Synthesis and Electrochemical Study of Benzothiazine and Phenothiazine Derivatives

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A number of benzothiazine and phenothiazine derivatives are prepared by reaction of 2-mercaptoaniline and cyclic β-diketo compounds or by reaction of bidentate nucleophiles on 4-chloro-3-nitrocoumarin by using the HSAB principle. The topological resonance energies per π-electron (TREPE's) are calculated for nine benzothiazine and phenothiazine derivatives and correlated with the first reversible peak potentials. The analysis of the data shows a good correlation between the TREPE values and the oxidation potentials. The chemical behavior of the electrochemically generated radical cations of the two related heterocyclic systems: 6,12-dihydro[1]benzopyrano[3,4-*b*][1,4]benzothiazin-6-one (1) and 2,3-dihydro-2,2-dimethylphenothiazin-6(1*H*)-one (2) are examined by using the electroanalytical techniques and preparative controlled potential electrolysis. HMO calculations are used to predict the most reactive sites toward the nucleophilic attack.

The continuous interest in the chemistry of phenothiazine and its derivatives is related to their wide range of applications as medicinal agents.[1-7] They were also subjects of a variety of theoretical studies within the frameworks of the MO theory[8,9] and QSAR approaches.[10,11] Significant improvements in the chemotherapeutic action of phenothiazines have been achieved by replacing the benzene rings with various heterocycles.[11-14] The electrochemical studies of phenothiazines have also been reported in a number of papers both in protic and aprotic media.[15,16]

We wish to report in the present work the synthesis and electrochemical behavior of benzothiazine, phenothiazine, and some novel derivatives of phenothiazine. These compounds are all depicted in Figure 1.

Results and Discussion

Synthesis. The compounds **1–6** were prepared via oxidative cyclization by heating the mixture of 2-mercaptoaniline and cyclic β-diketo compounds in dimethyl sulfoxide at 140–145 °C for 40 min according to the reaction scheme given in Figure 2. The compounds **2** and **4** were also synthetized according to the procedure by Miyano et al.,[17] and the synthesis of **1** was reported in our previous paper.[18] The structure of the products is confirmed by mass spectra, ^{1}H NMR spectra, and IR spectra of the compounds **1–6**. The mass spectra all show the intensive molecular ion. The ^{1}H NMR spectra all show signals for NH protons in the range δ 8.70–9.00. The IR spectra all show an NH absorption in the range 3240–3330 cm^{-1}. The compounds **5** and **6** appear to be a novel heterocyclic ring systems.

Table I. Oxidation Peak Potentials and TREPE's

compd	E_p, V vs. SCE	$E_p^a - E_p^c$, mV	TREPE
1	0.71	60	0.02030
	0.99	irrev	
3	0.67	60	0.01938
	0.77	irrev	
4	0.51	70	0.01679
	1.00	irrev	
5	0.50	55	0.015834
	1.10	irrev	
6	0.49	85	0.01557
	0.59	irrev	
7	0.89	60	0.0227124
	1.30	irrev	
8	0.66	80	0.0185155
	0.92	irrev	
9	0.69	90	0.200411
	0.93	irrev	
10	0.59	85	0.01779
	0.97	irrev	
11	1.03	irrev	
12	1.02	irrev	
13	1.44	irrev	

The synthesis of the compounds **7–9** was performed by reaction of bidentate nucleophiles on 4-chloro-3-nitrocumarin by using HSAB principle.[19,20]

Stirring of heterocyclic compound **1** or **2** with a haloderivative, RX, in two phase system consisting of an organic solvent (CH_2Cl_2) and a 25% aqueous sodium hydroxide solution in the presence of an ammonium salt, $PhCH_2N^+(CH)_3Cl^-$, leads to the cyclic sulfonium ylides **11–13**. The assignment of cyclic structures to the products **11–13** is supported by mass spectra and the ^{1}H NMR spectra of the compounds. The mass spectra all show, besides a molecular ion, a major fragment ion corresponding to the loss of an alkyl radical from the molecule.

