2024 © *1994 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **67**, *2024—2030(1994)* [Vol. 67, No. 8

Oxidation Potentials and Absorption Spectra of Phenothiazine Derivatives I. Benzophenothiazines and Triphenodithiazine

Naoyuki URASAKI, Sadamu YOSHIDA, Takashi OGAWA, Kozo KOZAWA, and Tokiko UCHIDA*
Department of Industrial and Engineering Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278

(Received December 28, 1993)

The homogeneous electrochemical oxidations of four phenothiazine derivatives, three isomers of benzophenothiazine and triphenodithiazine, were studied in acetonitrile solution together with phenothiazine itself. Their first and second redox potentials were determined by means of cyclic voltammetry. In all the materials examined, reversible one-electron oxidations were characterized. The electrogenerated cation radicals, except for triphenodithiazine, underwent a second one-electron oxidation and, after a subsequent chemical transformation, formed the corresponding benzophenothiazinium cations. For triphenodithiazine, only the first oxidation potential was observable under our experimental conditions. The electronic states of both the intermediates and the final products of electrolytic oxidation were identified by their electronic absorption spectra and electron spin resonance absorption spectra. The values of the first oxidation potential of the benzophenothiazines were proportional to the ionization energies, which were given by molecular orbital calculations.

Phenothiazine (PT) and its derivatives possess electron-donating properties and easily form charge-transfer (CT) complexes with various electron acceptors or Lewis acids.[1—13] In these complexes, especially "strong CT type" ones, they exist as stable cation radicals either in the solid state or in the solution state.[1—10] For several decades, the PT molecule has been known to undergo several stepwise oxidations, and the electronic spectra or electron spin resonance (ESR) spectra of the oxidation states have been studied by many researchers.[14—19]

In a series of structural and physicochemical studies of solid CT complexes of PT derivatives, we have tried to enlarge the intramolecular conjugation system of PT by condensing a benzene ring or thiazine ring to form benzophenothiazines (BPT's: having three isomers) or triphenodithiazine (TPDT). It has been found that BPT's can act as electron donors to form CT complexes as expected.[1—3] In particular, the iodine complex of benzo[*b*]phenothiazine has been found to be a metallic conductor around room temperature.[3] However, spectroscopic studies on the oxidation states of these compounds have not been reported, and consequently, their oxidized species have not been precisely described.

In this paper, we wish to report the oxidation states of the three BPT's and TPDT by means of cyclic voltammetry, electronic absorption spectra, and ESR absorption spectra.

Experimental

Materials. Benzo[*a*]phenothiazine (B[*a*]PT) and benzo[*c*]phenothiazine (B[*c*]PT) were synthesized by allowing sulfur to react with *N*-phenyl-1- and 2-naphthylamine, respectively, with a small amount of iodine as catalyst.[20] Benzo[*b*]phenothiazine (B[*b*]PT) was prepared by condensation of 2,3-naphthalenediol and *o*-aminobenzenethiol in trichlorobenzene.[21] These compounds were purified by recrystallization from benzene (B[*a*]PT and B[*c*]PT) or hexane (B[*b*]PT), and then sublimed in vacuo. Triphenodithiazine (TPDT) was obtained by reacting sulfur with *N*,*N*′-diphenyl-*p*-phenylenediamine, with a small amount of iodine in xylene. The product was purified by recrystallization from nitrobenzene, and subsequently by repeated sublimation in vacuo.[22] The materials used are shown in Chart 1 with their abbreviations.

Acetonitrile (AN) was distilled by an ordinary technique after dehydration on molecular sieves (4A 1/16, Wako). Analytical grade sulfuric acid (Wako), without special purification, and special grade ethanol (Wako), distilled after dehydration with molecular sieves (4A 1/16, Wako), were used for spectrometry. Tetrabutylammonium perchlorate

