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Dipole Moments of B-Trifluoro-, B-Trichloro-, and B-Tribromoborazine[1]

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Dielectric constants and specific volumes of dilute solutions of B-trifluoro- and B-tribromoborazine in benzene and of B-trichloroborazine in cyclohexane were measured as a function of concentration and temperature. Refractive indices of similar dilute solutions were measured as a function of concentration. These data were used to calculate total polarizations, orientation polarizations, electronic polarizations, and atomic polarizations of the three molecules in order to evaluate the contribution of each of these terms to the total polarization. The results suggest that these molecules have zero dipole moments and that most of the nonzero dipole moments previously reported for symmetrically substituted borazines can be accounted for by failure to correct properly for atomic polarization.

Introduction

X-Ray diffraction studies of solid B-trifluoro-[2] and B-trichloroborazine[3] and electron diffraction studies of gaseous borazine,[4] B-trifluoro-,[5] and B-trichloroborazine[6] have indicated that the borazine ring is planar and has D_{3h} symmetry. Furthermore, infrared spectra of about 140 symmetrically substituted borazines[7] and Raman spectra of six such compounds[8] have been readily interpreted in terms of D_{3h} symmetry. However, four dipole moment studies,[9–12] which yielded values from 0.18 to 1.23 D., have suggested that a number of symmetrically substituted borazines have dipole moments significantly greater than zero.

Except for the case of borazine gas, where partial decomposition may be cause for casting doubt on the experimental result,[9] these moments were attributed to solute–solvent interactions,[11] to nonplanarity of the borazine ring,[10] or to low-frequency vibrations which caused high atomic polarizations.[10] A significant dipole moment arising from solute–solvent interactions could be ruled out by spectral evidence of Mellon and Lagowski[13] and by noting that the dipole moments for B-trichloroborazine in benzene[10,11] and cyclohexane[12] were essentially the same. Nonplanarity significant enough to account for the observed moments seemed unlikely, particularly in solution where the molecules would be less constrained than in the solid phase. Values for atomic polarization were estimated to be quite small by Watanabe and Kubo[10] and were assumed to be negligible by other workers,[11,12] except for Ramaswamy,[9] whose method should have compensated for atomic polarization. Mellon and Lagowski[13] obtained data which suggested that hexamethylborazine was nonpolar and that the apparent dipole moment arose from large values of atomic polarization. The actual magnitude of atomic polarizations of borazines needed further investigation.

The purpose of this study was to determine the total molar polarizations of B-trifluoro-, B-trichloro-, and B-tribromoborazine as a function of temperature. By means of a Debye temperature-dependent plot each total polarization, p, could then be broken down into an orientation polarization, p_o, and the sum of an electronic and an atomic polarization ($p_e + p_a$). The latter two could be separated by calculating p_e by itself from refractive index data. One might then decide whether p_o is actually zero in agreement with D_{3h} symmetry, or whether it is decidedly greater than zero, thus indicating significant nonplanarity. Furthermore, one could determine the role which p_a played in this work and perhaps in previously reported results.

Experimental Section

Materials.—Matheson Coleman and Bell Spectroquality cyclohexane and Mallinckrodt analytical reagent grade carbon tetrachloride were used as standard solvents for calibration of the measuring condenser. Matheson Coleman and Bell cyclohexane (mp 5–6°) was used as a solvent for B-trichloroborazine. Mallinckrodt analytical reagent grade benzene was used as a solvent for B-trifluoro- and B-tribromoborazine. Benzene and cyclohexane were dried by refluxing over potassium and then fractionally distilling through a 1-m vacuum-jacketed column. Carbon tetrachloride was dried by refluxing over phosphorus pentoxide and fractionally distilling through the same column. Only the second of three nearly equivalent fractions was used in all cases. Any further handling of dried solvents was done in a dry nitrogen-filled glove bag.

