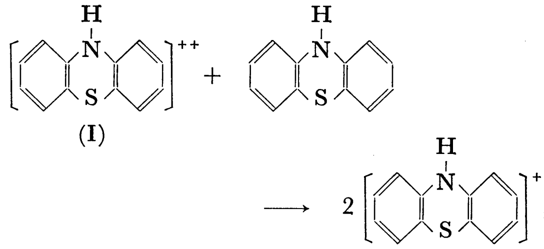
Yoshio MATSUNAGA and Yukio SUZUKI*
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received August 18, 1972)

The chloride, iodide, and perchlorate of benzo- and dibenzo-phenothiazine cation-radicals have been prepared by the reaction of an equimolar mixture of the thiazine and its *S*-oxide with an appropriate acid. The vibrational spectra of the products have been found to be in close agreement with those of the bromides made by the familiar oxidation of thiazines with bromine. The results of electronic spectral and ESR measurements have furnished further support for our conclusion that the thiazine cation-radical salts can be prepared by the above-mentioned reaction. The electronic spectra of the iodides of benzophenothiazines have been found to differ markedly from those of other salts and to bear a resemblance to those of the low-resistivity iodine complexes.

The cation-radical or semiquinoid salts derived from phenothiazine were described by Pummerer and Gassner and also by Kehrmann and Diserens over half a century ago.[1,2] These authors claimed the preparation of the following salts: bromide, periodide, sulfate, nitrate, perchlorate, and picrate. The first three salts were made by the oxidation of the parent compound with bromine, iodine, and concentrated sulfuric acid respectively. The next two were obtained as precipitates when the desired counter ion in an appropriate form was added to a dilute sulfuric acid solution of the sulfate thus prepared. The oxidation of phenothiazine with ferric chloride in the presence of picric acid resulted in the formation of the picrate. More recently, some new salts have been prepared by the oxidation of phenothiazine and its *N*-methyl derivative with antimony pentachloride.[3,4] Although halogens have been widely used as oxidizing agents in the preparation of cation-radicals, *e.g.*, those derives from aromatic diamines and tetrathiotetracene,[5-8] chlorine is not suited to the oxidation of either phenothiazine or diamines. Consequently, the use of ferric chloride has been proposed by Hatano *et al.* for the preparation of the chlorides of *p*-phenylenediamine and benzidine cation-radicals.[9] Moreover, the addition of iodine to phenothiazine has been known to produce a molecular complex with a 2: 3 mole ratio instead of the monoiodide.[10,11]

Earlier we studied the effects of iodine addition on the electrical resistivity and the electronic and vibrational spectra of the semiquinoid phenothiazine bromide.[12] A marked resistivity minimum was found to lie around the mole ratios from 1: 0.25 to 1: 0.30. The values in this composition range are from 4 to 5 ohm·cm, lower than those exhibited by the above-mentioned iodine complex, 13—20 ohm·cm.[10,12-14] The composition of this adduct corresponds approximately to $(\text{phenothiazine})_2\text{Br}_2\text{I}$. As the mixed halide ion, Br_2I^-, is a well-known species, the formation of a complex cation-radical salt, $(\text{phenothiazine})^+(\text{phenothiazine})^0\text{Br}_2\text{I}^-$, is very likely. In order to examine systems consisting of iodine and the chloride or iodide, the method of preparing these halides must first be established. In this paper, we wish to present a method based on the following reaction:



(I)

where the charge is proportionated between the protonated holoquinoid cation (I) and the phenothiazine molecule. The former species can be easily obtained when phenothiazine *S*-oxide is dissolved into strong acids.[1,2,15] A preliminary attempt to prepare the chloride and bromide by this reaction has already been reported by one of the present authors;[16] therefore, attention has here been directed towards the cation-radical salts derived from benzo[*a*]-, benzo[*c*]-, and dibenzo[*c*,*h*]-phenothiazines. As is indicated by the low energies of the charge-transfer absorptions in the *s*-trinitrobenzene and picric acid complexes listed in Table 1, the present compounds are expected to produce cation-radicals more easily than phenothiazine itself. The molecular orbital calculations made by Tyutyulkov *et al.* support this prediction.[17] In light of the size of the conjugated systems, the cation-radicals may be more stable than that of phenothiazine.