(1) Schenker, E.; Herbst, H. *Prog. Drug Res.* **1963**, *5*, 269.
(2) Gabay, S.; Harris, R. *Top. Med. Chem.* **1970**, *3*, 57.
(3) Ariëns, E. J. *Drug Des.* **1971**, *1*, 1.
(4) Ariëns, E. J. *Drug Des.* **1971**, *2*, 1.
(5) Büchi, J.; Perlia, X. *Drug Des.* **1972**, *3*, 243.
(6) Doukas, P. H. *Drug Des.* **1975**, *5*, 133.
(7) Mager, P. P. *Multidimensional Pharmacochemistry*; Academic: Orlando, FL, 1984.
(8) Kier, L. B. *Molecular Orbital Theory in Drug Research*; Academic: New York, 1971; p 154.
(9) Kauffman, J. J.; Koski, W. S. *Drug Des.* **1975**, *5*, 251.
(10) Golender, V. E.; Rozenblit, A. B. *Drug Des.* **1980**, *9*, 299.
(11) Gund, P.; Jensen, N. P. In *Quantitative Structure–Activity Relationships of Drugs*; Academic: New York, 1983; p 285.
(12) Okafor, C. O. *Int. J. Sulfur Chem.* **1971**, *B6*, 237.
(13) Okafor, C. O. *Phosphorus Sulfur* **1978**, *4*, 79.
(14) Okafor, C. O. *J. Heterocycl. Chem.* **1980**, *17*, 1587.
(15) Paduszek, B.; Kalinowski; M. K. *Electrochim. Acta* **1983**, *28*, 639.
(16) Lund, H.; Tabaković, I. *Adv. Heterocycl. Chem.* **1984**, *36*, 235.
(17) Miyano, S.; Abe, N.; Sumoto, K.; Termato, K. *J. Chem. Soc.; Perkin Trans. 1* **1976**, 1146.
(18) Tabaković, K.; Tabaković, I.; Trkovnik, M.; Jurič, A.; Trinajstič, N. *J. Heterocycl. Chem.* **1980**, *17*, 801.
(19) Tabaković, K.; Tabaković, I.; Trkovnik, M.; Trinajstič, N.; N. *Liebigs Ann. Chem.* **1983**, 1901.
(20) Tabaković, I.; Tabaković, K.; Grujič, Z.; Trinajstič, N.; Meič, Z. *Heterocycles* **1985**, *23*, 2539.

0022-3263/87/1952-4053$01.50/0

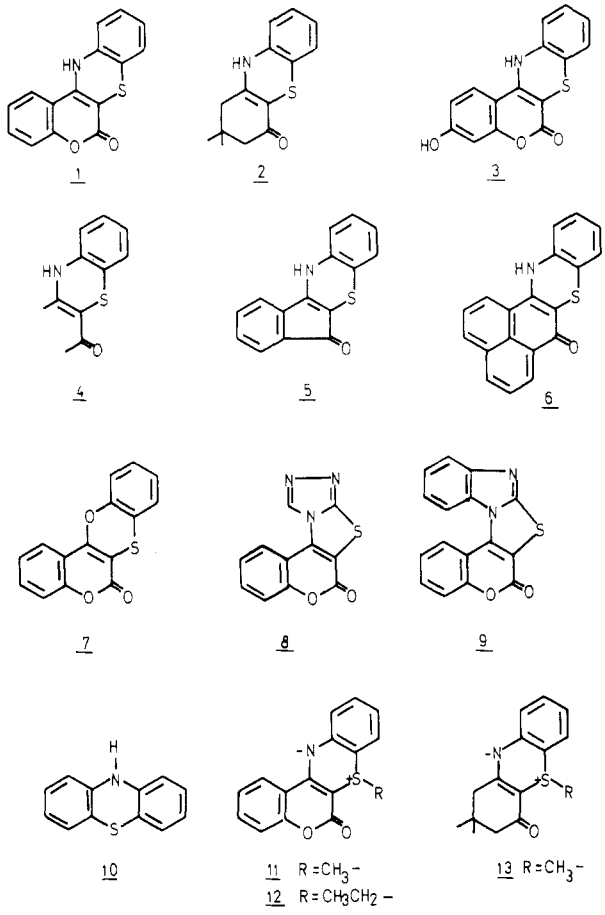


Figure 1. Schematic representation of studied phenothiazenes.

