four chlorides[19,20] to Tl^{3+}. In the bromide system ΔF is even more favorable for the binding of the first four bromides.[20] No equilibrium data are available for the addition of bromide to $TlBr_4^-$, but the synthesis of the rubidium salt of $TlBr_6^{3-}$ requires a considerably greater halide excess than is the case for any of a number of alkali metal $TlCl_6^{3-}$ salts.[10] It seems likely therefore that ΔF for reaction 1 is more unfavorable for bromide than for chloride. No compounds of TlI_6^{3-} are known. Apparently even very high iodide concentrations lead only to the formation of TlI_4^- salts.[10] Although Tl(III) is a typical class B metal[21] (soft acid[22]), in that the aquo cation binds bromide more strongly than chloride (iodide binding has not been measured because of its ready oxidation by Tl^{3+}), it appears to act as a class A metal (hard acid) with respect to reaction 1. This behavior is readily understood if all of the aqueous TlX_4^- ions are indeed tetrahedral. Steric repulsion with increasing ligand size increases much more rapidly in octahedral (or square-planar) than in tetrahedral complexes, and this could overcome the opposite trend of Tl(III) affinity for the halides.

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The Dipole Moments of Boron and Carbon Brominated Carboranes

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In agreement with theoretical considerations and earlier experimental evidence, dipole moment measurements of selectively substituted *o*- and *m*-carborane derivatives established that in the polar icosahedra of *o*-$B_{10}H_{10}C_2H_2$ and *m*-$B_{10}H_{10}C_2H_2$ the carbon atoms and the borons adjacent to them constitute the positive pole.

Introduction

During recent years, the icosahedral carboranes [dicarbaclovododecaboranes(12)] were discovered[2-5] and their chemistry has developed.[6] Structural elucidation of the three forms of this organoborane nucleus, which were identified as *ortho*, *meta*, and *para* isomers[7] with regard to the position of the nuclear carbon atoms, was established particularly by ^{11}B nmr spectroscopy.[8-11] Subsequently, conclusive proof of the *ortho* configuration was obtained *via* X-ray diffraction studies.[12,13]

The dipole moments of all three isomers in benzene solution have recently been reported.[14] The polarity decreases from the *ortho* through the *meta* form and becomes zero in the *para* configuration, as could be expected due to the change of distribution of the two carbon atoms in the framework. The direction of the dipole moment, however, remained undefined. From purely atomic considerations, such as electronegativity, the direction of the dipole moment in the cage would be expected to be in the direction of the carbon atoms. However, in these electron-deficient cage structures the carbon and boron atoms are hexacoordinated and their calculated charge distributions[15,16] indicate the direction to be exactly opposite.

This was substantiated by recent X-ray diffraction studies[17] on B-brominated *o*-carborane derivatives[18] which indicated that electrophilic substitution of *o*-carborane occurs first at the 9,12 boron atoms opposite the carbon atoms, thus demonstrating that these borons are the sites of highest electron density.