---

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

[1] R. Pummerer and S. Gassner, *Ber.*, **46**, 2310 (1913).

[2] F. Kehrmann and L. Diserens, *ibid.*, **48**, 318 (1915).

[3] Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, This Bulletin, **40**, 2539 (1967).

[4] Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, *ibid.*, **42**, 548 (1969).

[5] L. Michaelis and S. Granick, *J. Amer. Chem. Soc.*, **65**, 1747 (1943).

[6] G. K. Hughes and N. S. Hush, *J. Proc. Roy. Soc. N. S. W.*, **81**, 48 (1947).

[7] C. Marschalk and J. P. Niederhauser, *Bull. Soc. Chim. Fr.*, **1952**, 151.

[8] J. Honzl, K. Ulbert, V. Hadek, and M. Tlustakova, *Chem. Commun.*, **1965**, 440.

[9] K. Hatano, Y. Fujita, and T. Kwan, This Bulletin, **43**, 3022 (1970).

[10] Y. Matsunaga, *Helv. Phys. Acta.*, **36**, 800 (1963).

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

[12] Y. Matsunaga and K. Shono, This Bulletin, **43**, 2007 (1970).

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

[14] Y. Matsunaga and Y. Suzuki, *ibid.*, **45**, 3375 (1972).

[15] H. J. Shine and E. E. Mach, *J. Org. Chem.*, **30**, 2130 (1965).

[16] Y. Matsunaga, *Nippon Kagaku Zasshi*, **89**, 905 (1968).

[17] N. Tyutyulkov, D. Simov, and S. Stoyanov, *Compt. rend. Acad. bulg. Sci.*, **23**, 1095 (1970).

Table 1. Energies of charge-transfer absorption maxima in the *s*-trinitrobenzene complexes in chloroform and in the solid picric acid complexes (in kK) and energy coefficients of the highest occupied molecular orbitals of the thiazines (in β)

Donor	Acceptor		Energy coefficient of the HOMO[a)]
	s-Trinitrobenzene	Picric acid	
Phenothiazine	19.1	17.1[b)]	0.485
Benzo[*a*]-phenothiazine	*ca.* 18	16.2	0.382
Benzo[*c*]-phenothiazine	17.9	14.7	0.397
Dibenzo[*c,h*]-phenothiazine	17.4	14.1	0.346

a) Taken from Ref. 17.
b) 18.2 kK by Iida, Ref. 18.

Experimental

Materials. The examples cover only dibenzophenothiazine and its derivatives; however, they illustrate all of the preparative procedures which we employed.

Dibenzo[c,h]*phenothiazine*: β,β-Dinaphthylamine and sulfur were fused together in the presence of a small amount of iodine.[19)] The product was then recrystallized from benzene.

Dibenzophenothiazine S-*Oxide*: Following the procedure described by Pummerer and Gassner for phenothiazine *S*-oxide,[1)] dibenzophenothiazine, potassium hydroxide, and hydrogen peroxide in ethanol were gently heated for two hours. Subsequent recrystallization from ethanol gave yellow fine needles.

Dibenzophenothiazine Chloride and Iodide: An equimolar mixture of dibenzophenothiazine and its *S*-oxide was thoroughly ground in an agate mortar. The fine powder was spread in a beaker and moistened with concentrated hydrochloric acid. The reaction mixture was then dried in a vacuum desiccator containing potassium hydroxide pellets. Found: C, 67.2; H, 3.9; Cl, 10.0%. Calcd for $C_{20}H_{13}NS^+Cl^-\cdot H_2O$: C, 68.0; H, 4.3; Cl, 10.0%.