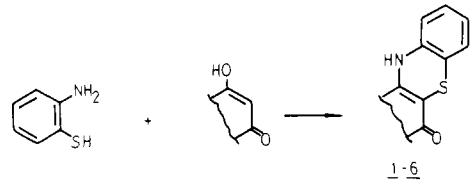


Figure 2. The reaction scheme for preparing phenothiazines 1–6.

The ^{1}H NMR spectra all show signals for *S*-alkyl group in the range δ 2.11–2.95. Compound **13**, having the same mp and identical spectra, was also synthetized by an independent synthetic procedure.[21] It is worthwhile to note that the anodic potential of the compounds **11–13** is shifted anodically between 0.98 and 0.59 V in comparison with the parent heterocycle. The reverse of this reaction, the dealkylation of the ylide, was readily achieved by heating the ylides with concentrated hydrochloric acid for the short period. In this way the ylides **11–13** were converted into the corresponding heterocyclic compounds **1** or **2**.

Correlation of Topological Resonance Energy per π-Electron (TREPE) and Oxidation Potential. In order to obtain a quantitative relationship for the oxidizability of the polynuclear heterocyclic compounds **1–13**, we first turned our attention to the determination of the peak potentials vs. saturated calomel electrode (SCE). Table I lists the values obtained by single-sweep voltammetry (sweep rate 100 mV/s) at platinum electrode. All measurements were made in acetonitrile containing 0.1 M tetraethylammonium perchlorate as the supporting electrolyte with 1 mM concentration of the substrate. As can

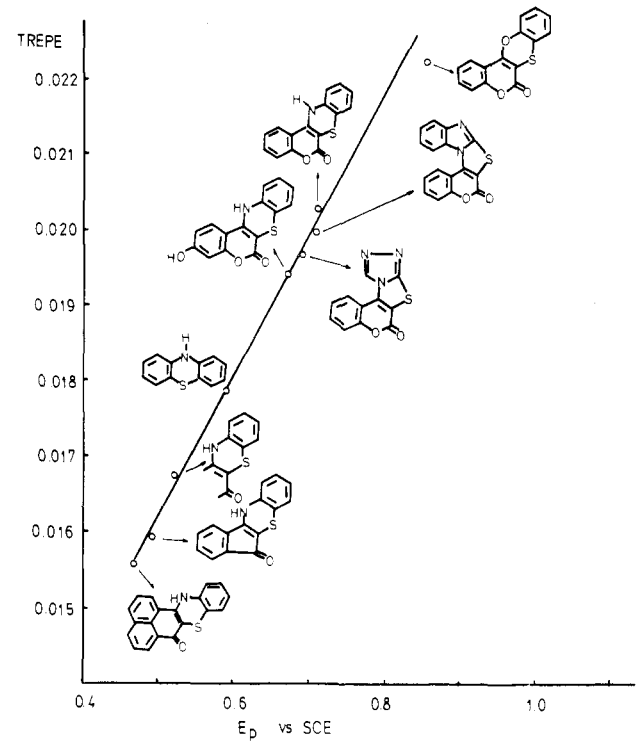


Figure 3. The TREPE indices vs. the first peak potentials (E_p) for a series of studied heterocycles.

be seen from Table I the compounds **1–10** exhibited two peaks. All the compounds gave first reversible and second irreversible peaks. The criteria for reversible cyclic voltammograms[22] $E_{pa} - E_{pc}$ close to 58 mV, the peak current ratio i_{pc}/i_{pa} equal to 1.0, and the current function $(i_p/v^{1/2}C)$ constant were found to be within the limits of experimental error for the compounds **1–10**. The compounds **11–13** showed one irreversible peak on the cyclic voltammogram.

We have compared our reversible peak potentials of the first wave with the theoretical calculations. The results are of theoretical interest because the electrochemical potential have been taken as a measure of the energy states of organic molecules. Since Maccoll first reported the correlation between polarographic oxidation potentials of aromatic compounds and their ionization potentials,[23] several examples of such correlation have appeared.[24] With the different approaches to the MO calculation, the energies calculated were correlated with the measured electrochemical potentials.[25-27]

We compared topological resonance energies per π-electron, TREPE's,[28] indices of aromaticity, with the first peak potentials, E_p, for a series of heterocycles studied. TREPE is calculated by means of the formula[28,29] in eq 1, where N is the total number of π-electrons in the con-

$$\text{TREPE} = \frac{1}{N}\sum_{i=1}^{N} g_i(x_i - x_i^{ac}) \qquad (1)$$

jugated molecule, x_i's are the Hückel eigenvalues, and x_i^{ac}'s

(21) Gilchrist, T. L.; Iskander, G. M. *J. Chem. Soc., Perkin Trans. 1* **1982**, 831.