B-Trichloro- and B-tribromoborazine were prepared by the hot-tube method,[14] respectively allowing boron trichloride to react with ammonium chloride and boron tribromide with ammonium bromide. The ammonium salts were mixed with powdered asbestos to prevent caking.[15] B-Trifluoroborazine was

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[15] F. B. Hutto, M.S. Dissertation, Cornell University, Ithaca, N. Y., 1950.

prepared by transhalogenation of B-trichloroborazine with titanium tetrafluoride.[16]

Three independent samples each of B-trifluoro-, B-trichloro-, and B-tribromoborazine were freshly purified by sublimation at appropriate temperatures. *Anal.* Calcd for $F_3B_3N_3H_3$: N, 31.25. Found: N, 31.23, 31.16, 31.22. Calcd for $Cl_3B_3N_3H_3$: N, 22.85. Found: N, 22.82, 22.82, 22.86. Calcd for $Br_3B_3N_3H_3$: N, 13.25. Found: N, 13.18, 13.28, 13.21. Any handling of these samples as solids was done in a nitrogen-filled drybox and as solutions in a dry nitrogen-filled glove bag.

Measurements.—Solutions of B-trihalogenoborazines of known concentration and specific volume were prepared by adding a sample of the solid B-trihalogenoborazine to a weighed 50-ml volumetric flask in a nitrogen-filled drybox. After another weighing, this flask was removed to a glove bag where approximately 50 ml of the appropriate solvent was added. The flask was again weighed. While thermostating the flask at 25° for at least 1 hr, it was periodically shaken and permitted to stand to allow complete dissolution of the sample. Making use of previous calibrations for the volumetric flask at 0.05-ml increments above and below the 50-ml line, an accurate volume of the solution (slightly different from 50 ml) could be determined. Accurate values at 25° of weight fraction, w_2, mole fraction, c_2, and specific volume of the solution, v_{12}, could be calculated from the above weight and volume data. The temperature dependence of v_{12} for any given concentration could be calculated by noting the change of volume with temperature in the measuring cell of the dipolemeter.

A dipolemeter, Type DM 01, manufactured by Wissenschaftlich-Technische Werkstätten of Weilheim, Germany, was used for the determination of dielectric constants. Technical data and principles of and procedures for operation of this instrument, which functions by the heterodyne-beat method, are given elsewhere.[17,18] The error in dielectric constant using this instrument was ±0.00004. Detailed descriptions of the measuring cell, Type DFL 1, can also be found elsewhere.[17] The glass tube to the ground-glass joint at the top of the cell was calibrated in 0.1-ml increments in order to facilitate measurement of volume changes of the solutions with temperature. The measuring condenser calibration constant was determined using vacuum, air, cyclohexane, and carbon tetrachloride as standards. This constant was independent of temperature from 10 to 70°.

A Bausch and Lomb dipping refractometer and a sodium D line source were used for the determination of refractive indices.[19] The factory-specified error for the refractometer was ±0.0004. An auxiliary prism, which allowed the use of only several drops of solution, was used for data for B-trifluoro- and B-tribromoborazine.

Constant temperature of both the measuring cell and the bath holding the dipping refractometer was maintained by a circulating thermostat. The control thermometer of this device was previously calibrated at 5° intervals from 10 to 70°. The adjustment accuracy of the control thermometer was ±0.04° with a fluctuation around the set temperature of ±0.08° during the heating and cooling cycles.

Calculations.—The following subscript nomenclature was used for all symbols: subscripts 1 and 2 denote solvent and solute, respectively; subscripts 10 and 20 denote values for solvent and solute, respectively, which have been determined by extrapolation to zero concentration; and subscript 12 denotes solution.

The total polarization at zero concentration, p_{20}, was calculated by two methods. The Halverstadt–Kumler method,[20] using the equation

$$p_{20} = \frac{3\alpha v_{10} M_2}{(\epsilon_{10} + 2)^2} + M_2(v_{10} + \beta)\frac{\epsilon_{10} - 1}{\epsilon_{10} + 2}$$

where ϵ denotes dielectric constant, M denotes molecular weight, and v denotes specific volume, made use of direct extrapolations of dielectric constant and specific volume data as a function of weight fraction to give the slopes α and β. Since errors in the determination of specific volume, v_{12}, were quite significant, the following procedures were used to obtain v_{10} and β. From literature density data v_{10} was determined as a function of temperature for cyclohexane and benzene[21] (and is hereafter designated as v_1) because this introduced less error than using v_{10} determined as the intercept of v_{12} *vs.* w_2. Experimental values of β had large errors attached to them (±6%) but were linear functions of temperature well within the experimental error. Thus the experimental β values were plotted as a function of temperature and smoothed β values were obtained from the best straight line. The Debye–Clausius–Mosotti method involved extrapolation to infinite dilution[22] of p_2 values obtained by the equation