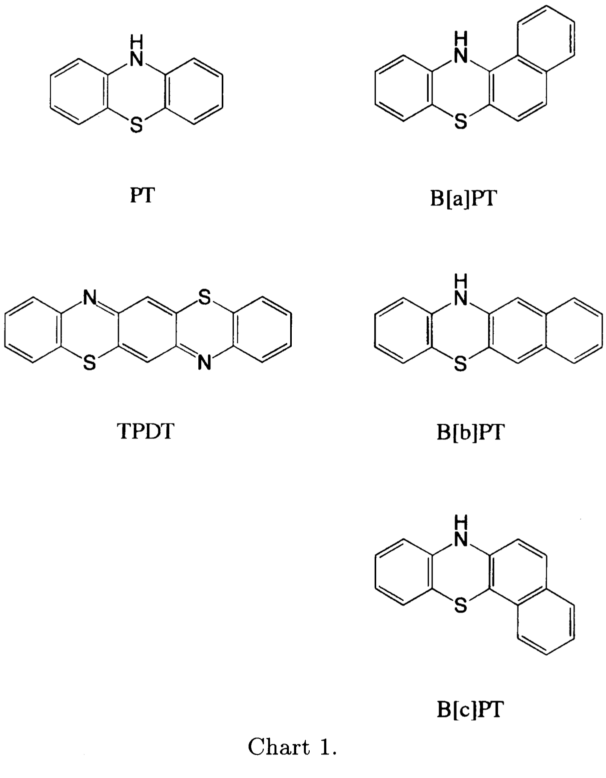


Chart 1.

(TBAP, Fulka) was purified by recrystallization from ethanol/water.

Cyclic Voltammetry and Spectrophotometric Measurements. The electrode assembly consisted of a platinum disk (area: 1.73 cm^2) as a working electrode, a Ag/AgCl (KCl saturated solution) electrode as a reference electrode, and a platinum wire as a counter electrode. All the measurements were performed in AN solution containing 0.1 $\mathrm{mol\,dm^{-3}}$ TBAP as a supporting electrolyte. The sample solutions were deoxygenated by bubbling with dry nitrogen gas for about 20 min prior to all the runs. The instrumentation used for CV consisted of an ADVANTEST TR6142 function generator and a Nikko Keisoku NPOT-2501 potentiostat, with a GRAPHTEC WX1200 X-Y recorder. A Hitachi 330 spectrometer was used for the electronic absorption measurements, and JEOL JES-PE-1 or JEOL JES-FE-3X spectrometers were used for the ESR spectra.

Results and Discussion

Cyclic Voltammetry (CV). The obtained cyclic voltammograms of the three BPT's and TPDT are shown in Fig. 1 together with that of PT. The electrode potential was scanned between 0 and 1.5 V vs. Ag/AgCl for PT and the three BPT's, and between 1.0 and 1.7 V vs. Ag/AgCl for TPDT. The scan rate was kept at 10 $\mathrm{mV\,s^{-1}}$ for all the measurements. In each scan, except for TPDT, two anodic peaks were clearly recognizable, and two cathodic peaks corresponding to the anodic ones. In the case of TPDT, only one anodic peak was observed under the adopted experimental conditions, and the small peak height reflected its poor solubility. Table 1 lists the cyclic voltammetric parameters for the five materials examined. E_{p}^{o1} and E_{p}^{o2} denote the anodic peak potentials, and E_{p}^{r1} and E_{p}^{r2} are cathodic peak potentials corresponding to E_{p}^{o1} and E_{p}^{o2}, respectively. It is well-known that the observed values of peak potentials frequently vary with the experimental conditions even in the same material. So, we observed the redox potentials of tetrathiafulvalene (TTF), and obtained a value of 0.40 V vs. Ag/AgCl for E_{p}^{o1}. Since that of PT was observed at 0.69 V vs. Ag/AgCl, the difference between the E_{p}^{o1} values of PT and TTF is 0.29 V. This value agrees with the value of 0.28 V, which can be derived from the E_{p}^{o1} values of PT and TTF (0.58 and 0.30 V vs. SCE, respectively) reported by Wheland and Gillson.[23)]

In the case of the three BPT's, though the values of $\Delta E_{\mathrm{p}1}$ $(=E_{\mathrm{p}}^{o1}-E_{\mathrm{p}}^{r1})$ and $\Delta E_{\mathrm{p}2}$ $(=E_{\mathrm{p}}^{o2}-E_{\mathrm{p}}^{r2})$, the differences between the anodic and cathodic peak potentials, are fairly different from the ideal value of 59 mV for a reversible one-electron transfer process, it can be assumed that two almost-reversible one-electron oxidations are involved in the electrode reactions. This presumption comes from the observation that the obtained cyclic voltammograms of the BPT's almost overlap with that of PT by moving the curves horizontally, since the two-step reversible oxidation process has already been confirmed for PT.[14,16,17)] Namely, the first anodic peak of PT corresponds to the oxidation of the neutral molecule to the cation radical, $\mathrm{PT}^{+\bullet}$, and the second anodic peak corresponds to the oxidation of the cation radical to the dication, PT^{2+}. Both processes involve electronic oxidation only. The overall redox reaction for B[*a*]PT is given in Scheme 1. For the other two BPT's, of course, a similar scheme is deducible. It was suggested by Billon that the cation radical of PT underwent another oxidation to form phenothiazinium ion (hereafter cation, PT^{+}), by releasing a proton.[16)] This subject will be discussed later.

