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The Polarizabilities and Diamagnetic Susceptibilities of Polyhedral Boranes and Haloboranes

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The electronic polarizabilities of the $B_{10}Cl_{10}^{-2}$, $B_{10}Br_{10}^{-2}$, $B_{12}H_{12}^{-2}$, $B_{12}Cl_{12}^{-2}$, $B_{12}Br_{12}^{-2}$, and $B_{20}H_{18}^{-2}$ ions were determined and an attempt was made to relate them to the structural features of these ions. From the magnetic susceptibilities of the $B_{10}H_{10}^{-2}$ and $B_{20}H_{18}^{-2}$ ions a Pascal constant was derived for boron in these systems and used to estimate the magnetic susceptibilities of the above listed hydrides and halides. These estimated values were compared and found to be in good agreement with magnetic susceptibilities calculated from the experimental polarizabilities. The great success of a conducting-sphere model in accounting for the physical properties of these ions is demonstrated, and simple general equations for calculating the polarizabilities and magnetic susceptibilities of polyhedral ions are derived.

Introduction

Despite their formal electron deficiency the $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ ions exhibit a remarkable chemical stability as far as integrity of the cage structure is concerned, though replacement of the H atoms by halogens and various organic groups can readily be achieved. Qualitatively the chemical behavior can best be rationalized by assuming that while each hydrogen is attached to a boron by an ordinary covalent bond the remaining electrons are delocalized over the entire cage producing a three-dimensional pseudo-aromatic system; this is one reason why the molecular orbital theory has been so successful in the study of these and other boron hydrides.[2] Such extensive delocalization would also be expected to produce unusually large diamagnetic susceptibilities and polarizabilities; these have, however, only been reported for the $B_{10}H_{10}^{-2}$ ion.[3] We have therefore undertaken an investigation of the polarizabilities and susceptibilities of the closed-cage ions since any optical or magnetic properties connected with their electronic structure can provide information useful for a better understanding of the chemical properties of these ions. The two ions though they differ by two borons and hydrogens are very similar in size; the most important difference, as far as polarizability and susceptibility are concerned, is in the geometry of the two cages (see Figure 1): in $B_{12}H_{12}^{-2}$ the borons form an icosahedron which can be inscribed in a sphere of radius $r = 1.68$ Å.,[4] but the borons in $B_{10}H_{10}^{-2}$ form a bicapped Archimedean antiprism which can be inscribed in a prolate spheroid with semi-axes $a = 1.88$ and $b = c = 1.43$ Å.[5] Whereas the polarizability of a spherical body is isotropic and proportional to the volume (for a conducting sphere in vacuum $\alpha = r^3$) this is not in general true for an ellipsoid, except when the eccentricity is very small. It is interesting therefore to find out over what range of eccentricities does the polarizability remain proportional to the volume. A charged conducting sphere and an ellipsoid of revolution will be used as models for the two types of cages.[3] The average polarizability of a prolate spheroid ($a > b = c$) is

$$\bar{\alpha} = (\alpha_1 + 2\alpha_2)/3 \qquad (1)$$

where α_1 is the component of the polarizability tensor along the major axis a, and α_2 the corresponding component along the minor axes b and c. For a conducting prolate spheroid under vacuum each component can be expressed as a function of the two semi-axes[6]: $\alpha_1 = 2/3A_1$ and $\alpha_2 = 2/3A_2$, where $A_1 = \int_0^\infty ds/(s + a^2)R_s$, $A_2 = \int_0^\infty ds/(s + b^2)R_s$, and $R_s = \sqrt{(s + a^2)(s + b^2)^2}$. Integration between the two limits yields

$$A_1 = -\left[2e + \ln\left(\frac{1 - e}{1 + e}\right)\right]/a^3e^3$$

$$A_2 = \left[2ea^2/b^2 + \ln\left(\frac{1 - e}{1 + e}\right)\right]/2a^3e^3$$

where $e = \sqrt{1 - b^2/a^2}$ is the eccentricity of the prolate spheroid. Attempts to find a simple analytical solution for the average polarizability in terms of the geometrical parameters yield an equation of the form

$$\bar{\alpha} = (1 + k)ab^2 \qquad (2)$$

where k, a complicated function of the eccentricity, has been evaluated for values of e between 0.1 and 0.9.

e	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
k	10^{-5}	0.00013	0.00072	0.0025	0.0067	0.016	0.038	0.091	0.26

Thus over a wide range of eccentricities, as long as $k \ll 1$, the polarizability will be proportional to the volume. The prolate spheroid formed by the B_{10} cage has an eccentricity $e = 0.65$, so that the ratio be-

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[2] For a detailed theoretical treatment of bonding in $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ ions see W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, Chapters II and III.

[3] A. Kaczmarczyk and G. B. Kolski, *J. Phys. Chem.*, **68**, 1227 (1964).

[4] Calculated from dimensions determined by J. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960).

[5] Calculated from dimensions determined by R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962).

[6] The equations are readily obtained from the general expression for the polarization of an ellipsoid in a parallel electric field derived by J. A. Stratton, "Electromagnetic Theory," McGraw-Hill Book Co., Inc., 1941, pp. 207–213.

