Table II
Thermal Decomposition of Arenesulfonyl Azides by Differential Scanning Calorimeter

Compd	T_m	T_d (40°/min)	T_d (80°/min)
3a	120–122	180	215
3b	170–172	192	212
3c	121	190	210
4		198	208

Experimental Section[7]

2-Hydroxyethyl 4-Azidosulfonylcarbanilate (3a). To an amount of 50.4 g (0.8 mol) of ethylene glycol in 500 ml of acetonitrile with cooling and stirring a solution of 43.2 g (0.2 mol) of 4-isocyanatobenzenesulfonyl chloride in 100 ml of acetonitrile was added over a period of 10 min at 2–8°. After disappearance of the N=C=O stretching in the infrared spectrum of the reaction mixture, 13 g (0.2 mol) of sodium azide was added and the reaction mixture was stirred at room temperature for 60 min. The precipitated sodium chloride was removed by filtration, and on evaporation of most of the solvent under vacuum and addition of water 52 g (91%) of 2-hydroxyethyl 4-sulfonylazidocarbanilate, mp 115–118°, was precipitated. Recrystallization from acetonitrile raises the melting point to 120–122°. The azidocarbanilates **3b–d** were prepared similarly.

Tris(4-azidosulfonylbenzene)isocyanurate (4). To 26 g (0.4 mol) of sodium azide suspended in 400 ml of acetonitrile a solution of 87 g (0.4 mol) of 4-isocyanatobenzenesulfonyl chloride[4] was added over a period of 20 min at 4–10°. After stirring at room temperature for 3 hr 600 ml of water was added to precipitate a mixture of product and sodium chloride, which was washed several times with water to remove the salt. Thus 79.7 g (89%) of 4 was obtained: mp ~200° (violent dec); ir (acetonitrile) 2132 (SO_2N_3), 1698 cm^{-1} (C=O).

4-Chlorosulfophthalic Anhydride (6). To 229.35 g (1.1 mol) of phosphorus pentachloride suspended in 1000 ml of acetonitrile, 228 g (1 mol) of 4-sulfophthalic anhydride (obtained from molten phthalic anhydride and sulfur trioxide) was added. The reaction mixture was refluxed for 150 min and the solvent was evaporated under vacuum. The residue was dissolved in 1000 ml of methylene chloride and washed twice with 300 ml of water. The organic layer was dried with magnesium sulfate, the solvent was evaporated, and vacuum distillation of the residue gave 163.2 g (66.2%) of 4-chlorosulfonylphthalic anhydride: bp 170° (0.5 mm); mp 91–92° (CCl_4); ir ($CHCl_3$) 1869, 1786 cm^{-1} (C=O).

Anal. Calcd for $C_8H_3ClO_5S$: C, 38.95; H, 1.22; Cl, 14.37. Found: C, 38.80; H. 1.53; Cl, 14.16.

4-Azidosulfonylphthalic Anhydride (7). To a solution of 12.3 g (0.05 mol) of 4-chlorosulfonylphthalic anhydride in 125 ml of acetonitrile, 3.25 g (0.05 mol) of sodium azide was added. After stirring for 4 hr at room temperature the precipitated sodium chloride was removed by filtration and the solvent was removed under vacuum. Trituration of the residue with diethyl ether gave 8.8 g (69.5%) of **7**: mp 93–94°; ir ($CHCl_3$) 2137 (SO_2N_3), 1869 and 1786 cm^{-1} (C=O).

Anal. Calcd for $C_8H_3N_3O_5S$: C, 37.94; H, 1.18; N, 16.60. Found: C, 38.27; H, 1.09; N, 16.23.

Registry No.—**1**, 6752-38-1; **3a**, 33780-21-1; **3b**, 34280-60-9; **3c**, 34235-62-6; **3d**, 34235-60-4; **4**, 31328-33-3; **5**, 134-08-7; **6**, 39871-41-5; **7**, 37696-57-4; ethylene glycol, 107-21-1; 1,2,3-propanetriol, 56-81-5; 2-(hydroxymethyl)-2-methyl-1,3-propanediol, 77-85-0; sodium azide, 26628-22-8.

References and Notes

(1) The use of isocyanatobenzenesulfonyl azides[2] and 3-sulfonylazidobenzoyl chloride[3] to graft onto hydroxy group containing linear polymers are the only reported examples.
(2) H. Holtschmidt and G. Oertel, *Angew. Makromol. Chem.*, **9**, 1 (1969).
(3) Agfa Gevaert, A.-G., French Patent 1,455,154 (1966); *Chem. Abstr.*, **67**, 109254 (1967).
(4) L. M. Alberino, H. Ulrich, and A. A. R. Sayigh, *J. Polym. Sci., Part A*, **5**, 3212 (1967).
(5) F. A. Stuber, H. Ulrich, D. V. Rao, and A. A. R. Sayigh, *Photogr. Sci. Eng.*, **17**, 446 (1973).
(6) A. A. R. Sayigh, F. A. Stuber, and H. Ulrich, U.S. Patent 3,751,393 (1973).
(7) Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn.; ir spectra were taken on a Beckman IR-8 spectrophotometer. All melting points (uncorrected) were determined on a Fisher-Johns apparatus.