The iodide was prepared similarly. Found: C, 52.9; H, 2.9; N, 3.1; I, 32.8%. Calcd for $C_{20}H_{13}NS^+I_{1.15}^-$: C, 53.0; H, 2.9; N, 3.2; I, 32.8%.

Dibenzophenothiazine Bromide: The thiazine dissolved in a mixture of acetone and ether was cooled with an ice-salt mixture, and then bromine corresponding to less than one equivalent in cold ether was added, drop by drop. A black precipitate was then filtered out and washed with ether. Found: C, 63.1; H, 3.4; N, 3.2; Br, 21.5%. Calcd for $C_{20}H_{13}NS^+Br^-$: C, 63.3; H, 3.4; N, 3.7; Br, 21.1%.

Dibenzophenothiazine Perchlorates: An equimolar mixture of dibenzophenothiazine and its *S*-oxide was added to perchloric acid cooled with an ice-salt bath. A black precipitate appeared immediately. Found: C, 61.3; H, 3.3; N, 3.0%. Calcd for $C_{20}H_{13}NS^+ClO_4^-$: C, 60.2; H, 3.3; N, 3.5%.

If dibenzophenothiazine *S*-oxide alone is employed in place of the mixture, the holoquinoid perchlorate can be isolated. Found: C, 59.5; H, 3.0; N, 3.2; Cl, 9.2%. Calcd for $C_{20}H_{12}NS^+ClO_4^-$: C, 60.3; H, 3.0; N, 3.5; Cl, 8.9%.

Dibenzophenothiazine Picrate: The thiazine dissolved in ethanol was cooled with an ice-salt mixture and was then oxidized by adding it to an ethanolic solution containing an equimolar amount of ferric chloride and an excess of picric acid. The black picrate precipitated immediately. Found: C, 58.4; H, 2.8; N, 10.5%. Calcd for $C_{20}H_{13}NS^+C_6H_3N_3O_7^-$: C, 59.2; H, 2.9; N, 10.6%.

Measurements. The vibrational and electronic spectra of the solid salts were examined as have been reported elsewhere.[12)] The ESR measurements were carried out by means of a JEOL model JES-ME-3X spectrometer in the temperature range from −100 to 100°C. The spin concentrations were estimated at room temperature by comparing the signal intensities due to the sample and the standard material, violanthrone (8.1×10^{19} spins/g) with the aid of a multimode cavity model JES-MCX-1.

Results and Discussion

Syntheses. Although the preparation of phenothiazine chloride by the above-mentioned reaction was not satisfactory,[16)] the composition of the dibenzophenothiazine chloride agrees well with the calculated one. With the benzo derivatives the results were less satisfactory; those results were: C, 65.0; H, 4.1; N, 4.5; Cl, 10.9% for benzo[*a*]phenothiazine chloride, and C, 62.6; H, 4.0; N, 4.5; Cl, 10.7% for benzo[*c*]phenothiazine chloride. Calcd for $C_{16}H_{11}NS^+Cl^-\cdot H_2O$: C, 63.5; H, 4.3; N, 4.6; Cl, 11.7%.

A monoiodide hitherto unknown could be prepared by this method. In the case of benzo[*a*]phenothiazine, we obtained the following analytical results: C, 48.8; H, 2.6; N, 3.6; I, 35.3%. Calcd for $C_{16}H_{11}NS^+I_{1.07}^-$: C, 49.9; H, 2.9; N, 3.6; I, 35.3%. As for benzo[*c*]-phenothiazine iodide, C, 49.7; H, 2.8; N, 3.9; I, 34.8%. Calcd for $C_{16}H_{11}NS^+I_{1.05}^-$: C, 50.2; H, 2.9; N, 3.7; I, 34.9%. In all three, the presence of free iodine produced from hydroiodic acid during the preparation accounts for iodine contents higher than those expected for a 1 : 1 composition.