(22) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.
(23) Maccoll, A. *Nature (London)* **1949**, *163*, 178.
(24) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1978**, 101, 1308 and references therein.
(25) Dewar, M. J. S.; Hashmall, J. A.; Trinajstić, N. *J. Am. Chem. Soc.* **1970**, *92*, 5555.
(26) Wiberg, K. B.; Lewis, T. P. *J. Am. Chem. Soc.* **1970**, *32*, 7154.
(27) Shawali, A. S; Herndon, W. C.; Párkányi, C. *Electrochim. Acta* **1982**, *27*, 817.
(28) Gutman, I.; Milun, M.; Trinajstić, N. *J. Am. Chem. Soc.* **1977**, *99*, 1962.
(29) Trinajstić, N. *Chemical Graph Theory*; CRC: Boca Raton, FL, 1983; Vol. II, Chapter 1.

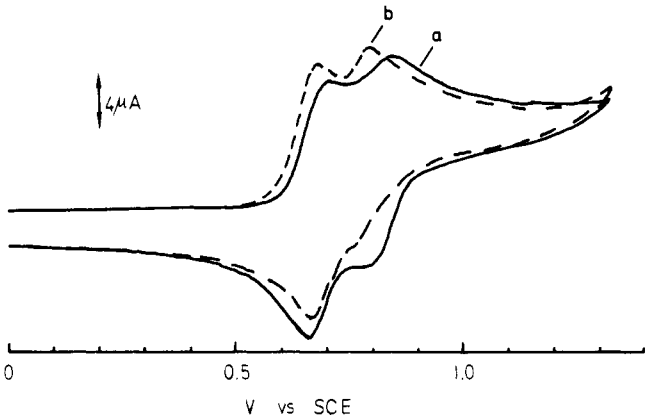


Figure 4. Typical cyclic voltammograms for oxidation of 1 mM solution of 1 at platinum electrode with scan rate 100 mV s^{-1}: (a) CH_3CN–0.1 M Et_4NClO_4; (b) CH_3CN–0.1 M Et_4NClO_4; water (200 L).

are those of the reference polynomial. The g_i is the orbital occupancy number. The computation of TREPE and the computer program are detailed elsewhere.[30] Parameters for heteroatoms are taken from Purcell and Singer.[31] In addition, Wheland and Pauling's parameter for the methyl group is used.[32]

The numerical values of the TREPE indices for molecules **1** and **3–10** are also given in Table I. All these molecules are predicted to be aromatic. Systems **11–13** are not studied because the TREPE model in the present form is not applicable to ionic systems of this kind.

The TREPE values have been correlated with the first peak potentials of compounds **1** and **3–10**. This is shown in Figure 3.

As it can be seen from Figure 3, more aromatic compounds possess more positive oxidation potentials. The least-squares analysis of the data shows that the results of the correlation can be modeled by eq 2. Putting the

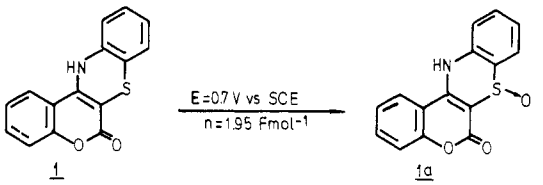
$$\text{TREPE} = 0.15822345E_p^3 - 0.28940219E_p^2 + 0.1959779E_p - 0.0295862 \quad (2)$$

TREPE value for benzene (0.045) in this equation one can predict the reversible peak potential for benzene in acetonitrile (2.36 V vs. SCE).