$$p_2 = \frac{1}{c_2}\left[\left(\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2}\right)(c_1 M_1 v_{12}) + \left(\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2}\right)(c_2 M_2 v_{12}) - \left(\frac{\epsilon_{10} - 1}{\epsilon_{10} + 2}\right)(c_1 M_1 v_1)\right]$$

where c denotes mole fraction, ϵ denotes dielectric constant, M denotes molecular weight, and v denotes specific volume. v_{12} values given in Tables IV–VI and used for calculation of p_2 by the above equation were obtained from values of v_1 and the smoothed β values. All slopes and intercepts obtained by extrapolation over either concentration or temperature ranges were determined by least-squares regression analyses on a Control Data Corp. digital computer, No. 1604.

Debye plots of p_{20} values from both methods *vs.* the reciprocal of absolute temperature were performed. The slope of such plots yielded values of the temperature-dependent p_o and the intercept yielded values of the temperature-independent $p_e + p_a$.

Making use of refractive index data as a function of concentration, p_e was calculated from an expression similar to the Halverstadt–Kumler relation.[20] However, in this expression dielectric constants were replaced by squares of refractive indices. This method gives a maximum value for p_e when the sodium D line source is used. Thus the values of p_a calculated by difference from $p_e + p_a$ may be slightly smaller than the true value.

Results

Tables I–III contain dielectric constant data as a function of weight fraction and temperature for B-trifluoroborazine in benzene, B-trichloroborazine in cyclohexane, and B-tribromoborazine in benzene. Tables IV–VI contain specific volume data as a function of mole fraction and temperature, and Table VII contains refractive index data as a function of weight fraction for the same three molecules in the same solvents. Table VIII contains values of total molar polarization at infinite dilution as a function of temperature, and Table IX contains values of orientation polarization and the sum of electronic and atomic polarization, as determined from a Debye plot of the p_{20} values of Table VIII.

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(20) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 224.

(21) "International Critical Tables," McGraw-Hill Book Co., Inc., Vol. III, New York, N. Y., 1928, p 29.

(22) Reference 20, p 223.

TABLE I

DIELECTRIC CONSTANT, ϵ_{12}, AS A FUNCTION OF WEIGHT FRACTION, w_2, AND TEMPERATURE FOR B-TRIFLUOROBORAZINE IN BENZENE, FROM WHICH α CAN BE DETERMINED

	10^2w_2							
	2.6157	1.9009	0.8065	0.6419	0.6292	0.4074	0.0000	
T, °C	ϵ_{12}						ϵ_{10}	$10^{-1}\alpha$
10.00	2.3079	2.3063	2.3031	2.3024	2.3021	2.3020	2.3007	2.8131
15.00	2.2982	2.2966	2.2938	2.2927	2.2927	2.2924	2.2912	2.7358
20.00	2.2885	2.2865	2.2837	2.2827	2.2826	2.2824	2.2811	2.8303
25.00	2.2785	2.2766	2.2738	2.2731	2.2730	2.2728	2.2715	2.6651
30.00	2.2686	2.2668	2.2641	2.2633	2.2631	2.2629	2.2617	2.6662
35.00	2.2590	2.2574	2.2546	2.2539	2.2535	2.2535	2.2522	2.6417
40.00	2.2493	2.2471	2.2447	2.2440	2.2438	2.2437	2.2424	2.5790
45.00	2.2396	2.2374	2.2350	2.2346	2.2344	2.2342	2.2330	2.4598
50.00	2.2303	2.2279	2.2254	2.2251	2.2250	2.2249	2.2235	2.5001
55.00	2.2206	2.2184	2.2161	2.2158	2.2156	2.2155	2.2143	2.3035
60.00	2.2113	2.2090	2.2069	2.2066	2.2065	2.2062	2.2051	2.2467
65.00	2.2017	2.1996	2.1972	2.1973	2.1968	2.1968	2.1956	2.2511
70.00	2.1922	2.1899	2.1881	2.1878	2.1875	2.1873	2.1863	2.1435

TABLE II

DIELECTRIC CONSTANT, ϵ_{12}, AS A FUNCTION OF WEIGHT FRACTION, w_2, AND TEMPERATURE FOR B-TRICHLOROBORAZINE IN CYCLOHEXANE, FROM WHICH α CAN BE DETERMINED