Preparation and Anodic Peak Potentials of Salts of Coordination Compounds Derived from Boric Acid and Polyhydric Phenols

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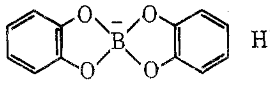
The coordination compounds derived from boric acid and dihydric phenols have the spiran structure shown in I, for the compound from boric acid and catechol. They have been studied since the late 19th century, and this work has been reviewed in a comprehensive manner by Steinberg.[1] Salts of these coordination compounds are now being used extensively as the solute in the electrolyte of electrolytic capacitors.[2] As a result we have had occasion to prepare the salts listed in Table I.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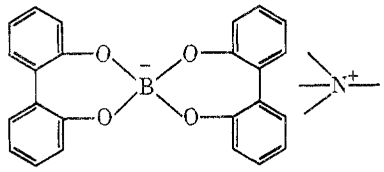
II

Alkali metal and amine salts have been reported previously,[1] but quaternary ammonium salts have been described only in the patent literature.[2] The bis-2,2′-dihydroxybiphenylborate salts are of special interest, since they have the structure, shown in II, where the spiran rings about the boron atom are seven-membered, and the four aromatic rings are very probably forced into two planes, one perpendicular to the other. These geometrical requirements, the seven-membered spiran rings and the largely planar configuration for the two biphenyl ring systems, do not result in any difficulty in the preparation of these salts, since they are readily obtained in high yield and are extremely stable once formed.

Peak potentials for the anodic oxidation of the free phenols and the salts were determined at a platinum anode by cyclic voltammetry at a scan rate of 200 mV/sec in dimethyl sulfoxide containing 0.1 *M* tetrabutylammonium fluoroborate as the supporting electrolyte. The results are shown in Table II. Since in each case studied there is no significant change in potential in going from the free phenol to the salt, the initial anodic process must be the same for both the free phenol and the salt and must consist of an electron transfer from an aromatic ring to form a cation radical. This must be true for the salts even though the negative charge is centered on the boron atom. It also follows that the change from free phenol to coordination compound is not accompanied by any significant perturbation of the electronic structure of the aromatic rings.

The current functions, $i_p/V^{1/2}C^*$, where i_p is the peak current, V is the scan rate, and C^* is the bulk concentration of the electroactive species, decreased with increasing scan rate. This is indicative of a chemical reaction coupled with the electron transfer. It is highly probable that catechol, 2,3-naphthalenediol, and 2,2′-dihydroxybiphenyl are electrochemically equivalent, since the observed current function values were similar. Catechol and 4-methylcatechol have been reported to undergo a two-electron oxidation coupled with a nucleophilic addition reaction.[3] The current function values for the complexes were consistently

Table I
Salts of Coordination Compounds Derived from Boric Acid and Dihydric Phenols

Registry no.	Cation	Yield, %	Mp, °C	N calcd	N found
	A. Biscatecholborate Salts				
53992-90-8	Dimethylammonium	86	325–350 dec	5.12	4.97
53992-91-9	Di-2-propylammonium	83.7	211–214	4.26	4.19
22364-89-2	Tetramethylammonium	83	290–291	4.65	4.50
53992-92-0	Tetraethylammonium	78	125–127	3.94	3.92
20234-44-0	Benzyltrimethylammonium	78	166–168	3.71	3.67
53992-93-1	*p*-Nitrobenzyltrimethylammonium	59.7	276–277	6.63	6.51
53992-95-3	*p*-Xylylene bis(triethylammonium)	87.6	222–225	3.68	3.61
	B. Bis-*p*-*tert*-butylcatecholborate Salts				
53992-97-5	Benzyltrimethylammonium	62.9	290–292	2.86	2.75
	C. Bis-2,3-naphthalenediolborate Salts				
53992-99-7	Tetramethylammonium	80.5	291 dec	3.49	3.27
53993-00-3	Benzyltrimethylammonium	67	257–259	2.93	2.91
53993-01-4	*p*-Nitrobenzyltrimethylammonium	82.6	318–319 dec	5.36	5.31
	D. Bis-2,2′-dihydroxybiphenylborate Salts				
53993-03-6	Dimethylammonium	85.6	260–262	3.29	3.07
53993-04-7	Di-2-propylammonium	86.1	317–321	2.91	2.92
53993-05-8	Tetramethylammonium	95	352–355	3.09	3.18
53993-06-9	Benzyltrimethylammonium	89	286–288	2.65	2.69

Table II
Peak Potentials for Anodic Oxidation of the Free Phenols and the Salts in Dimethyl Sulfoxide

Compd	E_p, V vs. Ag/Ag$^+$ (0.1 M)
Catechol	0.69
Dimethylammonium borodicatecholate	0.68
2,3-Naphthalenediol	0.80
Tetramethylammonium borodi(2,3-naphthalenediolate)	0.82
2,2′-Dihydroxybiphenyl	0.96
Benzyltrimethylammonium borodi(*o*,*o*′-biphenolate)	0.94

greater than those for the free phenols, and this may be attributed to either a difference in the diffusion rate or a difference in the rate of the coupled chemical reaction. The peak potentials also changed with scan rate, with the peak potentials increasing by approximately 100 mV when the scan rate was increased from 50 to 500 mV/sec.