Chemical Behavior of Radical Cations. We have examined the chemical behavior of the electrochemically generated radical cations of the two related heterocyclic systems: 6,12-dihydro[1]benzopyrano[3,4-*b*][1,4]benzothiazin-6-one (**1**) and 2,3-dihydro-2,2-dimethylphenothiazin-6(1*H*)-one (**2**). The electrochemical studies were conducted with an acetonitrile–0.1 M tetraethylammonium perchlorate solution. A one-compartment cell was employed; the platinum anode and cathode and saturated calomel electrode (SCE) as the reference electrode were used.

The precise mechanism of electrochemical oxidation of **1** and **2** is of interest, but it may be quite complex. Our results are limited but do allow the formulation of the main mechanistic features.

Typical cyclic voltammograms for oxidation of compound **1** are shown in Figure 4. The cyclic voltammogram obtained in dry acetonitrile, which was added to the cell through the column with activated alumina, exibits two reversible anodic waves at 0.71 and 0.84 V. The first wave



1 1a

Figure 5. The preparative electrochemical oxidation of 1.

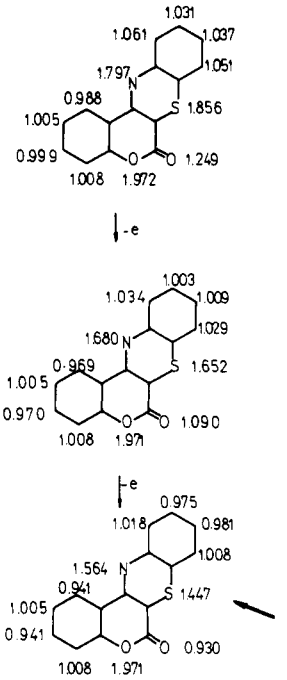


Figure 6. The HMO charge densities of 1 and its cation radical and dication.

corresponds to the formation of the radical cation and the second to the formation of the dication. By adding the 200 μL of water the cathodic counterpart disappeared, indicating that the dication is kinetically active species.

Coulometry at 0.75 and 0.9 V, corresponding to the first and second plateau of the current–potential curve, obtained by rotating disk electrode voltammetry, shows that the overall electrode reaction is a two-electron oxidation. The difference between two peak potentials, $\Delta E = 0.13$ V, implies that the disproportionation of radical cations generated at the first anodic potential seems feasible (Kd = $10^{-2.2}$).[33] The preparative electrochemical oxidation of **1** at the controlled potential ($E = 0.75$ V vs. SCE) gave a good yield of 6,12-dihydro[1]benzopyrano[3,4-*b*][1,4]benzothiazin-6-one 5-oxide (**1a**) (Figure 5).

One major advantage of the present reaction lies in its regioselectivity with the regard to the position of nucleophilic attack. According to the proposed mechanism it is to be expected that the atom of higher positive charge in the dication would react more readily with water as a nucleophile. In order to predict the most reactive sites, toward the nucleophilic attack, the standard HMO calculations have been performed. The charge density distribution of the compound **1** and its radical cation and dication are given in Figure 6. The greatest positive charge is on the sulfur atom, marked with an arrow, in accord with the product obtained.

Cyclic voltammograms for oxidation of compound **2** run in dry acetonitrile showed two reversible anodic waves at 0.75 and 1.05 V (see Figure 7). By the addition of the 200

(30) Mohar, B.; Trinajstić, N. *J. Comput. Chem.* **1982**, *3*, 28.
(31) Purcell, W. P.; Singer, J. A. *J. Chem. Eng. Data* **1967**, *12*, 235.
(32) Wheland, G. W.; Pauling, L. *J. Am. Chem. Soc.* **1935**, *57*, 2086.
(33) Weinberg, N. L., Ed. *Techniques of Electroorganic Synthesis*; Wiley: New York, 1974; Part I, p 545.

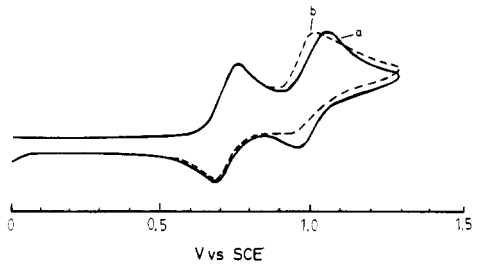


Figure 7. Typical cyclic voltammograms for oxidation of 1 mM solution of **2** at a platinum electrode with scan rate 100 mV s^{-1}: (a) CH_3CN–0.1 M Et_4NClO_4; (b) CH_3CN–0.1 M Et_4NClO_4; water (200 L).