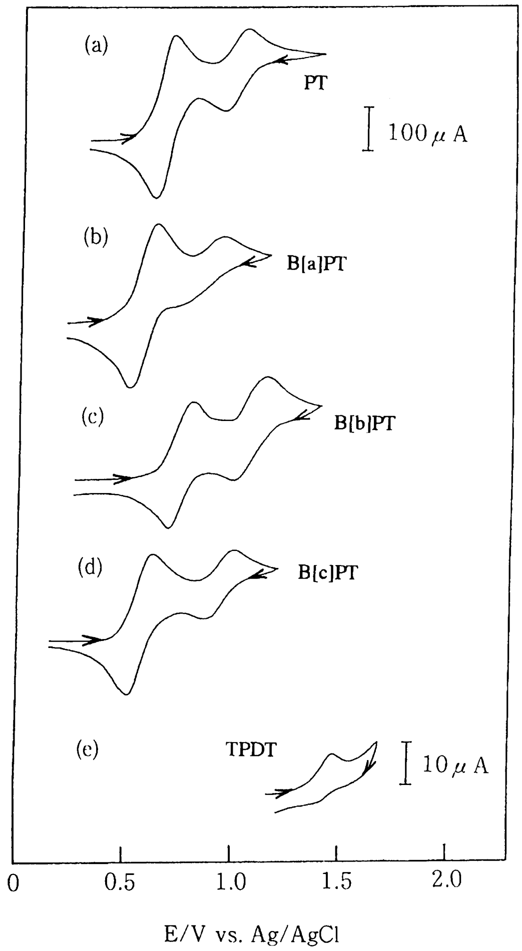
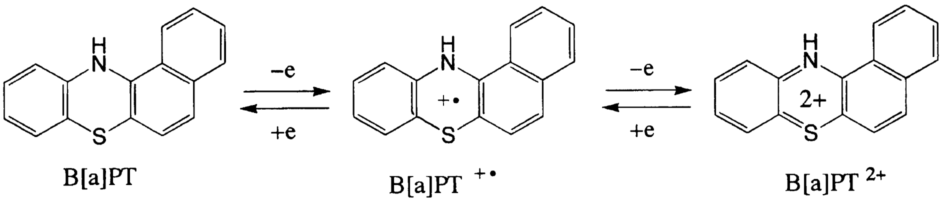


Fig. 1. Cyclic voltammograms of PT, BPT's, and TPDT in AN containing 0.1 $\mathrm{mol\,dm^{-3}}$ TBAP. Material and its concentration (in $\mathrm{mol\,dm^{-3}}$) in the observed solution are: (a), PT 2.0×10^{-3}; (b), B[*a*]-PT 2.0×10^{-3}; (c), B[*b*]PT 2.0×10^{-3}; (d), B[*c*]PT 2.0×10^{-3} and (e), TPDT in saturated solution. All the measurements were done at 19.5±0.3°C, and scan rate 10 $\mathrm{mV\,s^{-1}}$.

In polycyclic aromatic hydrocarbons, it is generally known that, the more the fused benzene rings increase, the smaller the ionization energy value becomes. In this connection, the BPT's are expected to possess a lower oxidation potential value than that of PT. Comparing the observed first oxidation potentials, B[*a*]PT and

Table 1. CV Parameters of PT, BPT's and TPDT (E/V vs. Ag/AgCl, 10 mV s^{-1})

Compound	E_p^{o1}	E_p^{o2}	ΔE_{p1}	ΔE_{p2}	i_p^{r1}/i_p^{o1}	i_p^{r2}/i_p^{o2}
PT	0.69	1.04	0.08	0.10	1.04	1.04
B[*a*]PT	0.62	0.94	0.11	0.16	0.96	0.97
B[*b*]PT	0.79	1.13	0.08	0.14	1.01	1.05
B[*c*]PT	0.62	1.00	0.09	0.13	1.00	1.03
TPDT	1.46	—	—	—	—	—



Scheme 1.

B[*c*]PT exhibit lower values than that of PT, whereas B[*b*]PT has a higher value than that of PT. The ionization potential (I_p) values of these molecules were calculated by a semiempirical molecular orbital method.[24] The calculated values are 7.97, 7.85, 8.03, 7.86, and 8.07 eV for PT, B[*a*]PT, B[*b*]PT, B[*c*]PT, and TPDT, respectively. As shown in Fig. 2, the values of I_p and E_p^{o1} exhibit an approximately linear relationship for the former four molecules, whereas only the plot of TPDT is in a deviated position. This deviation can be understood, since, in the PT derivatives examined, only the TPDT molecule possesses two thiazine rings, which directly participate in the electrooxidation reaction.