	10^2w_2							
	5.3885	4.2200	2.8505	2.2092	1.2191	0.5098	0.0000	
T, °C	ϵ_{12}						ϵ_{10}	$10^{-1}\alpha$
10.00	2.0534	2.0501	2.0467	2.0447	2.0421	2.0402	2.0388	2.7078
15.00	2.0155	2.0121	2.0089	2.0069	2.0043	2.0023	2.0310	2.6825
20.00	2.0374	2.0342	2.0309	2.0290	2.0259	2.0244	2.0229	2.7054
25.00	2.0293	2.0252	2.0227	2.0206	2.0183	2.0164	2.0151	2.5542
30.00	2.0212	2.0181	2.0148	2.0133	2.0101	2.0083	2.0071	2.6327
35.00	2.0136	2.0101	2.0068	2.0051	2.0023	2.0004	1.9991	2.6647
40.00	2.0052	2.0019	1.9987	1.9968	1.9942	1.9923	1.9910	2.6278
45.00	1.9974	1.9939	1.9909	1.9896	1.9864	1.9841	1.9832	2.6379
50.00	1.9893	1.9859	1.9827	1.9808	1.9783	1.9763	1.9750	2.6372
55.00	1.9814	1.9778	1.9749	1.9732	1.9704	1.9685	1.9673	2.5873
60.00	1.9737	1.9701	1.9672	1.9654	1.9624	1.9605	1.9593	2.6586
65.00	1.9660	1.9621	1.9591	1.9575	1.9545	1.9528	1.9514	2.6634
70.00	1.9581	1.9541	1.9512	1.9493	1.9464	1.9446	1.9432	2.7122

TABLE III

DIELECTRIC CONSTANT, ϵ_{12}, AS A FUNCTION OF WEIGHT FRACTION, w_2, AND TEMPERATURE FOR B-TRIBROMOBORAZINE IN BENZENE, FROM WHICH α CAN BE DETERMINED

	10^2w_2							
	3.7043	2.2986	2.0346	1.5533	0.6760	0.2865	0.0000	
T, °C	ϵ_{12}						ϵ_{10}	$10^{-1}\alpha$
10.00	2.3110	2.3075	2.3072	2.3059	2.3037	2.3029	2.3022	2.3830
15.00	2.3015	2.2979	2.2976	2.2962	2.2940	2.2930	2.2923	2.4791
20.00	2.2916	2.2881	2.2876	2.2862	2.2839	2.2828	2.2822	2.5649
25.00	2.2814	2.2780	2.2776	2.2763	2.2741	2.2731	2.2725	2.4241
30.00	2.2721	2.2689	2.2686	2.2671	2.2647	2.2638	2.2632	2.4687
35.00	2.2619	2.2586	2.2584	2.2568	2.2546	2.2540	2.2532	2.3798
40.00	2.2523	2.2491	2.2486	2.2473	2.2448	2.2442	2.2434	2.4360
45.00	2.2425	2.2393	2.2385	2.2374	2.2352	2.2345	2.2337	2.3769
50.00	2.2330	2.2296	2.2293	2.2278	2.2256	2.2249	2.2241	2.4157
55.00	2.2236	2.2201	2.2200	2.2183	2.2161	2.2155	2.2147	2.4308
60.00	2.2142	2.2109	2.2106	2.2089	2.2068	2.2060	2.2053	2.4460
65.00	2.2049	2.2014	2.2010	2.1995	2.1971	2.1964	2.1956	2.5230
70.00	2.1949	2.1917	2.1913	2.1898	2.1874	2.1869	2.1861	2.4149

Discussion

A detailed error analysis of the results is pertinent before any conclusions are drawn from them. The absolute errors in the Halverstadt–Kumler (H–K) p_{20} values of Table VIII were estimated to be ±2, ±3, and ±5 cm^3 for B-trifluoro-, B-trichloro-, and B-tribromoborazine, respectively. These errors resulted primarily from the uncertainty in β values in the second term of this expression. However, the use of smoothed β values should have greatly reduced the relative errors in the p_{20} values for the same compound at different temperatures. Thus the relative error between successive H–K values for any one compound in Table VIII was estimated to be ±0.6 cm^3. Both the absolute and the relative errors in the Debye–Clausius–Mosotti (D–C–M) values of Table VIII are considerably greater than errors in the H–K values because the D–C–M intercept is strongly affected by the p_2 value at lowest concentration and with largest uncertainty.