The reaction was also successfully applied to the preparation of the semiquinoid perchlorate. In addition to the dibenzophenothiazine perchlorate described above, we obtained the salts derived from benzo[*a*]- and benzo[*c*]-phenothiazines by the same technique. Found: C, 53.8; H, 3.0; N, 3.9; Cl, 10.5% for the former salt and C, 54.8; H, 3.1; N, 4.0% for the latter. Calcd for $C_{16}H_{11}NS^+ClO_4^-$: C, 55.1; H, 3.2; N, 4.0; Cl, 10.2%.

In the present work, the dibenzophenothiazine bromide was prepared by a method analogous to that reported by Pummerer and Gassner; however, it has already been shown that phenothiazine bromide can be obtained by the reaction described above.[16)]

The present work seems to provide justification for our hypothesis that the addition of an equimolar mixture of a thiazine and its *S*-oxide to a strong acid is a convenient method for preparing the semiquinoid salts, provided that the cation-radical is stable in the acid. As will be discussed in the following sections, the physical properties of the salts so prepared support this conclusion.

Vibrational Spectra. If the chloride and iodide are indeed of the cation-radical, their vibrational spectra must be identical with that of the bromide prepared

---

[18)] Y. Iida, This Bulletin, **44**, 663 (1971).

[19)] E. Knoevenagel, *J. Prakt. Chem.*, (2) **89**, 1 (1914).

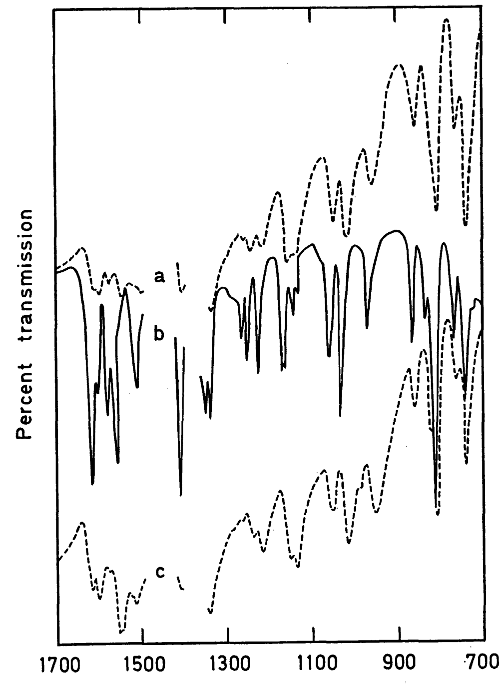


Fig. 1. Vibrational spectra of (a) dibenzophenothiazine chloride, (b) the bromide, and (c) the iodide.

by the authentic oxidation with bromine. The spectra of the three salts of dibenzophenothiazine are compared with each other in Fig. 1. As we noted earlier in the cases of phenothiazine and its benzo derivatives,[12,14)] the bromide gives a spectrum distinctly different from that of the parent compound. The bands in the chloride and iodide are overlapped by the electronic absorption to be described later and are not well resolved; however, it is easy to see that their general features are in essential agreement with those of the bromide. The spectrum of the semiquinoid perchlorate is dominated by strong broad absorption bands due to the anion. Nevertheless, this is also in good accordance with that of the bromide, as far as we can compare them. It must be added that the spectrum of the holoquinoid perchlorate differs appreciably from that of the corresponding semiquinoid salt. Thus, the vibrational spectra of the chloride, iodide, and perchlorate prepared by our method are definitely those of the cation-radical. This conclusion is also valid for the salts derived from benzophenothiazines.

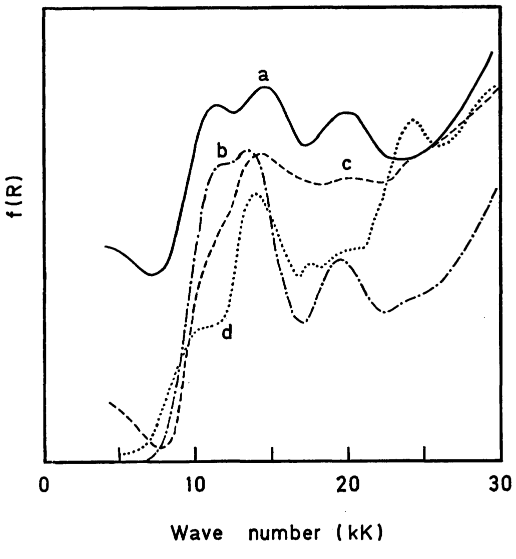


Fig. 2. Diffuse reflection spectra of (a) dibenzophenothiazine chloride, (b) the bromide, (c) the iodide, and (d) the picrate.