$B_{10}H_{10}^{-2}$ $B_{12}H_{12}^{-2}$

Figure 1.—The boron cage structure in $B_{1}\,H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ ions. Boron atoms are located at the corners.

tween the polarizabilities of a B_{10} and a B_{12} cage should have a value $\sim 1.03ab^2/r^3$. Moreover, the apparent radius that one calculates from the average polarizability will be proportional to the *geometric* average of the three semi-axes ($r_{\text{app}} = \sqrt[3]{ab^2}$).

Having determined the polarizability of the $B_{10}H_{10}^{-2}$ ion[3] we were interested in seeing how it compares with that of the structurally related but somewhat less reactive $B_{12}H_{12}^{-2}$ ion. By further extending the study to chlorides and bromides, which it should be pointed out exhibit remarkable thermal and chemical stabilities,[7] in addition to obtaining valuable data on a very interesting series of ions one has a chance to test the validity of the conducting-sphere model in several ways: (a) Since the electrons of the B–X bonds in a $B_{10}X_{10}^{-2}$ ion are assumed to interact very little with the remaining 22 cage electrons[8] the hydride, chloride, and bromide should yield approximately the same "bare-cage" polarizability after contributions from the B–X bonds are subtracted; the same argument applies to the $B_{12}X_{12}^{-2}$ series of compounds. (b) The ratio between the "bare-cage" polarizabilities in corresponding $B_{10}X_{10}^{-2}$ and $B_{12}X_{12}^{-2}$ ions should remain approximately constant and close to 0.83, the ratio calculated for the $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ cages from the values of parameters a, b, and r based on X-ray diffraction measurements.

Once the polarizabilities of these salts had been determined it became apparent that the data could also be used to estimate their diamagnetic susceptibilities. New compounds and derivatives are nowadays synthesized at such a rapid rate and frequently in such small yields that it is unlikely that the susceptibilities of any sizable fraction of them will ever be measured, and consequently a self-consistent set of Pascal constants would be extremely useful. The constant normally listed for boron, -7.3,[9] is derived from measurements done on borates in which the boron forms three or four normal electron-pair bonds; this value also appears to be satisfactory for the trihalides (the calculated magnetic susceptibility of BCl_3 is -58.9×10^{-6} cm.^{3}/mole, experimental -59.9). However, attempts to use this value for boron in hydrides result in serious discrepancies between the calculated and experimental susceptibilities as is well illustrated by the following four examples: (a) BH_4^-, $\chi_M = -15 \times 10^{-6}$ cm.^{3}/mole[10,11]; removal of a hydride ion, for which -3.7 is allowed,[11,12] leaves a neutral BH_3 species in which the boron appears to contribute -2.6 if the normal -2.9 is allowed for the hydrogens.[9] (b) B_2H_6, $\chi_M = -17 \times 10^{-6}$ cm.^{3}/mole[13]; if equal weight is given to all six hydrogens we are left with $+0.4$ for the two borons! If the figure cited above is correct (the work has never been published) we have to either drastically reduce the Pascal constant for all the hydrogens or treat the terminal and bridge hydrogens separately allowing the normal value for the former and -1.5 to nothing for the latter. This second approach, which is more readily justified and consistent with the nature of the hydrogen-bridge bonding,[2] yields a residue of between -1.2 and -2.7 per boron. The second figure is clearly in excellent agreement with the number obtained from BH_4^-. (c) $B_{10}H_{14}$, $\chi_M = -116 \times 10^{-6}$ cm.^{3}/mole[10,14]; if all fourteen hydrogens are weighed equally there remains -7.5 per boron, but if we disregard the four bridge hydrogens we are left with -8.7 per boron. (d) $B_{10}H_{12}\cdot 2(C_2H_5)_3N$, $\chi_M = -279 \times 10^{-6}$ cm.^{3}/mole[10]; after the susceptibilities of the two covalently bonded triethylamines (-81.4×2) are subtracted -116×10^{-6} cm.^{3}/mole remains for the boron hydride residue. This is what one would expect, since the cage structure and dimensions in $B_{10}H_{12}L_2$ compounds (where L is any electron pair donor) are almost identical with those of the parent compound, $B_{10}H_{14}$; the difference resides primarily in the number and positions of the hydrogen bridges.[15] Again, we can either weigh all the hydrogens equally, which leaves -8.1 per boron, or count only the ten terminal hydrogens, in which case we get -8.7 as in $B_{10}H_{14}$.

Needless to point out, for the two sets of related compounds more consistent results are obtained when only the terminal hydrogens are assigned the full Pascal constant of -2.9. If one recalls that BH_4^- and B_2H_6 are isoelectronic with methane and ethylene, respectively, while $B_{10}H_{14}$ and $B_{10}H_{12}\cdot 2(C_2H_5)_3N$ have a highly delocalized system of electrons, analogous to the π-electron system in benzene, then by using the same arguments as are used for the analogous organic compounds[16] it is not too difficult to explain, qualitatively at least, the relative magnetic susceptibilities of the four hydrides cited above. The apparent zero contribution from bridge hydrogens is not as surprising as it may appear at first sight if one recalls that the use of normal Pascal constants for carbon and hydrogen in

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(7) W. H. Knoth, M. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

(8) W. N. Lipscomb, ref. 2, pp. 88, 112.