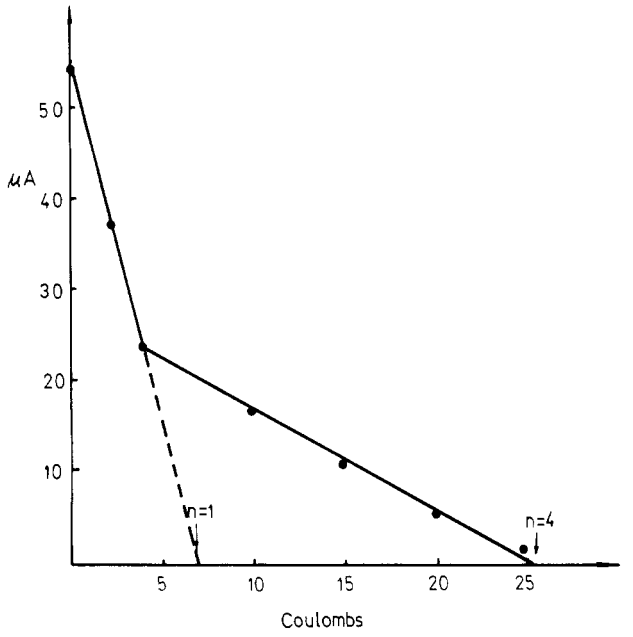


Figure 8. Coulometry for oxidation at +0.75 V of **2** (1.5×10^{-3} M) in CH_3CN–0.1 M Et_4NClO_4 at a platinum–gauze anode.

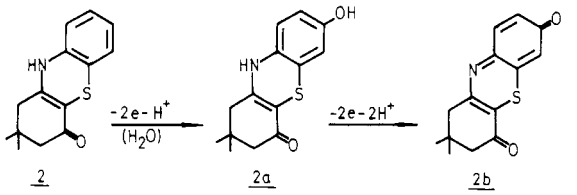


Figure 9. The preparative electrochemical oxidation of **2**.

μL of water, the second peak shifted cathodically and the cathodic counterpart corresponding to the dication formation disappeared, indicating that the dication is a reactive species. Cyclic voltammograms with constant condition were obtained, during controlled potential electrolysis at the potential of the first wave (E = 0.75 V vs. SCE), as a function of charge passed, and the results indicated that both waves decreased at a rate corresponding to the consumption of 1 F mol^{-1} in the beginning of the electrolysis and to 4 F mol^{-1} in exhausted electrolysis (Figure 8). The preparative electrochemical oxidation of **2** at the controlled potential (E = 0.75 V vs. SCE) gave good yield of 2,3-dihydro-2,2-dimethyl-1*H*-phenothiazine-4,7-dione (**2b**). The formation of the product **2b**, can be explained by the formation of the intermediary phenothiazine **2a** hydroxylated in position 7, which is the final product **2b** by loss of two electrons and two protons (Figure 9).

Providing that the hydroxylation occurs at the stage of the dication leading to the intermediate **2a**, it is to be expected that the atom of the highest positive charge is

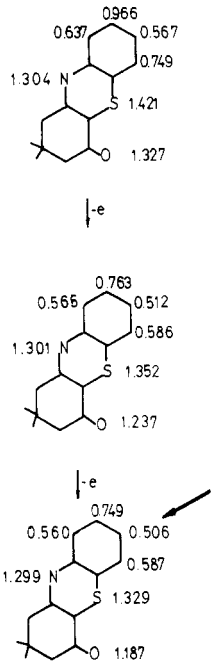


Figure 10. The HMO charge densities of the conjugated subsystem of **2** and its oxidation products.

in position 7 of the substrate **2**. In order to predict the most reactive sites, toward the nucleophilic attack, the HMO calculations showed that the greatest positive charge is on the carbon atom at position 7 marked with an arrow in Figure 10.

Experimental Section

Apparatus and Materials. An Amel 550 potentiostat, HI-TEK DT2101 potentiostat, HI-TEK PRRI wave form generator, and Gould x–y recorder were used. A one-compartment cell was used in all voltammetric experiments with the platinum anode ($2r$ = 3 mm), platinum cathode, and saturated calomel electrode. For rotating disk electrode studies, a Tacussel rotating electrode-type EDI was employed.