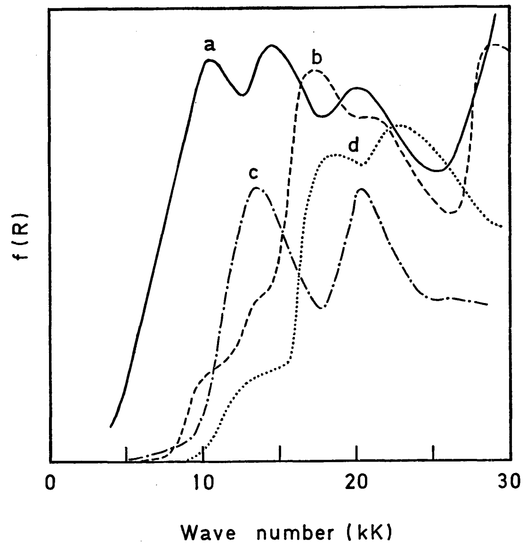


Fig. 3. Diffuse reflection spectra of (a) semiquinoid dibenzophenothiazine perchlorate, (b) the holoquinoid perchlorate, (c) semiquinoid phenothiazine perchlorate, and (d) the holoquinoid perchlorate.

Electronic Spectra. The dibenzophenothiazine cation-radical in hydrochloric acid-acetic acid (1: 1 by volume) exhibits absorption maxima at 14.3, 17.9, and 20.4 kK, with an intensity ratio of 1: 0.44: 0.52. The diffuse reflection spectra of the solid chloride, bromide, iodide, and picrate are presented in Fig. 2, and that of the perchlorate, in Fig. 3. The spectrum of the bromide includes bands at 11.6, 13.4, and 19.6 kK. The spectra of the chloride, iodide, and perchlorate prepared by our method also show bands around 11, 14, and 20 kK. Among the five, the picrate gives the most complicated spectrum, consisting of bands located at 10.3, 13.9, 17.4, about 20, and 24.2 kK. The last band can be assigned to the picrate anion. The locations of the second and third are close to those of the two strong ones observed in the solution spectrum; however, the one appearing around 11 kK is undoubtedly characteristic of the solid cation-radical salts. By analogy with the spectra of the phenothiazine cation-radical salts,[18)] this band may arise from the pair-by-pair interaction between the cations. In addition to this, the chloride and iodide have bands located below 4 kK, indicating some difference in the mode of interaction. It must be noted that the relative intensities of the bands located at about 11 kK in the iodide and picrate are appreciably weaker than those in the other two. The nature of the extra band appearing at 17.4 kK in the picrate will be speculated on in connection with the ESR data.

In Fig. 3 the spectrum of the perchlorate of dibenzophenothiazine is compared with that of the holoquinoid perchlorate. Although the holoquinoid salt absorbs also down to 10 kK, the intensities in the region below 15 kK are much diminished and the locations of the absorption maxima above 15 kK differ substantially from those of the cation-radical salt. A similar comparison is made for the semiquinoid and holoquinoid phenothiazine perchlorates in the same figure. The spectrum of this semiquinoid perchlorate is simpler than those of the phenothiazine bromide, bisulfate, and picrate reported earlier;[12,18] that is, a band near 23 kK common to the latter three is not observed here.