(9) P. Pascal, "Chimie Generale," Masson et Cie., Paris, 1949.

(10) S. Schulman, A. Kaczmarczyk, and W. N. Lipscomb, unpublished data, 1962. The value cited here is the average obtained from KBH_4 (-28.8) and $NaBH_4$ (-19.3).

(11) K. Knox and A. P. Ginsberg, *Inorg. Chem.*, **1**, 945 (1962), report the value of -28×10^{-6} for $NaBH_4$ from which they get -5.3 per hydride ligand. Our value for the borohydride ion is based on susceptibilities of two salts and yields for the hydride ligand -3.7, a much more reasonable value in view of the net -1 charge for four covalently-bonded hydrides as contrasted with an ionic hydride such as LiH which yields only -4 for the hydride ion (see ref. 12).

(12) S. Freed and H. G. Thode, *J. Chem. Phys.*, **3**, 212 (1935).

(13) S. Freed and H. G. Thode, unpublished results cited by S. H. Bauer, *Chem. Rev.*, **31**, 43 (1942).

(14) R. Bottei and A. W. Laubengayer, *J. Phys. Chem.*, **66**, 1449 (1962).

(15) W. N. Lipscomb, ref. 2, pp. 7 and 20.

(16) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, Chapters VI and VII.

calculating the magnetic susceptibility of ethylene requires a +5.5 structural correction factor for the double bond to make the calculated and experimental values agree. A similar correction factor could be expected for diborane, which is not only isoelectronic with ethylene but has the same symmetry too; the correction factor just about cancels out the contribution from the two hydrogens.

To avoid or reduce, at least, the problem of the hydrogen bridge it seemed advisable to start a systematic susceptibility study and establishment of a self-consistent set of Pascal constants for boron with the higher boranes and particularly with closed-cage compounds which are highly symmetrical, contain only terminal hydrogens (and/or halogens), and can be investigated under normal laboratory conditions. There are a number of ways of calculating magnetic susceptibilities from polarizabilities, not all of them simple and reliable. For the structurally related series of compounds discussed in this paper we decided to use a recently derived semiempirical equation[17]

$$-\chi_M = (\pi f r^2/2F\lambda_0^2)\alpha_\infty \qquad (3)$$

where f is the effective number of electrons contributing to the diamagnetic current in a loop of radius r, F is the number of dispersion electrons, and λ_0 is the characteristic wave length in the classical dispersion equation. As the authors of the paper have shown, for several "homologous" series of ions and of salts with a common ion λ_0^2 is a linear function of fr^2/F; surprisingly enough, since the temperature-independent paramagnetic term of the Van Vleck equation[16] was entirely neglected in the derivation of eq. 3, not only does the relationship between χ_M and α_∞ remain linear over a wide range of ionic sizes but the line also passes through the origin. That being so, one would be justified in writing a simple empirical relationship

$$\chi_M = Q\alpha_\infty \qquad (4)$$

where Q is a coefficient to be calculated from the experimentally determined susceptibility and polarizability of at least one member of the homologous series. In our case that member was $Cs_2B_{10}H_{10}$.

The reason for including $B_{20}H_{18}^{-2}$ in this study was to check whether the apparent excess in the polarizability of this ion, excess over that of two "$B_{10}H_9$" units, was true or only the result of a possible discrepancy between the data for $B_{10}H_{10}^{-2}$ and data from an anisotropic crystal of the $B_{20}H_{18}((C_2H_5)_3NH)_2$ salt.[3] By varying the cation and the solvent we hoped to get a more reliable figure for the average polarizability of the $B_{20}H_{18}^{-2}$ ion, and see how much electronic interaction there is between the two cages.

Experimental

Materials.—The preparation and purification of B_{10}, B_{12}, and B_{20} salts are reported in detail in three recent publications.[7,18,19] Eastman Spectrograde nitromethane was used as solvent for $(N(C_2H_5)_3H)_2B_{20}H_{18}$, and Baker Analyzed dimethyl sulfoxide for all other salts.

Apparatus.—The refractive indices of pure solvents were determined with a Bausch and Lomb Abbé-3L refractometer. The refractive index differences were measured in a Brice-Phoenix differential refractometer[20] equipped with 436 and 546 mμ glass filters. Weld specific gravity bottles of 2 and 5 ml. capacity were used for density determinations. The temperature in all the density and refractive index measurements was maintained at 25.0 ± 0.1°.

Procedures.—The refractometer cell was calibrated with aqueous KCl solutions[21] and solvent correction determined prior to each set of solution readings. Each refractive index difference is the result of five readings. The density of each solution was measured on the average four times; for the more dilute solutions determinations were continued until the mean deviation from the average density was reduced below ±0.0005 g./cc. It may also be appropriate to mention that the unpublished susceptibilities cited in this paper were all measured on a Gouy balance.