The H–K p_{20} value at 25° for B-trichloroborazine

TABLE IV

SPECIFIC VOLUME, v_{12}, AS A FUNCTION OF MOLE FRACTION, c_2, AND TEMPERATURE FOR B-TRIFLUOROBORAZINE IN BENZENE, FROM WHICH β CAN BE DETERMINED

T, °C	10^2c_2							β
	1.5350	1.1155	0.4733	0.3736	0.3662	0.2371	0.0000	
	v_{12}						v_1	
10.00	1.1090	1.1132	1.1196	1.1205	1.1206	1.1219	1.1243	−0.5881
15.00	1.1155	1.1199	1.1264	1.1273	1.1274	1.1287	1.1311	−0.5921
20.00	1.1225	1.1268	1.1333	1.1342	1.1343	1.1356	1.1380	−0.5961
25.00	1.1293	1.1336	1.1402	1.1412	1.1412	1.1426	1.1450	−0.6001
30.00	1.1362	1.1405	1.1471	1.1481	1.1482	1.1495	1.1520	−0.6040
35.00	1.1434	1.1477	1.1544	1.1554	1.1555	1.1568	1.1592	−0.6070
40.00	1.1505	1.1549	1.1616	1.1626	1.1627	1.1640	1.1665	−0.6120
45.00	1.1577	1.1622	1.1689	1.1699	1.1700	1.1714	1.1738	−0.6150
50.00	1.1651	1.1695	1.1763	1.1774	1.1774	1.1788	1.1813	−0.6200
55.00	1.1727	1.1772	1.1840	1.1850	1.1851	1.1865	1.1890	−0.6239
60.00	1.1803	1.1848	1.1916	1.1926	1.1927	1.1941	1.1967	−0.6279
65.00	1.1881	1.1926	1.1995	1.2005	1.2006	1.2020	1.2046	−0.6319
70.00	1.1960	1.2006	1.2076	1.2086	1.2087	1.2102	1.2126	−0.6359

TABLE V

SPECIFIC VOLUME, v_{12}, AS A FUNCTION OF MOLE FRACTION, c_2, AND TEMPERATURE FOR B-TRICHLOROBORAZINE IN CYCLOHEXANE, FROM WHICH β CAN BE DETERMINED

T, °C	10^2c_2							β
	2.5359	1.9860	1.3245	1.0232	0.5665	0.2369	0.0000	
	v_{12}						v_1	
10.00	1.2371	1.2440	1.2520	1.2556	1.2616	1.2657	1.2689	−0.5887
15.00	1.2440	1.2510	1.2591	1.2630	1.2689	1.2731	1.2762	−0.5945
20.00	1.2514	1.2584	1.2665	1.2704	1.2763	1.2805	1.2837	−0.6002
25.00	1.2586	1.2657	1.2740	1.2778	1.2839	1.2881	1.2913	−0.6060
30.00	1.2661	1.2733	1.2816	1.2855	1.2916	1.2958	1.2991	−0.6118
35.00	1.2736	1.2809	1.2894	1.2933	1.2995	1.3038	1.3070	−0.6176
40.00	1.2816	1.2888	1.2974	1.3013	1.3075	1.3120	1.3151	−0.6234
45.00	1.2894	1.2967	1.3053	1.3094	1.3157	1.3201	1.3235	−0.6292
50.00	1.2975	1.3050	1.3136	1.3176	1.3240	1.3284	1.3318	−0.6350
55.00	1.3057	1.3132	1.3220	1.3260	1.3324	1.3369	1.3403	−0.6407
60.00	1.3142	1.3217	1.3305	1.3346	1.3411	1.3456	1.3490	−0.6465
65.00	1.3227	1.3303	1.3393	1.3433	1.3499	1.3544	1.3579	−0.6523
70.00	1.3314	1.3391	1.3481	1.3523	1.3588	1.3635	1.3669	−0.6581

TABLE VI

SPECIFIC VOLUME, v_{12}, AS A FUNCTION OF MOLE FRACTION, c_2, AND TEMPERATURE FOR B-TRIBROMOBORAZINE IN BENZENE, FROM WHICH β CAN BE DETERMINED