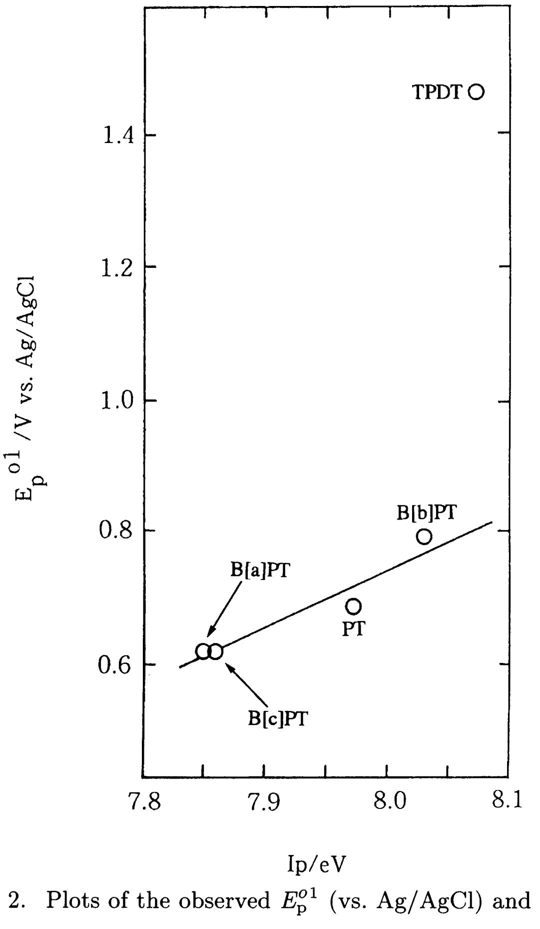


Fig. 2. Plots of the observed E_p^{o1} (vs. Ag/AgCl) and I_p.

In preparing CT complexes with these materials used as electron donors, the qualitative "readiness" of complex formation was found to follow the order of the E_p^{o1} or IP values. For example, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) can react with B[*b*]PT or B[*a*]PT to precipitate solid complexes from solution, but a higher concentration of B[*b*]PT than B[*a*]PT is necessary for complex formation.

Electronic States of Oxidized Products. Benzophenothiazines: Figures 3, 4, 5, and 6 show the typical electronic absorption spectra of the neutral solution and the two kinds of oxidized sample solutions, which were prepared by controlled potential electrolysis. The first oxidation step was controlled at the potential between E_p^{o1} and E_p^{o2}, and the second oxidation step was controlled at a potential above E_p^{o2}. In each procedure, the electrolysis was continued until the electrolytic current became negligibly small. In the case of B[*a*]PT, the intense absorption band of the neutral species at 272 nm gradually shifted to a longer wavelength range by the stepping oxidation, and the new bands grew in the visible range as shown in Fig. 3. Similar spectral changes were also observed for PT oxidized in AN containing TBAP (0.1 mol dm^{-3}), and they agreed with the electrochemically-oxidized PT spectra observed by Billon in an acidic medium (0.1 mol dm^{-3} perchloric acid in AN).[16]

In order to determine whether the first-step oxidized products were cation radicals or not, two methods were applied, ESR and ultraviolet/visible (UV-vis) spectroscopy. When observation of ESR was carried out for each sample solution after its controlled potential

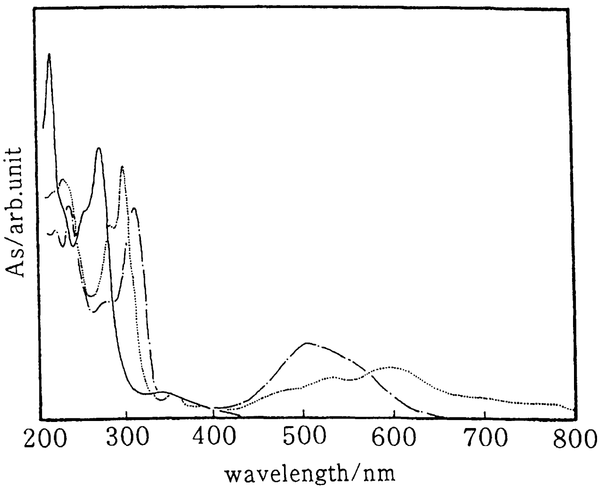


Fig. 3. Absorption spectra of B[*a*]PT in AN containing 0.1 mol dm^{-3} TBAP: (a), before electrolysis (—); (b), after electrolysis at 0.8 V vs. Ag/AgCl (····); and (c), after electrolysis at 1.1 V vs. Ag/AgCl (–··–).