For calculating polarizabilities we used the Lorenz-Lorentz equation for binary systems in a form which separates the gravimetric from the optical data[22]

$$4\pi N_A\alpha/3 = \phi_0(\Phi + \Pi) \qquad (5)$$

where $\phi = (n^2 - 1)/(n^2 + 2)$; $\Phi = [M_1 - 1000(d - d_0)C^{-1}]/d_0$; and $\Pi = 1000(\phi - \phi_0)/\phi_0 C$. The subscript zero refers to the pure solvent, n is the refractive index, d is density, M_1 is the molecular weight of the solute, and C the solute concentration. It is customary to tabulate polarizabilities at the Na D-line and $\lambda = \infty$, and these were calculated from α_{436} and α_{546} by means of the classical dispersion equation[23] reduced to a convenient form

$$\alpha_\infty = \alpha(1 - \lambda_0^2/\lambda^2) \qquad (6)$$

where λ_0 is the characteristic wave length and α_∞ is the polarizability at infinite wave length. Use of this equation was justified by the fact that none of the investigated compounds had any electronic absorption bands within 1400 Å. from the experimental wave lengths. The ultimate accuracy of the experimental polarizability depends primarily on the precision with which the $d - d_0$ and $n - n_0$ differences are measured. Previous experience with $B_{10}H_{10}^{-2}$ indicated that concentrations in the range from 0.02 to 0.2 M would be most suitable for these highly polarizable compounds. Thus, though water is an extremely convenient solvent to work with it had to be excluded since the Cs^+ salts of $B_{12}H_{12}^{-2}$, $B_{10}Cl_{10}^{-2}$, $B_{12}Cl_{12}^{-2}$, $B_{10}Br_{10}^{-2}$, and $B_{12}Br_{12}^{-2}$ are only sparingly soluble in water at room temperature. Of the several organic solvents tested dimethyl sulfoxide proved most suitable.

Results and Discussion

Densities.—The density of dimethyl sulfoxide was 1.0957 ± 0.0002 g./cc. (result of six determinations) at 25.0°. The nitromethane had a density of 1.1304 ± 0.0002. The experimental density differences, $\Delta d = d_{soln} - d_0$, listed in Tables I and II are all accurate to at least ±0.5 mg./cc.

Refractive Indices.—The refractive indices of dimethyl sulfoxide at 436 and 546 mμ were calculated from the experimental n^{25}D 1.4771 and literature dispersion data[24]; they were 1.4883 and 1.4795, respectively. The corresponding refractive indices of nitromethane

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(17) S. K. K. Jatkar, V. S. Jatkar, and A. J. Mukhedkar, *J. Inorg. Nucl. Chem.*, **25**, 1372 (1963).

(18) A. Kaczmarczyk, R. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).

(19) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and M. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

(20) Phoenix Precision Instrument Co., Philadelphia 40, Pa.

(21) W. H. Orttung, *J. Phys. Chem.*, **67**, 1003 (1963).

(22) W. Geffcken, *Z. physik. Chem.*, **B5**, 81 (1929).

(23) C. J. F. Bottcher, "Theory of Electric Polarization," Elsevier Publishing Co., Amsterdam, 1952, Chapter VIII.

(24) W. Strecker and R. Spitaler, *Ber.*, **59**, 6 (1926).

TABLE I

THE POLARIZABILITIES OF $B_{10}X_{10}^{-2}$ AND $B_{12}X_{12}^{-2}$ SALTS

Molarity	$\Delta d \times 10^3$ g./cc.	$\Delta n_{436} \times 10^3$	$\Delta n_{546} \times 10^3$	α_∞, Å.^{3}	α_D, Å.^{3}
			$Cs_2B_{12}H_{12}$		
0.2056	45.0	10.458	10.155	28.22	29.07
0.1439	31.7	7.505	7.256	28.14	29.10
0.1028	21.7	5.023	4.929	28.73	29.55
0.05139	10.8	2.505	2.421	28.13	29.33
			Av.	28.30 ± 0.21	29.26 ± 0.18
			$Cs_2B_{10}Cl_{10}$		
0.1710	71.2	9.574	9.220	43.60	44.96
0.1509	59.2	8.448	8.191	43.43	44.71
0.1003	40.3	5.653	5.451	42.68	44.09
0.0855	34.4	4.994	4.839	43.11	44.49
0.06018	23.5	3.360	3.234	43.45	45.03
0.05015	19.9	2.852	2.733	42.78	44.49
			Av.	43.17 ± 0.32	44.62 ± 0.27
			$Cs_2B_{12}Cl_{12}$		
0.1331	57.7	8.408	8.211	50.48	51.83
0.1102	48.4	7.134	7.007	50.32	51.59
0.0954	41.8	6.156	6.002	50.13	51.56
0.0665	29.1	4.518	4.432	50.92	52.35
0.0572	25.1	3.548	3.483	49.59	51.03
0.0477	20.9	3.232	3.109	49.95	51.85
			Av.	50.23 ± 0.38	51.70 ± 0.31
			$Cs_2B_{10}Br_{10}$		
0.1670	131.6	15.730[a]	15.064[a]	55.21	57.14
0.1551	121.5	14.505[a]	13.891[a]	55.53	57.47
0.1419	114.0	14.013[a]	13.527[a]	54.92	56.68
0.08350	66.1	7.915	7.601	54.92	56.90
0.04175	32.6	3.839	3.642	54.57	57.06
			Av.	55.03 ± 0.27	57.05 ± 0.21
			$Cs_2B_{12}Br_{12}$		
0.1413	130.3	15.424[a]	14.893[a]	63.03	65.01
0.07065	64.8	7.649	7.391	63.21	65.32
0.06150	56.2	6.554	6.309	63.02	65.26
0.03532	32.1	3.975	3.827	64.21	66.75
0.03075	28.0	3.422	3.278	63.55	66.29
			Av.	63.40 ± 0.38	65.72 ± 0.60