T, °C	10^2c_2							β
	0.9376	0.5755	0.5084	0.3932	0.1711	0.0725	0.0000	
	v_{12}						v_1	
10.00	1.1020	1.1104	1.1120	1.1149	1.1201	1.1225	1.1243	−0.6023
15.00	1.1085	1.1170	1.1187	1.1216	1.1270	1.1294	1.1311	−0.6085
20.00	1.1151	1.1238	1.1255	1.1284	1.1338	1.1361	1.1380	−0.6148
25.00	1.1220	1.1307	1.1324	1.1354	1.1408	1.1432	1.1450	−0.6210
30.00	1.1287	1.1375	1.1392	1.1422	1.1477	1.1502	1.1520	−0.6274
35.00	1.1356	1.1445	1.1462	1.1493	1.1548	1.1572	1.1592	−0.6335
40.00	1.1427	1.1517	1.1535	1.1566	1.1622	1.1646	1.1665	−0.6397
45.00	1.1499	1.1590	1.1606	1.1638	1.1695	1.1720	1.1738	−0.6459
50.00	1.1571	1.1662	1.1680	1.1711	1.1768	1.1793	1.1813	−0.6520
55.00	1.1647	1.1739	1.1756	1.1788	1.1845	1.1870	1.1890	−0.6583
60.00	1.1721	1.1814	1.1832	1.1864	1.1922	1.1947	1.1967	−0.6645
65.00	1.1798	1.1891	1.1909	1.1941	1.2000	1.2025	1.2046	−0.6706
70.00	1.1875	1.1970	1.1989	1.2022	1.2080	1.2106	1.2126	−0.6769

(43.1 cm^3) is, within the estimated absolute experimental error (±3 cm^3), in agreement with the value of 45.3 cm^3 reported by Watanabe and Kubo.[10] However, this agreement is fortuitous since Watanabe and Kubo used very different α and β values in the H–K expression to obtain their result. The difference in α values cannot be explained, but changes in α cause only small changes in the absolute value of p_{20} anyway. Watanabe and Kubo obtained their β value by applying corrections to density data for borazine. The β value in this work, determined from measured specific volume data, should be closer to the actual value. The fact that the H–K and D–C–M values of Table VIII for any one compound are nearly equal is also an indication that the specific volume and β data are reasonably good. Otherwise, the H–K and D–C–M methods, which make use of different functions of specific volume, would give very different results.

TABLE VII

SQUARE OF REFRACTIVE INDEX, $(n^{25}\text{D})_{12}^2$, AS A FUNCTION OF WEIGHT FRACTION, w_2, FOR B-TRIFLUOROBORAZINE IN BENZENE, B-TRICHLOROBORAZINE IN CYCLOHEXANE,[12] AND B-TRIBROMOBORAZINE IN BENZENE

$F_3B_3N_3H_3$		$Cl_3B_3N_3H_3$[12]		$Br_3B_3N_3H_3$	
10^2w_2	$(n^{25}\text{D})_{12}^2$	10^2w_2	$(n^{25}\text{D})_{12}^2$	10^2w_2	$(n^{25}\text{D})_{12}^2$
2.9474	2.24526	1.92	2.02792	5.6815	2.24815
2.5811	2.24514	1.76	2.02803	3.2453	2.24632
1.6157	2.24493	1.67	2.02792	3.0983	2.24620
0.7497	2.24481	1.40	2.02772	1.9001	2.24587
0.4434	2.24472	1.21	2.02772	0.9795	2.24524
0.0760	2.24460	1.03	2.02763	0.6254	2.24503
0.0000	2.24460	0.91	2.02752	0.4409	2.24491
		0.80	2.02752	0.0000	2.24460
		0.68	2.02743		
		0.00	2.02713		