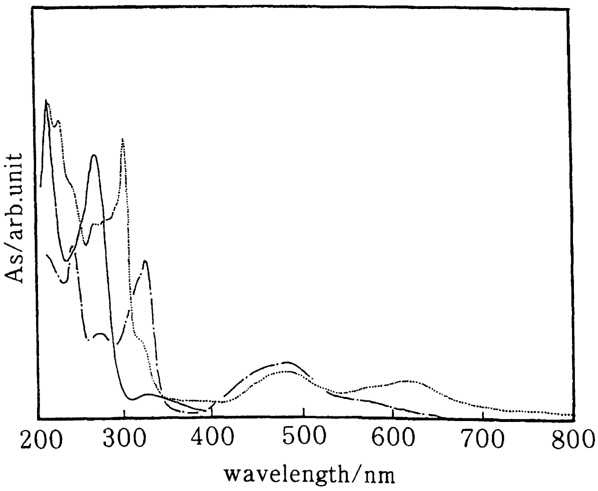


Fig. 5. Absorption spectra of B[*c*]PT in AN containing 0.1 mol dm^{-3} TBAP: (a), before electrolysis (—); (b), after electrolysis at 0.8 V vs. Ag/AgCl (····); and (c), after electrolysis at 1.2 V vs. Ag/AgCl (–··–).

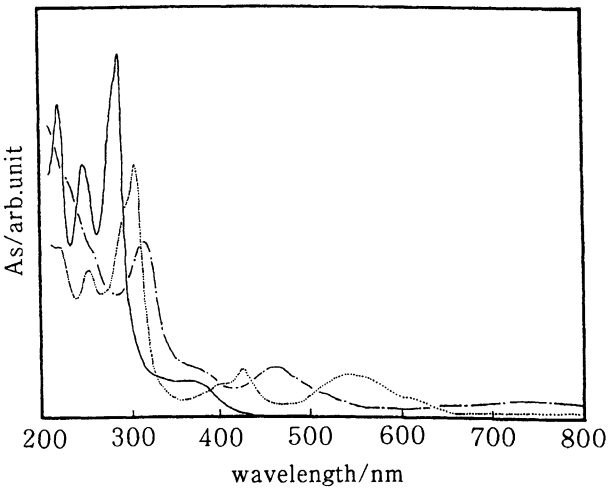


Fig. 4. Absorption spectra of B[*b*]PT in AN containing 0.1 mol dm^{-3} TBAP: (a), before electrolysis (—); (b), after electrolysis at 1.0 V vs. Ag/AgCl (····); and (c), after electrolysis at 1.4 V vs. Ag/AgCl (–··–).

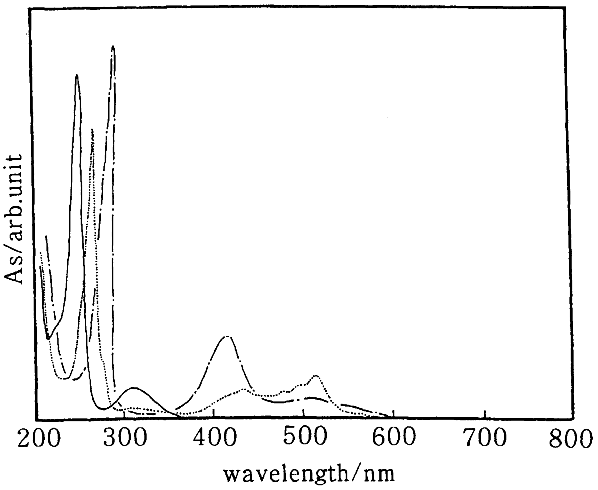


Fig. 6. Absorption spectra of PT in AN containing 0.1 mol dm^{-3} TBAP: (a), before electrolysis (—); (b), after electrolysis at 0.9 V vs. Ag/AgCl (····); and (c), after electrolysis at 1.4 V vs. Ag/AgCl (–··–).

electrolysis, an absorption signal was obtained for every sample solution examined. The observed *g*-values were in the range 2.002—2.005, exhibiting the ordinary values of organic radicals in which an unpaired electron is delocalized. Secondly, we applied the method reported by Shine and Mach, who observed the PT cation radical in solutions of phenothiazine 5-oxide in 59% H_2SO_4 by UV-vis and ESR spectroscopy.[14] When *S*-oxides of the three BPT's were prepared and their UV-vis spectra were observed in sulfuric acid solutions, their spectra agreed with those obtained by corresponding electrochemical oxidation. Thus, these results indicate that the first-step electrooxidation products of the BPT's are the corresponding cation radicals.