[a] Extrapolated values (see the Results and Calculations section).

were found to be 1.3914 and 1.3823.[25] The tabulated experimental refractive index differences, $\Delta n = n_{\text{soln}} - n_0$, are accurate to within $\pm 10^{-5}$. The figures marked *a* were outside the refractometer range and were obtained by extrapolation from data at lower concentrations.

Polarizabilities.—The refractive index and density data listed in Tables I and II when substituted in eq. 5 yield polarizabilities at 436 and 546 mμ, from which polarizabilities at $\lambda = \infty$ and $\lambda = 589.3$ mμ (Na D-line) are calculated with the help of eq. 6. To get the ionic polarizabilities listed in Table III we subtracted from the polarizabilities listed in Table I the contribution from the Cs^+ ions, for which $\alpha_D = 3.34$ Å.^{3} and $\alpha_\infty = 3.14$ Å^3.[26]

As an independent check on the solvent effect on polarizability we also determined the density, $d^{25}{}_4$ 1.88, and the refractive index, $n^{25}{}_D$ 1.588, of solid $Cs_2B_{12}H_{12}$. For these optically isotropic crystals the simple Lorenz–Lorentz equation yields $\alpha_D = 28.9$ Å.^{3}, which is in excellent agreement with the figure obtained in solution.

Subtraction of the appropriate number of B–X bond polarizabilities from the ionic polarizabilities left a residual value which was a measure of the polarizability of the extensively delocalized system of electrons on the bare cage. The B–H, B–Cl, and B–Br bond polarizabilities were calculated from the polarizabilities of BH_4^- ($\alpha_D = 3.96$),[27] BCl_3 ($\alpha_D = 8.27$),[28] and BBr_3 ($\alpha_D = 11.73$),[28] respectively.

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(25) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Amsterdam, 1950, p. 578.

(26) J. R. Tessman, A. H. Kahn, and W. S. Shockley, *Phys. Rev.*, **92**, 890 (1953).

(27) W. H. Stockmayer, D. W. Rice, and C. C. Stephenson, *J. Am. Chem. Soc.*, **77**, 1980 (1955).

TABLE II

POLARIZABILITY OF $B_{20}H_{18}^{-2}$

Molarity	$\Delta d \times 10^3$ g./cc.	$\Delta n_{436} \times 10^3$	$\Delta n_{546} \times 10^3$	α_∞, Å.^{3}	α_D, Å.^{3}
			$[(CH_3)_4N]_2B_{20}H_{18}$		
0.1815	−9.2	17.042	16.130	59.48	61.78
0.09075	−4.6	8.664	8.030	58.69	61.59
0.0565	−3.1	5.382	4.991	58.90	61.92
0.0483	−2.5	4.662	4.304	58.52	61.70
0.0395	−2.0	3.905	3.640	59.07	62.17
			Av.	58.93 ± 0.27	61.83 ± 0.17
			$(CH_3)_4N^+$ ion	8.7[a]	8.93[a]
			$B_{20}H_{18}^{-2}$ ion	41.5	43.9
			$[(C_2H_5)_3NH]_2B_{20}H_{18}$		
0.1742	−17.7	21.328	20.191	65.23	68.19
0.0749	−9.2	9.161	8.665	66.67	69.72
0.05009	−6.1	6.152	5.887	67.22	69.90
0.02020	−2.7	2.473	2.341	66.50	69.52
0.01503	−2.1	1.891	1.790	67.09	70.15
			Av.	66.54 ± 0.54	69.50 ± 0.52
			$(C_2H_5)_3NH^+$ ion	12.8[b]	13.1[b]
			$B_{20}H_{18}^{-2}$ ion	40.9	43.3

[a] Calculated from α_D = 11.9 Å.^{3} reported for $(CH_3)_4NCl$ [W. R. Gilberson and J. L. Stewart, *J. Phys. Chem.*, **65**, 1465 (1961)] and α_D = 2.97 Å.^{3} for Cl^- [J. R. Tessman, A. H. Kahn, and W. S. Shockley, *Phys. Rev.*, **92**, 890 (1953)]; the α_∞ value was calculated from α_D by assuming dispersion to be similar to that of $(C_2H_5)_3NH^+$. [b] A. Kaczmarczyk and G. B. Kolski, *J. Phys. Chem.*, **68**, 1227 (1964), Table II.