All melting points are uncorrected. The IR spectra (KBr pellets) were recorded on a Perkin-Elmer M-377 spectrophotometer, the NMR spectra were recorded on a Perkin-Elmer R 12A spectrometer using tetramethylsilane as an internal standard, and mass spectra were recorded on a Hitachi Perkin-Elmer RMV-GL mass spectrometer.

Acetonitrile (Merck) was purified by refluxing over potassium permanganate for 1 h, followed by distillation over P_2O_5. Tetraethylammonium perchlorate (Eastman) was recrystallized twice from water, then dried in an oven at 110 °C, and kept in a desiccator over P_2O_5.

9-Hydroxy-6,12-dihydro[1]benzopyrano[3,4-*b*][1,4]benzothiazin-6-one (3). 4,7-Dihydroxycoumarin (1.78 g, 10 mmol), 2-mercaptoaniline (1.25 mL, 10 mmol), and dimethyl sulfoxide (4 mL) were stirred and heated together at 145–150 °C for 3 h. The product crystallized on cooling; it was filtered off: 0.98 g (34%). Recrystallization from EtOH–H_2O (7:3) gave **3** with mp 282–284 °C: IR (KBr pellet) 3450 (OH), 3325 (NH), 1660 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.7 (br s, 1 H, NH) 7.05–8.04 (m, 7 H, Ar); MS, m/e (relative intensity) 283 (100), 282 (25), 255 (28) 251 (19), 227 (15), 186 (20), 142 (31), 120 (14), 108 (18), 69 (20). Anal. Calcd for $C_{15}H_9NSO_2$ (267): C, 67.41; H, 2.99; N, 5.24. Found: C, 67.08; H, 2.98; N, 5.19.

11*H*-1-Benzo[3,4]cyclopenta[1,2-*b*][1,4]benzothiazin-5-one (5). 1,3-Indandione (1.46 g, 10 mmol), 2-mercaptoaniline (1.25 mL, 10 mmol), and dimethyl sulfoxide (4 mL) were stirred and heated together at 145–150 °C for 5 min. The product crystallized on cooling; it was filtered off: 1.74 g (50%). Recrystallization from acetone gave **5** with mp 232–234 °C: IR (KBr pellet) 3241 (NH), 1620 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.77 (br s, 1 H, NH), 6.72–7.80 (m, 8 H, Ar); MS, m/e (relative intensity) 251 (38), 223 (15), 222 (8), 219 (5) 121 (13), 111 (7), 83 (9), 82 (100), 42 (22),

41 (18), 40 (15). Anal. Calcd for $C_{15}H_9SNO$ (251): C, 71.71; H, 3.61; N, 5.58. Found: C, 71.47; H, 3.65; N, 5.46.

13*H*-Naphtho[1',8':3,4,5]cyclohexa[1,2-*b*][1,4]benzothiazin-6-one (6). Phenalenedione (1.96 g, 10 mmol), 2-mercaptoaniline (1.25 mL, 10 mmol), and dimethyl sulfoxide (6 mL) were stirred and heated together at 145–150 °C for 1 h. The product crystallized on cooling; it was filtered off: 1.4 g (47%). Recrystallization from DMF gave **6** with mp 306–308 °C: IR (KBr pellet) 3330 (NH), 1630 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.80 (br s, 1 H, NH), 6.20–8.50 (m, 10 H, Ar); MS, *m/e* (relative intensity) 301 (100), 274 (7), 273 (33) 272 (11), 269 (11), 241 (10), 240 (10), 151 (19), 137 (10) 135 (8), 120 (9). Anal. Calcd for $C_{19}H_{11}NSO$ (301): C, 75.74; H, 3.68; N, 4.65. Found: C, 75.48; H, 3.62; N, 4.60.

Ylides by Phase-Transfer Alkylation. General Procedure. A mixture of the compound **1** or **2** (4 mmol), methyl or ethyl iodide (20 mmol), and methylenechloride (10 mL) was stirred with a 50% aqueous sodium hydroxide solution (10 mL) containing benzyltrimethylammonium chloride (0.3 mmol) at room temperature for 2 h. The organic layer was then separated, washed with water, dried (Na_2SO_4), and evaporated. The crude product was recrystallized from the appropriate solvent.