The oxidized products generated by the second step potentiostatic electrolysis were identified by electronic spectroscopy, though their chemical conversion in AN solutions made it slightly complicated. The characterization process was as follows:

(i) The typical absorption spectra of PT and the BPT's are shown in Figs. 3, 4, 5, and 6. After the second-step potentiostatic oxidation, the cation radical absorption band of B[*a*]PT$^{+\bullet}$ at 299 nm decreased in intensity and shifted to 309 nm. At the same time, an intensity decrease took place at the 597 nm band, and a new intense band grew at 500 nm (Fig. 3). Similar spectral changes were also obtained for B[*b*]PT$^{+\bullet}$, B[*c*]PT$^{+\bullet}$, and PT$^{+\bullet}$ (Figs. 4, 5, and 6, respectively). There have been many studies on the oxidized states of PT or its substituted derivatives, mainly for pharmaceutical interests.[14,16,17,25,26] Referring to these reports, the present spectrum of PT corresponds to that of the

Table 2. Observed Absorption Maxima of PT and BPT's with Their Oxidation States in AN

Compound	Absorption maximum / nm						
B[*a*]PT	218		272	325			
B[*a*]PT$^{+\cdot}$	230		299				597
B[*a*]PT^{+}	235		309			500	
B[*a*]PT^{2+} a)		241	307	326	402		594
B[*b*]PT	219	247	285	365			
B[*b*]PT$^{+\cdot}$			305		425	540	
B[*b*]PT^{+}			318		460		
B[*b*]PT^{2+} a)		261	300	331		526	
B[*c*]PT	218		270	326			
B[*c*]PT$^{+\cdot}$	234		302				608
B[*c*]PT^{+}		242	318		470		
B[*c*]PT^{2+} a)		242	316		398		593
PT	253		315				
PT$^{+\cdot}$			271			515	
PT^{+}			281		419		
PT^{2+} b)			287		455		

a) Observed in H_2SO_4/ethanol solution. b) Ref. 14.

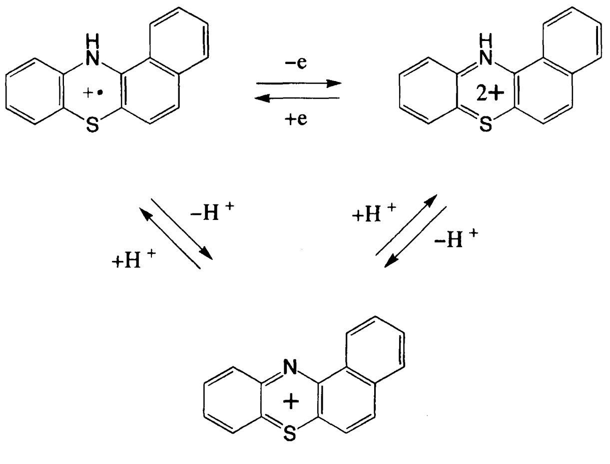
cation, PT^{+}, which arises by a proton extraction from the cation radical. Billon observed the electrochemically oxidized spectrum of PT in acidic media, and he assigned his product also as PT^{+}. The observed UV-vis absorption bands are summarized in Table 2.

(ii) The CV results suggest that the second-step oxidized product should be the dication, (BPT)$^{2+}$, which has no unpaired electron. However, the ESR observation gave a slight absorption signal for the sample solution of B[*a*]PT electrolyzed at a potential larger than $E_{\mathrm{p}}^{\mathrm{o}2}$. This fact reveals that there exists an ESR-active chemical species, perhaps a cation radical, which comes from a chemical conversion in the electrolyzed solution.

(iii) Shine and Mach observed the dication state of PT by UV-vis spectra in concentrated H_2SO_4 solution. By applying a similar method, we found that PT^{2+} and the (BPT's)$^{2+}$, in concentrated H_2SO_4 solution, gave absorption maxima which were different from those of the electrooxidized samples (see Table 2).

(iv) We prepared the perchlorate salt of B[*a*]PT according to the literature,[27] since the PT^{+} state has been known to exist stably in this salt.[14] The infrared vibrational spectrum of this salt did not give the N–H stretching peak. Its UV-vis spectrum agreed with that of our "second-step oxidized product" of B[*a*]PT. So, we feel sure that the final product of B[*a*]PT after the second-step electrostatic oxidation is the cation state (B[*a*]PT^{+}). We characterized the cation state of B-[*c*]PT (B[*c*]PT^{+}) similarly. However, the perchlorate salt of B[*b*]PT (B[*b*]PT^{+}) was unstable in AN solution, though the UV-vis spectral behaviors of B[*b*]PT were very similar to those of the other two BPT's in each electrooxidized step.