TABLE III

POLARIZABILITIES (IN Å.^{3}) AND RADII (IN Å.) OF $B_{10}X_{10}^{-2}$ AND $B_{12}X_{12}^{-2}$ IONS

	$B_{10}X_{10}^{-2}$				$B_{12}X_{12}^{-2}$				Bare cage	
	α_∞	α_D	r_{app}	r_{ion}[b]	α_∞	α_D	r_{app}	r_{ion}[b]	α_D, B_{10},	α_D, B_{12}
H	18.9[a]	19.3[a]	2.66	2.8	22.0	22.6	2.80	2.9	9.4	10.7
Cl	36.9	37.9	3.33	3.3	44.0	45.0	3.53	3.4	10.3	11.9
Br	48.7	50.4	3.65	3.5	57.1	59.0	3.85	3.6	11.0	12.1

[a] Calculated from $K_2B_{10}H_{10}$ polarizability, A. Kaczmarczyk and G. B. Kolski, ref. 3. [b] Calculated from the cage dimensions and B–X bond lengths cited in this paper.

That the simple model proposed for the closed cage compounds is essentially sound is borne out by the fact that the bare cage polarizabilities for the two sets of cages do remain practically constant (see Table III). The slight upward trend observed as one proceeds from the hydrides to halides can be accounted for by back bonding between the halogen and the cage. For example, the significant shortening of the B–Cl bond in the closed cage halide B_8Cl_8, 1.70 Å. *vs.* 1.75 Å. in BCl_3, has been attributed to increased partial double-bond character.[29] The hydrides, chlorides, and bromides yield B_{10}/B_{12} bare-cage polarizability ratios of 0.87, 0.87, and 0.91, respectively, not too far off from the predicted 0.83.

The polarizability of $((C_2H_5)_3NH)_2B_{20}H_{18}$ in nitromethane differs by about 5% from the average polarizability of crystalline $((C_2H_5)_3NH)_2B_{20}H_{18}$[3]; in view of the anisotropy of the solid a difference was to be expected. The triethyl- and tetramethylammonium salts, though dissolved in fairly different solvents, yield polarizabilities for the ion which agree to within about 1% and which are still in excess of that for two $B_{10}H_{10}^{-2}$ ions. This fact can only be interpreted as indicating that charge transfer can take place between the two cages with relative ease.

Even though the nature of the bond between the two cages in $B_{20}H_{18}^{-2}$ has not been established,[18,30] the geometry of the ion is known.[18,31] If we again regard each cage as a conducting ellipsoid of revolution, two limiting possibilities have to be considered in dealing with the B_{20} twin-cage system: (a) flow of electrons from one cage to another is entirely forbidden, in which case the polarizability of the two linked bare cages would simply be the sum of two separate cages; (b) electrons can flow freely from one cage to the other, so that the system behaves as an enlarged ellipsoid of the following dimensions: $A = 2a$, $B = b$, and $C = 1.5b$, where a and b are the semi-axes of the ellipsoid generated by a single cage and the coefficients are estimated from the structure. In the first case the B_{20}/B_{10} bare-cage polarizability ratio would be 2. In the second case it would be 3. The experimental value is 25.8:9.4, or 2.75:1, which is obviously much closer to case *b* than case *a*.

Ionic Radii.—Table III lists also the apparent ionic radii, $r = \sqrt[3]{\alpha_\infty}$, calculated on the usual assumption of a perfect spherical conductor,[32] and the average radii of the ellipsoids and spheres circumscribing the ligands which were calculated from dimensions determined by X-ray diffraction.[33] The following B–X bond lengths

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[28] From refractive index data in Landolt-Börnstein, "Physikalisch-Chemische Tabellen," 5th Ed., Springer Verlag, Berlin, 1923, Vol. II, p. 966.

[29] W. N. Lipscomb and R. Lewin, Advances in Chemistry, No. 42, American Chemical Society, Washington, D. C., 1964, p. 314.

[30] R. L. Pilling, M. F. Hawthorne, and E. A. Pier, *J. Am. Chem. Soc.*, **86**, 3568 (1964).

[31] B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1451 (1964).

[32] S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, pp. 541–543.

[33] W. N. Lipscomb and R. Lewin, ref. 29, pp. 315–316.

were used: B–H = 1.2 Å., B–Cl = 1.7 Å., B–Br = 1.9 Å.; figures were rounded off to the first decimal place to allow for variations of up to 0.06 Å. observed in various compounds.[33] In the spherically symmetrical $B_{12}X_{12}^{-2}$ ions (Figure 1) the respective B–X bond lengths were added directly to the cage radius, 1.68 Å. The apical borons in $B_{10}X_{10}^{-2}$ ions are located 1.88 Å. away from the center while the eight nonapical borons are 1.52 Å. away.[5] Simple calculations show that the ions form ellipsoids of revolution of the following dimensions (in Å.): hydride a = 3.11, b = 2.65; chloride a = 3.63, b = 3.18; bromide a = 3.81, b = 3.36, where a and b are the two semi-axes. For reasons explained in the Introduction the apparent radii were compared with the geometric averages of the semi-axes. The high symmetry and the extensive delocalization of bonding electrons are reflected in the close agreement between the apparent and calculated radii.