TABLE VIII

TOTAL MOLAR POLARIZATION AT INFINITE DILUTION, p_{20}, AS A FUNCTION OF TEMPERATURE FOR B-TRIFLUORO-, B-TRICHLORO-, AND B-TRIBROMOBORAZINE

	p_{20}, cm³					
	$F_3B_3N_3H_3$		$Cl_3B_3N_3H_3$		$Br_3B_3N_3H_3$	
T, °C	H–K[a]	D–C–M[b]	H–K	D–C–M	H–K	D–C–M
10.00	28.7	28.6	43.8	42.7	63.9	62.9
15.00	28.6	28.8	43.7	43.2	64.4	66.4
20.00	28.9	29.3	43.8	43.4	64.8	62.0
25.00	28.6	29.1	43.1	42.8	64.0	63.8
30.00	28.6	28.4	43.5	42.0	64.2	63.5
35.00	28.7	29.9	43.7	43.4	63.6	61.6
40.00	28.6	29.2	43.5	43.9	64.0	64.7
45.00	28.4	29.5	43.6	41.5	63.6	66.8
50.00	28.5	29.6	43.7	42.9	63.9	62.7
55.00	28.1	28.8	43.5	42.1	64.0	63.3
60.00	28.1	28.1	43.9	42.7	64.1	63.2
65.00	28.2	28.5	44.0	43.3	64.7	62.7
70.00	28.0	29.5	44.3	44.2	64.0	64.0
Av	28.5	29.0	43.7	42.9	64.1	63.7

[a] Halverstadt–Kumler. [b] Debye–Clausius–Mosotti.

TABLE IX

ORIENTATION POLARIZATION, p_o, AND THE SUM OF ELECTRONIC AND ATOMIC POLARIZATION, $p_e + p_a$, FOR B-TRIFLUORO-, B-TRICHLORO-, AND B-TRIBROMOBORAZINE

Compound	Method	p_o, cm³, at 25°	$p_e + p_a$, cm³
$F_3B_3N_3H_3$	H–K[a]	4.1	24.5
	D–C–M[b]	−0.2	29.3
$Cl_3B_3N_3H_3$	H–K	−2.3	45.9
	D–C–M	−1.4	44.3
$Br_3B_3N_3H_3$	H–K	0.5	63.7
	D–C–M	1.8	62.0

[a] Halverstadt–Kumler. [b] Debye–Clausius–Mosotti.

If one examines the results of Table IX in detail, it is difficult to draw any meaningful conclusions. No p_o values are very large, but neither are they quite zero. Furthermore, the negative p_o values are not theoretically acceptable. The results in Table IX must have large errors attached to them for two reasons. Firstly, the Debye equation has previously proved valid primarily for cases where the extrapolation could be made over temperature ranges up to 10 times the range used in this work and often where larger total polarizations were involved. However, the 60° temperature range used in this work was the maximum possible in terms of the liquid range of suitable solvents of accurately known dielectric constant and in terms of thermal stability of the B-trihalogenoborazines. The second reason is that the extrapolation was performed using p_{20} values which themselves had a 1–3% relative error attached to them. One can only conclude that the Debye plot may not be quantitatively useful in this case.

Qualitative examination of the p_{20} data in Table VIII does show an approximate constancy of p_{20} values with temperature. This constancy is indicative of the fact that p_{20} for each of the three molecules is composed primarily of significant contributions of p_e and p_a. p_o is then essentially zero, and a zero dipole moment also follows.

If one assumes that $p_o = 0$ on the basis of the above arguments, then $p_{20} = p_e + p_a$. Thus, averaging the 13 p_{20} values, as in Table VIII, gives average values for the sum of $p_e + p_a$. From the refractive index data p_e equals 22.0, 34.1, and 52.5 cm³ for B-trifluoro-, B-trichloro-, and B-tribromoborazine, respectively. This is in line with the increase in polarizability from fluorine to chlorine to bromine atoms. By difference p_a equals 6.5, 9.6, and 11.6 cm³ for the same three molecules if the H–K ($p_e + p_a$) values are used. Considering B-trichloroborazine, if p_a were neglected or assumed to be very small as in previous studies and if such a value were instead attributed to p_o, this would give a dipole moment of 0.67 D., in exact agreement with a previously determined value where a correction was made for p_e but where p_a was neglected.[12] This result indicates that all or certainly a large portion of the dipole moments previously calculated for B-trichloroborazine can be accounted for by atomic polarization.