Experimental Section

The salts were generally prepared by dissolving the dihydric phenol and amine or aqueous solution of a quaternary ammonium hydroxide in methanol. A solution of the requisite amount of boric acid in hot water was then added, and the resultant solution was distilled to dryness at the water pump. The crude product was then crystallized, most commonly from methanol–ether or acetone–ether. The preparation of tetramethylammonium borodicatecholate described below is typical.

Tetramethylammonium Borodicatecholate. Catechol (220.2 g, 2 mol) was mixed with 912 ml of 10% aqueous tetramethylammonium hydroxide, and methanol was added to complete solution. A solution of boric acid (61.8 g, 1 mol) in hot water was added, and the resultant solution was distilled at the water pump. The residue was crystallized from 2-propanol–methanol–ether to yield 250 g (83%) of the salt. A sample, recrystallized for analysis, had mp 290–291°.

Anal. Calcd for $C_{16}H_{20}BNO_4$: C, 63.81; H, 6.69; N, 4.65. Found: C, 64.03; H, 6.92; N, 4.50.

The dimethylammonium salts can be prepared as above, using dimethylamine, or, more simply, by heating a solution of the dihydric phenol and boric acid in the molar ratio of 2:1 in dimethylformamide at 125–130° for 24 hr.

Dimethylammonium Borodi(*o*,*o*′-biphenolate) A solution of 2,2′-dihydroxybiphenyl (9.3 g, 0.05 mol) and boric acid (1.55 g, 0.025 mol) in dimethylformamide (125 ml) was heated for 24 hr at 125–130°. Cooling and addition of ether gave 9.7 g (91.5%) of the salt, mp 258–261°, crystallized from dimethylformamide. As prepared in this manner the salt incorporates a molecule of dimethylformamide.

Anal. Calcd for $C_{29}H_{31}BN_2O_5$: N, 5.62. Found: N, 5.51.

The salt may be obtained free of dimethylformamide as follows. A solution, prepared by mixing solutions of 2,2′-dihydroxybiphenyl (18.6 g, 0.1 mol) in warm methanol (100 ml) and boric acid (3.1 g, 0.05 mol) in boiling methanol (60 ml), was cooled in an ice bath and treated with anhydrous dimethylamine (3.4 g, 0.076 mol). Hexane (100 ml) was added to complete precipitation and the mixture was cooled in the freezer. The yield was 18.2 g (85.6%), mp 260–262° after crystallization from methanol–ether. A sample for analysis was dried in vacuo at 80° for 2.5 hr.

Anal. Calcd for $C_{26}H_{24}BNO_4$: N, 3.29. Found: N, 3.07.

When the above analytical sample was crystallized from dimethylformamide a molecule of the amide was again incorporated in the salt.

Anal. Calcd for $C_{29}H_{31}BN_2O_5$: N, 5.62. Found: N, 5.18.

Oxidation Potentials. These were determined on a PAR 170 Electrochemistry unit. A single compartment cell containing a silver wire reference electrode and platinum wire working and auxiliary electrodes was used. *p*-Phenylenediamine, $E_p = -0.15$ V vs. Ag/Ag$^+$ (0.1 M) in dimethyl sulfoxide, was used to calibrate the reference electrode. The observed anodic waves were all irreversible, and cathodic currents were not observed even at sweep speeds of 500 V/sec.

Registry No.—Boric acid, 10043-35-3; dimethylamine, 124-40-3; di-2-propylamine, 108-18-9; tetramethylammonium hydroxide, 75-59-2; tetraethylammonium hydroxide, 77-98-5; benzyltrimethylammonium hydroxide, 100-85-6; *p*-nitrobenzyltrimethylammonium hydroxide, 53993-52-5; *p*-xylylene bis(triethylammonium hydroxide), 29059-91-4; catechol, 120-80-9; 2,3-naphthalenediol, 92-44-4; 2,2′-dihydroxybiphenyl, 1806-29-7; dimethylformamide, 68-12-2; dimethylammonium borodi(*o*,*o*′-biphenolate) salt with dimethylformamide, 53993-07-0.

References and Notes

(1) H. Steinberg, "Organoboron Chemistry", Vol. 1, Interscience, New York, N.Y., 1964, Chapter 15.
(2) S. D. Ross, R. C. Petersen, and M. Finkelstein, U.S. Patent 3,403,304 (1968); R. W. Santway and R. S. Alwitt, U.S. Patent 3,403,305 (1968).
(3) G. Sivaramiah and V. R. Krishnan, *Indian J. Chem.*, **4**, 541 (1966); R. N. Adams, M. D. Hawley, and S. W. Feldberg, *J. Phys. Chem.*, **71**, 851 (1967).