The above-mentioned experimental results are summarized as follows: In the second-step electrooxidized solutions of PT, B[*a*]PT, and B[*c*]PT, the cation states were observed as the main products by electronic spectra, and a relatively small amount of the cation radical states were also observed by ESR spectra, but the dication states were not observed, in spite of expectations from the CV behaviors. To elucidate the observed results, we propose the following mechanism as illustrated in Schemes 1, 2, and 3. The electrolytic oxidation proceeds first from the neutral molecule to the stable cation



B[a]PT^{+}

Scheme 2.

$$\mathrm{B[a]PT}^{+\bullet} \xrightarrow{-e} \mathrm{B[a]PT}^{2+}$$

$$\mathrm{B[a]PT}^{2+} + \mathrm{B[a]PT} \longrightarrow 2\,\mathrm{B[a]PT}^{+\bullet}$$

$$\mathrm{B[a]PT}^{2+} \xrightarrow{-H^{+}} \mathrm{B[a]PT}^{+}$$

Scheme 3.

radical, and then to the unstable dication (Scheme 1). Since the generated dication is unstable under these experimental conditions, it changes to a more stable cation state by releasing a proton or to a cation radical state by taking an electron (Schemes 2 and 3).

TPDT: Although we could not observe the ESR spectra of the electrolytic oxidized species of TPDT due to its poor solubility in AN, its electronic absorption spectra were observed, and are shown in Fig. 7. To confirm its electronic state, chemical oxidation was attempted in an ethanolic solution of H_2SO_4. When TPDT is dissolved in mixed H_2SO_4/ethanol solutions, the color of the solution gradually changes from red to violet and finally to blue with increasing H_2SO_4concentration. Figure 8 shows the UV-vis absorption spectra of TPDT in acidic solutions, in which the concentrations of H_2SO_4 in ethanol are 0, 0.01, and 14% (in volume). This color change suggests that TPDT can undergo a two-step oxidation by a chemical reaction. By comparing Figs. 7 and 8, it can be understood that the first-step oxidized product of TPDT is the same species whether generated by electrolytic oxidation or by chemical oxidation.

Subsequently, we prepared a CT complex of TPDT with $SbCl_3$ as an electron acceptor. This Lewis acid has been known to make a CT complex with PT (exactly, PT-$SbCl_4$), which exists as a cation radical state in the complex.[2,4,5] In this case, the TPDT-$SbCl_3$ complex was obtained in the solid state, and its 1,2-dichloroethane solution displayed almost the same electronic absorption spectrum as that of TPDT in the first-step oxidized state. Moreover, this solid complex gave an ESR absorption signal. So, it was proved that the first-step oxidation of TPDT gives its cation radical state.

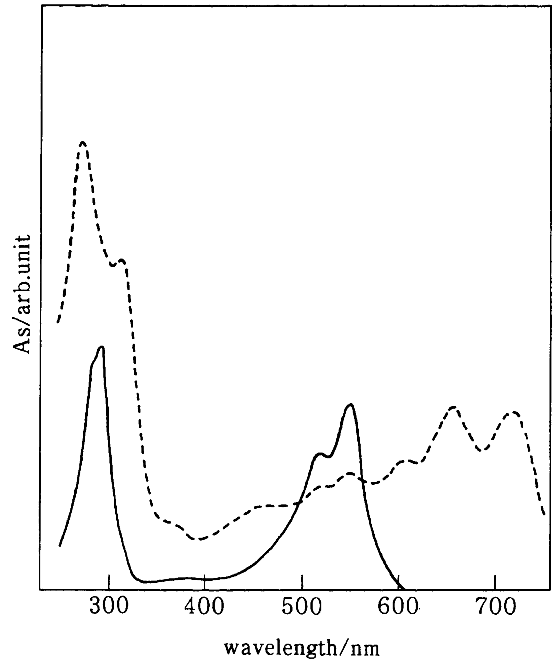


Fig. 7. Absorption spectra of TPDT in AN containing 0.1 mol dm^{-3} TBAP: (a), before electrolysis (—); and (b), after electrolysis at 1.6 V vs. Ag/AgCl (····).