It is likely that all previously reported nonzero dipole moments, except for that of B-trichloro-N-triphenylborazine, can be explained in terms of failure to correct for atomic polarization. The 1.23 D. value for $Cl_3B_3N_3(C_6H_5)_3$,[11] on the other hand, must be accounted for by failure to correct properly for both electronic and atomic polarization. Rysz does not give refractive index data to verify his conclusion that the slope of n_{12}^2 *vs.* w_2 equals zero. It is, however, unlikely that the slope, a_n, equals zero for this molecule and that there would be no p_e correction in Rysz's Guggenheim expression. Total molar electronic polarizations previously determined for various borazines range from 22 to 122 cm³.[10] A large part of this p_e arises from the second term of the Halverstadt–Kumler expression, and this part would not be present in the Guggenheim expression. However, except for $H_3B_3N_3H_3$ and for $R_3B_3N_3R'_3$ where R and R′ are the same or different alkyl groups, a significant part of p_e still arises from the first term of the H–K expression, and this part would be reflected in the Guggenheim expression.

Further insight into the contribution made by atomic polarization can be gained by a closer scrutiny of the data for the B-trihalogenoborazines. The result of high values of p_a and of increasing p_a from B-trifluoro- to B-trichloro- to B-tribromoborazine could have been anticipated in the following way. One can calculate p_a by an independent method making use of absolute absorption intensities from infrared spectra of gases.[23] Thus, p_a is found to be proportional to the absolute absorption intensity of an infrared-active line (which alters the dipole moment of a molecule) and inversely proportional to the square of the frequency, ν, of the line. Therefore, molecular vibrations involving low frequencies and involving atoms carrying partial charges (which tend to cause increased intensity) would make the largest contributions to p_a. Boron and nitrogen,[24] and probably also halogens, carry partial charges. Therefore, contributing modes in B-trihalogenoborazines would be those involving B–X in-plane and out-of-plane bending and B–N ring in-plane and out-of-plane torsion. Three infrared-active lines for B-trichloroborazine have been calculated by Watanabe and co-workers[25] to fall at 106, 118, and 368 cm^{-1}. By mass arguments these three lines should fall at higher frequencies for B-trifluoroborazine and at lower frequencies for B-tribromoborazine. If they were of similar intensity, p_a would reflect the $1/\nu^2$ dependence by increasing from B-trifluoro- to B-trichloro- to B-tribromoborazine.

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Chemistry of Boranes. XXVII.[1] New Polyhedral Borane Anions, $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$

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Salts of two novel polyhedral borane anions, $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$, have been prepared and characterized. The alkali metal salts of $B_9H_9^{2-}$ possess a high thermal stability comparable to that of the salts of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. At 600°, $Cs_2B_{11}H_{11}$ is converted to a mixture of $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$. The B_9 and B_{11} anions are hydrolytically unstable in acidic media; the B_9 anion is more rapidly degraded than the B_{11} anion. In solution, the $B_9H_9^{2-}$ ion appears to be best described as a symmetrically tricapped trigonal prism (D_{3h}) of boron atoms each of which has a terminally attached hydrogen atom.

Introduction

The complete series of triangulated coordination polyhedra from the tetrahedron to the icosahedron is established for boron chemistry. This structural series with examples[2–10] is presented in Table I. However, the simple binary hydride series is as yet incomplete; missing members include $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_{11}H_{11}^{2-}$. We report in this paper the isolation and characterization of salts of $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$. Analogous to $B_9H_9^{2-}$ are the chlorononaboranes[7] B_9Cl_8H and $B_9Cl_8H^{2-}$ and the carborane[11] $B_7H_7C_2(CH_3)_2$, although these boranes may not necessarily comprise an isostructural series. The new $B_{11}H_{11}^{2-}$ ion is isoelectronic with the $B_9C_2H_{11}$ carborane.[9]

Synthesis.—Alkali metal salts of the $B_3H_8^-$ ion decompose smoothly under vacuum at 200–230° with liberation of hydrogen. About 1.6 moles of hydrogen is liberated per mole of triborohydride salt.[12] The solid residue from the pyrolysis consists of a mixture of salts of BH_4^-, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, and $B_9H_9^{2-}$. Yields of the B_9 salt are substantially greater than those of the B_{10} salt. Under ideal conditions the yield of the B_{12} salt is quite low; however, the presence of ethers in the triborohydride starting material leads to a significant increase in the yield of $B_{12}H_{12}^{2-}$. (The preparation of the $B_{12}H_{12}^{2-}$ ion in good yields by pyrolysis of ether complexes of triborohydride salts[13] and by heating ethereal solutions of triborohydride[14] salts has been described. However, we have found that $B_9H_9^{2-}$ is formed in low yield when a solution of NaB_3H_8 in diglyme is heated to 100°.)

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