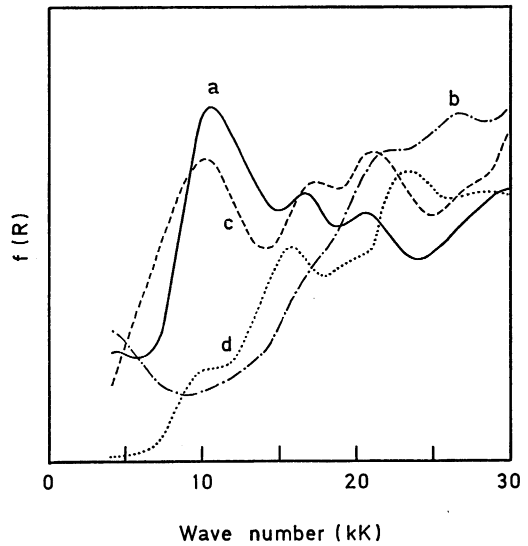


Fig. 4. Diffuse reflection spectra of (a) benzo[*c*]phenothiazine chloride, (b) the iodide, (c) the perchlorate, and (d) the picrate.

The diffuse reflection spectra of the cation-radical salts of benzo[*c*]phenothiazine prepared by our method are shown in Fig. 4, together with that of the picrate shown for the sake of comparison. The iodide was found to give a spectrum quite different from the others. This spectrum resembles that of the low-resistivity iodine complex presented in a previous paper.[14] The pattern of these two may be assigned to the cation-radicals in a more-than-by-pairs interaction. However, the band around 15 kK seen in the iodine complex is much diminished in the iodide. On the other hand, the absorption above 25 kK is intensified, resulting in the appearance of a maximum at 26.4 kK. Here again, bands at 16—17 and about 21 kK common to the chloride, perchlorate, and picrate are located close to the bands observed in the solution spectrum: 16.8 and 21.1 kK, with an intensity ratio of 1 : 0.70. The absorption located at about 10 kK is possibly due to the pair-by-pair interaction between the cation-radicals. A similarity in the spectrum was also noted between the iodide of benzo[*a*]phenothiazine and the iodine complex.

In spite of the coincidence in the locations of the absorption maxima, the whole spectrum of the solid salt varies considerably with the counter ion. Such pronounced variations are not unexpected in the solid-state spectrum of ion-radicals.[20,21]

Spin Concentrations. Electron-spin-resonance absorption was detected in all the salts which were supposed to be of cation-radicals, but not in the holoquinoid perchlorate. The absorptions are all symmetric except in the case of the benzo[*a*]phenothiazine perchlorate, where the g-values estimated by the method according to Kneubühl are as follows: $g_{//}=2.0027$ and $g_{\perp}=2.0074$.[22] The distance between the points of the maximum slope measured at room temperature are in the range from 7 to 12 Gauss, and the spin concentrations, in the range from 0.01 to 0.10 spins per molecule. Thus, the major fraction is diamagnetic. This finding is in accordance with the electronic spectral behavior discussed above. Besides, the concentrations were found to be temperature-independent; therefore, the observed spins must be ascribed to some imperfections and impurities in crystals. The dibenzophenothiazine picrate gave an exceptionally wide absorption; that is, a distance of 34 Gauss was observed. Moreover, a spin concentration as high as 0.30 was detected in this salt. One should recall the observation that this solid salt shows an electronic absorption maximum at 17.4 kK, corresponding to the weakest band in the spectrum of the monomeric cation-radical. The high spin concentration may be correlated with the appearance of this band in the solid-state spectrum. However, the weakness of the absorption at 10—11 kK is common in the solid picrates and cannot be correlated with the spin concentration. The benzo[*c*]phenothiazine salt has a spin concentration as low as 0.01.

The authors wish to express their thanks to Professor Minoru Kinoshita of the University of Tokyo for his gift of the sample of violanthrone. The ESR spectrometer was obtained with a grant-in-aid from the Ministry of Education.

---

20) Y. Iida and Y. Matsunaga, This Bulletin, **41**, 2615 (1968).

21) Y. Matsunaga and Y. Narita, *ibid.*, **45**, 408 (1972).

22) F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).