Magnetic Susceptibilities.—In calculating the susceptibilities per boron listed in column 3 of Table IV we used the following ionic susceptibilities (cm.³/mole): −13 for K^+,[34] −31 for Cs^+,[34] -65×10^{-6} for $(C_2H_5)_3NH^+$ (calculated from an experimental value of -91×10^{-6} for triethylammonium chloride[10]), and −2.9 for hydrogen.[9] The Pascal constant for boron decreases markedly in the order: $B_{10}H_{10}^{-2}$, $B_{10}H_{14}$, $B_9H_{13}\cdot NH(C_2H_5)_2$, in full accord with the departure from spherical symmetry, decreasing area of electron delocalization, and declining number of cage electrons per boron.[2] The first of the three factors mentioned above not only tends to increase the positive temperature-independent paramagnetic term in the Van Vleck equation[16] but also reduces the diamagnetic term, $C\sum_i n_i r_i^2$, where n_i is the number of electrons generating diamagnetic currents in loops of radius r_i, and C is a constant. The other two factors reduce r^2 and n, respectively, in the diamagnetic term. To calculate the magnetic susceptibilities listed in column 4 of Table IV we assumed that the average electronic environment of a boron in the two types of cages is the same (not a bad assumption[2]), and that due to the pseudo-aromatic behavior of the closed cage compounds halogens attached to the cage resemble aromatic halogens more than aliphatic.[7]

The magnetic susceptibility of $Cs_2B_{10}H_{10}$ (Table IV) combined with the polarizability of the salt, 25.2 Å.³ (calculated from that of $K_2B_{10}H_{10}$[3]), converts eq. 4 into the expression

$$\chi_M = -7.86\alpha_\infty \tag{7}$$

which should be valid for the entire family of $Cs_2B_{10}X_{10}$ and $Cs_2B_{12}X_{12}$ compounds, where X is hydrogen or a halogen. The magnetic susceptibilities calculated from eq. 7 agree very well with the ones calculated from additive Pascal constants, as can clearly be seen in Figure 2. The figure also shows that for the anions the agreement between the calculated and extrapolated susceptibilities is not as good. This is in line with the behavior of alkali metal halides where the use of eq. 4 is much more satisfactory for the entire salts than for

TABLE IV

MOLAR MAGNETIC SUSCEPTIBILITIES, $-\chi_M \times 10^6$ CM.³/MOLE

Compound	Exptl.[a]	Per boron	Calcd.[b]	From eq. 7
$((C_2H_5)_3NH)_2B_{10}H_{10}$	262	10.3	265	...
$K_2B_{10}H_{10}$ (solid)	162	10.7	161	...
$K_2B_{10}H_{10}$ (solution)	164	10.9	161	...
$Cs_2B_{10}H_{10}$	198	10.6	197	198
$Cs_2B_{12}H_{12}$	...	(10.6)	224	222
$Cs_2B_{10}Cl_{10}$	...	(10.6)	340	339
$Cs_2B_{12}Cl_{12}$	...	(10.6)	396	394
$Cs_2B_{10}Br_{10}$	...	(10.6)	433	432
$Cs_2B_{12}Br_{12}$	...	(10.6)	507	498
$((C_2H_5)_3NH)_2B_{20}H_{18}$	388	10.3	394	...
$B_{10}H_{14}$	116	8.7	...	...
$B_{10}H_{12}\cdot(N(C_2H_5)_3)_2$[c]	279	8.7	...	...
$B_9H_{13}\cdot N(C_2H_5)_2H$[c]	156	7.4	...	...

[a] The experimental values, including that for $B_{10}H_{14}$ which was independently determined by R. Bottei and A. W. Laubengayer, ref. 14, were obtained by S. Schulman, G. Eaton, A. Kaczmarczyk, and W. N. Lipscomb, unpublished results, 1962. [b] We used the average value per boron in $B_{10}H_{10}^{-2}$ (10.6) together with 17.2 for Cl and 26.5 for Br, the Pascal constants for the respective halogens in aromatic compounds (ref. 9). [c] The susceptibilities of $N(C_2H_5)_3$ and $NH(C_2H_5)_2$ are −81.4 and -56.8×10^{-6}, respectively (M. Foëx, "Constantes Seléctionées, Diamagnetisme et Paramagnetisme," Masson et Cie., Paris, 1957, p. 140).