5-Methyl-6-oxo-6*H*-[1]benzopyrano[3,4-*b*][1,4]benzothiazinium Hydroxide Inner Salt (11). Recrystallization from ethanol gave **11** (0.84 g, 75%) with mp 197–199 °C: IR (KBr pellet 2920 (CH_3), 1660 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.40–8.40 (m, 8 H, Ar), 2.11 (s, 3 H, CH_3); MS, *m/e* (relative intensity) 281 (47), 266 (100), 238 (14), 211 (3.), 209 (12), 132 (14), 120 (9), 119 (10). Anal. Calcd for $C_{16}H_{11}O_2SN$ (281): C, 68.32; H, 3.94; N, 4.98. Found: C, 67.97; H, 3.76; N, 4.64.

5-Ethyl-6-oxo-6*H*-[1]benzopyrano[3,4-*b*][1,4]benzothiazinium Hydroxide Inner Salt (12). Recrystallization from benzene gave **12** (0.35 of, 59%) with mp 172–174 °C: IR (KBr pellet) 2980, 2860 (CH_3CH_2), 1660 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.13–8.44 (m, 8 H, Ar), 2.95 (q, 2 H, CH_2), 1.02 (t, 3 H, CH_3); MS, *m/e* (relative intensity) 295 (8), 266 (100), 238 (10), 210 (3), 209 (3), 91 (4). Anal. Calcd for $C_{17}H_{13}O_2SN$ (295): C, 69.15; H, 4.41; N, 4.75. Found: C, 68.84; H, 4.11; N, 4.31.

2,3-Dihydro-2,2,5-trimethyl-4-oxo-1*H*-phenothiazinium Hydroxide Inner Salt (13). Recrystallization from acetonitrile gave **13** (0.65 g, 63%) with mp 179–181 °C (lit.[17] mp 179–181 °C).

Preparative Electrolysis of 1 and 2. General Procedure. Into the anodic compartment of the divided cell with Pt-gauze anode (3 × 5 cm) and a Ni cathode filled with a 0.1 M solution of Et_4NClO_4 in acetonitrile (150 mL) was added the substrate **1** or **2** (0.15–0.25 g). The potential was maintained at a fixed value (0.75 V vs. SCE) with initial currents, generally 200–700 mA. Electrolysis was usually discontinued when the current dropped to 2–5 mA. During controlled potential electrolysis an electronic integrator was used to record the quantity of electricity passed. The solution was evaporated to ca. 10 mL and 150 mL of water was added. The precipitated products **1a** and **2b** was isolated by filtration and recrystallized from the appropriate solvent.

6,12-Dihydro[1]benzopyrano[3,4-*b*][1,4]benzothiazin-6-one 5-Oxide (1a). Recrystallization from ethanol gave **1a** (73%) with mp 240–242 °C: IR (KBr pellet) 3230 (NH), 1700 (C=O), 1150 (S=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.93 (br s, 1 H, NH), 7.10–8.30 (m, 8 H, Ar); MS, *m/e* (relative intensity) 267 (100), 266 (35), 239 (9), 238 (13), 227 (24), 212 (15), 211 (13), 134 (7), 120 (8), 108 (27). Anal. Calcd for $C_{15}H_9O_3NS$ (267): C, 63.60; H, 3.18; N, 4.95. Found: C, 3.32; H, 3.31; N, 4.58.

2,3-Dihydro-2,2-dimethyl-1*H*-phenothiazine-4,7-dione (2b). Recrystallization from ethanol gave **2b** (76%) with mp 159–161 °C: IR (KBr pellet) 2980 (CH), 1720 (C=O), 1660 (C=O quinoneimine) cm^{-1}; MS, *m/e* (relative intensity) 259 (55), 245 (16), 216 (8), 162 (6), 149 (5), 136 (51), 135 (48), 108 (16), 82 (5), 71 (5), 69 (10), 60 (8), 56 (92), 45 (100), 41 (80). Anal. Calcd for $C_{14}H_{13}O_2SN$ (259): C, 64.86; H, 5.02; N, 5.41. Found: C, 65.01; H, 5.32; N, 5.12.

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