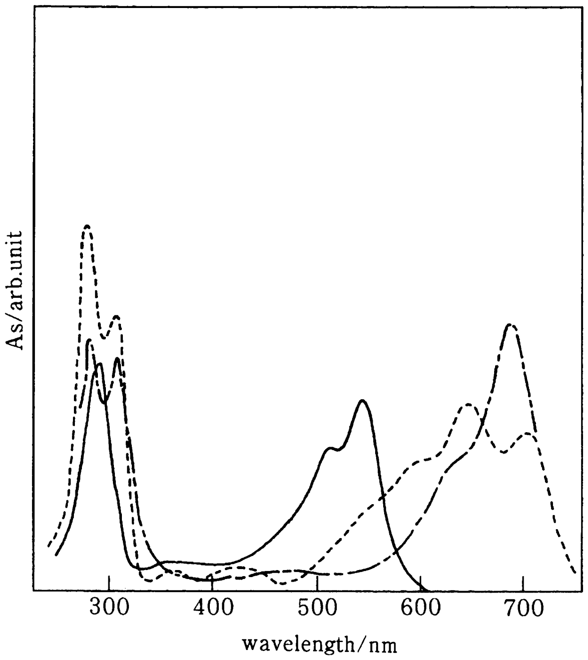


Fig. 8. Absorption spectra of TPDT in ethanolic solution of H_2SO_4. The concentration of H_2SO_4 are 0% (—), 0.01% (····), and 14% (– · –), respectively.

The authors express their hearty thanks to Mrs. Yaeko Goto and Dr. Minoru Suzuki of the University of Tokyo for ESR measurements. The authors are also grateful to Mr. Satoru Yamanaka, Mr. Koji Oneyama, and Mr. Atsushi Ogawa for their technical assistance.

References

1) K. Kozawa and T. Uchida, *Acta Crystallogr., Sect. C*, **49**, 267 (1993).

2) K. Kozawa, T. Hoshizaki, and T. Uchida, *Bull. Chem. Soc. Jpn.*, **64**, 2039 (1991).

3) T. Someno, T. Hoshizaki, K. Kozawa, T. Uchida, H. Hayashi, T. Sugano, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **64**, 921 (1991).

4) K. Kozawa and T. Uchida, *Acta Crystallogr., Sect. C*, **46**, 1006 (1990).

5) T. Uchida, H. Seki, M. Ito, C. K. Nakano, T. Hoshizaki, and K. Kozawa, *Chem. Lett.*, **1986**, 999.

6) T. Uchida, M. Ito, and K. Kozawa, *Bull. Chem. Soc. Jpn.*, **56**, 577 (1983).

7) R. B. Von Dreele and J. Harris, *Acta Crystallogr., Sect. C*, **39**, 170 (1983).

8) A. Obata, H. Kawazura, and H. Miyamae, *Acta Crystallogr., Sect. C*, **40**, 45 (1984).

9) A. Obata, M. Yoshimori, K. Yamada, and H. Kawazura, *Bull. Chem. Soc. Jpn.*, **58**, 437 (1985).

10) A. Singhabhandhu, D. P. Robinson, J. H. Fang, and W. E. Geiger, *Inorg. Chem.*, **14**, 318 (1975).

11) R. Anthonj, N. Karl, B. E. Robertson, and J. J.

Stezowski, *J. Chem. Phys.*, **72**, 1244 (1980); B. E. Robertson and J. J. Stezowski, *Mol. Cryst. Liq. Cryst.*, **52**, 319 (1979).

12) H. Kobayashi, *Acta Crystallogr., Sect. B*, **30**, 1010 (1974).

13) C. J. Fritchie, Jr., *J. Chem. Soc. A*, **1969**, 1328.

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

15) Y. Iida, *Bull. Chem. Soc. Jpn.*, **44**, 663 (1971).

16) J. P. Billon, *Ann. Chim. (Paris)*, **7**, 183 (1962).

17) D. M. Chapman, A. C. Buchanan, and G. Mamantov, *J. Am. Chem. Soc.*, **108**, 654 (1986).

18) B. Paduszek and M. K. Kalinowski, *Electrochim. Acta*, **28**, 639 (1983).

19) M. Opallo and A. Kapturkiewicz, *Electrochim. Acta*, **30**, 1301 (1985).

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

21) J. A. VanAllen, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.*, **27**, 1659 (1962).

22) J. Garbarczyk and A. Zuk, *Phosphorus Sulfur*, **6**, 351 (1979).

23) R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, **98**, 3916 (1976).

24) CAche system, MOPAC ver. 6.04 (SONY Tektronix).

25) P. C. Dwivedi, K. G. Rao, S. N. Bhat, and C. N. R. Rao, *Spectrochim. Acta, Part A*, **31**, 120 (1975).

26) K. Yasukouchi, I. Taniguchi, H. Yamaguchi, J. Ayukawa, K. Ohtsuka, and Y. Tsuruta, *J. Org. Chem.*, **46**, 1659 (1981).

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