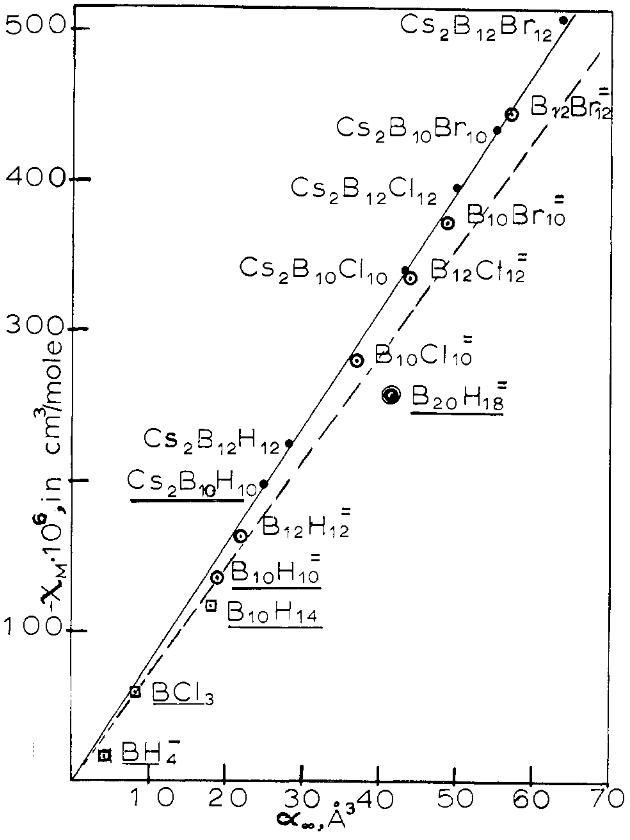

Figure 2.—The polarizabilities and magnetic susceptibilities of boron hydrides and halides. The polarizabilities are all experimental values; the experimental susceptibilities are underlined. The salts and anions are represented by solid circles ● and circled dots ⊙, respectively. The solid line represents eq. 7 extrapolated through the $Cs_2B_{10}H_{10}$ point; the dashed line represents the corresponding equation for the ions.

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(34) P. W. Selwood, ref. 16, p. 78.

the ions alone; effects of polarization on the additivity of the component group properties have been blamed for the irregular behavior of ions.[17]

In view of what has been said about the polarizability of $B_{20}H_{18}^{-2}$, it may seem strange that the magnetic susceptibility of the ion differs from that of two $B_{10}H_{10}^{-2}$ ions by an amount almost equivalent to the contribution from the two lost hydrogens. However, examination of a somewhat analogous case of benzene and biphenyl reveals that although the polarizability of biphenyl exceeds that of two C_6H_5 units joined by a C–C bond by about 6% the magnetic susceptibility of $C_{12}H_{10}$ is almost exactly double that of two phenyl groups, indicating that the two diamagnetic ring currents remain relatively independent of each other.[35] This explains the anomalous position of $B_{20}H_{18}^{-2}$ in Figure 2. The other hydrides and halides at the bottom of Figure 2 were included for comparison.

Conclusion

In developing the molecular orbital theory of polyhedral molecules Hoffman and Lipscomb have shown[36] that the calculations can be considerably simplified, without significantly altering the final results, by factoring out all the localized covalent bonds directed outward from the molecular center and treating them separately. Our results indicate that the dielectric and magnetic properties of polyhedral boranes and their derivatives can be treated in a somewhat analogous fashion. The total property of such ions or molecules can be expressed as a sum of two terms, one giving the contribution from the boron framework electrons, the other from the attached atoms or side groups. Thus for the polarizability of any of the astronomically large number[37] of possible substituted boranes we can write

$$\alpha_T = \alpha_C + \sum_i n_i \alpha_i \tag{8}$$

and similarly for the magnetic susceptibility

$$\chi_T = \chi_C + \sum_i n_i \chi_i \tag{9}$$

where α_T and χ_T are the total polarizability and susceptibility, respectively, of an ion or molecule; α_C and χ_C are the respective contributions from the delocalized cage electrons; n_i is the number of external localized covalent bonds of polarizability α_i or the number of atoms or radicals of magnetic susceptibility χ_i attached to the cage. α_C = 10, 11, and 26 Å.[3] at the Na D-line and $\chi_C = -106$, -127, and -212×10^{-6} cm.^{3}/mole for the $B_{10}X_{10}^{-2}$, $B_{12}X_{12}^{-2}$, and $B_{20}X_{18}^{-2}$ ions, respectively; for the χ_i of the halogens the aromatic Pascal constants should be used.[9]

The cage parameters are very satisfactory for the ionic hydrides and halides, but it remains to be seen whether any correction factors will be needed when hydrogen is replaced by ligands such as N_2^+, NH_3^+, and CO^+ which alter the charge of the cage[38] and for neutral carboranes, such as $B_{10}C_2H_{12}$.

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[35] P. W. Selwood, ref. 16, pp. 115–116.

[36] R. Hoffman and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962); see also W. N. Lipscomb, ref. 2, pp. 88, 112.

[37] The number of derivatives of the general composition $B_{12}H_aF_bCl_cBr_dI_e^{-2}$ that could in principle be synthesized from $B_{12}H_{12}^{-2}$ is 1820 (16!/4!12!), which does not even include the various possible isomers.

[38] W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 115 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND
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Organosilyl Sulfides and Organogermyl Sulfides

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The convenient preparation of compounds of the type $(CH_3)_nSi(SCH_3)_{4-n}$, n = 1, 2, 3, from the corresponding silyl halide and methylthiomagnesium iodide is described together with the applicability of this reaction to similar systems. Organogermyl sulfides are prepared more conveniently from the interaction of the germyl halide and the mercaptan in the presence of pyridine. Bis(trimethylsilyl) telluride is reported. Some properties and reactions of these compounds are discussed.

Introduction

Several methods for the preparation of organosilanes containing the silicon–sulfur link are described in the literature.[2] However, the only report of polysubstituted thiosilanes of the type $R_nSi(SR')_{4-n}$ was made by Schmeisser and Müller,[3] who prepared a series of ethyl compounds by redistribution reactions followed by reaction of the ethylthiochlorosilanes with ethylmagnesium bromide.

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