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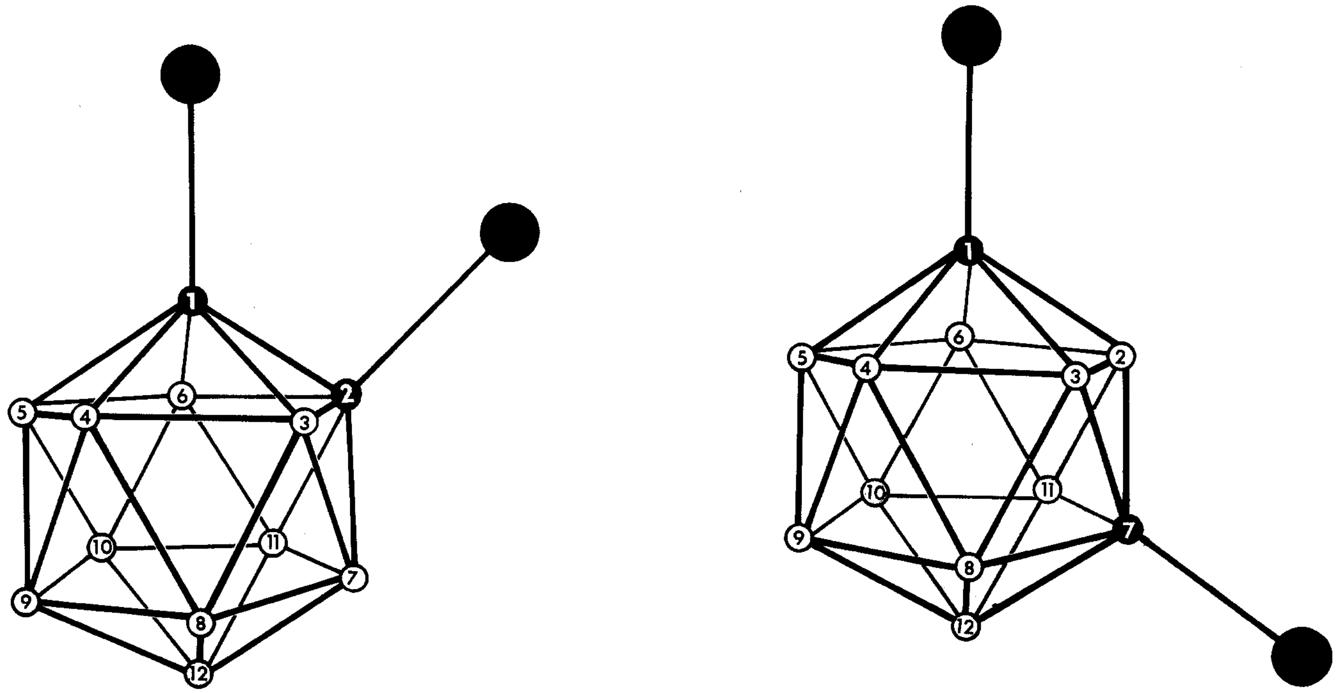
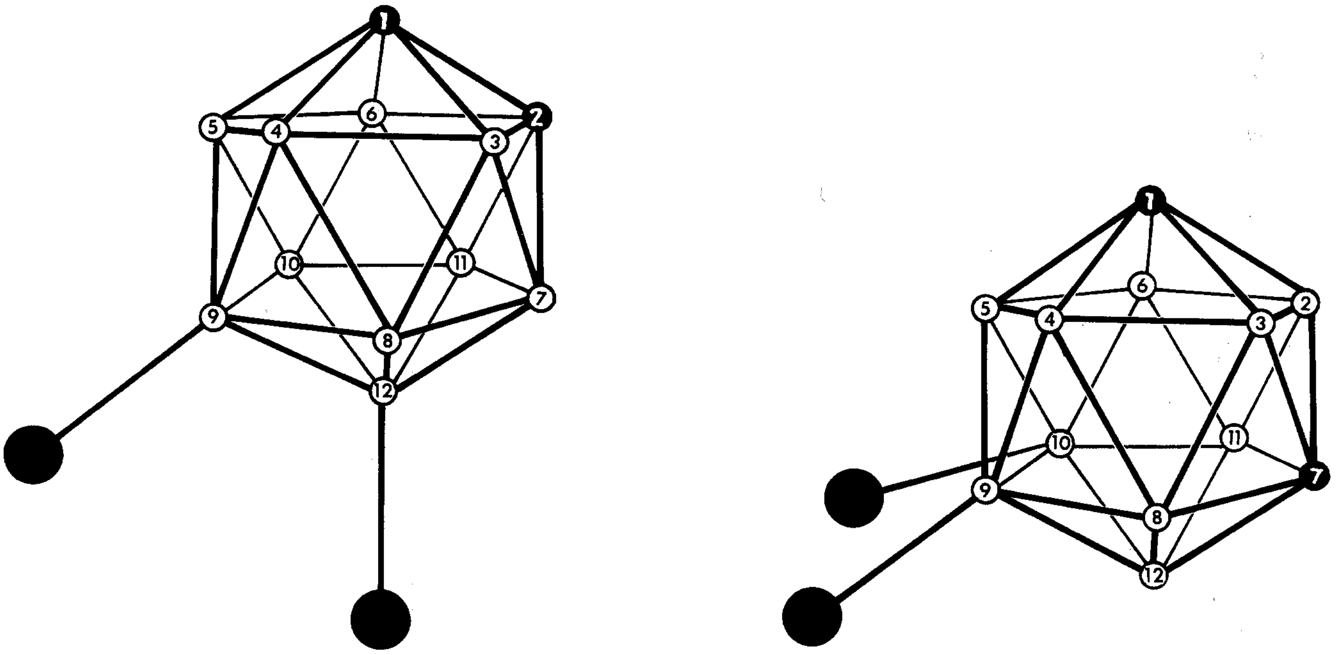


1,2-Dibromo-*o*-carborane

1,7-Dibromo-*m*-carborane



9,12-Dibromo-*o*-carborane

9,10-Dibromo-*m*-carborane

Figure 1.—Dibromo isomers of *o*- and *m*-carboranes (hydrogens not shown).

The successful synthesis of C,C′-dibromo-*o*- and -*m*-carborane[19] has now made possible a comparison of the dipole moments of, for example, such series of compounds as *o*-carborane, 1,2-dibromo-*o*-carborane,[19] and 9,12-dibromo-*o*-carborane[17,18] (Figure 1). The presence of electronegative halogens on the carborane cage at opposite locations should in one case increase, in the other decrease the polarity relative to the unsubstituted carborane cage, thus clearly pointing out the direction of the dipole moment.

Experimental Section

In this study, highly purified samples of *o*-carborane, *m*-carborane, 9,12-dibromo-*o*-carborane, and 9,10-dibromo-*m*-carborane were employed. 1,2-Dibromo-*o*-carborane (mp 228°) and 1,7-dibromo-*m*-carborane (mp 122°) were prepared by treating *o*-$B_{10}H_{10}C_2Li_2$ and *m*-$B_{10}H_{10}C_2Li_2$, respectively, with elemental bromine in petroleum ether and recrystallized from acetonitrile.[19,20]

Very dry cyclohexane was used as solvent because it was thought to offer less chance of interaction with the solute samples

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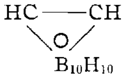
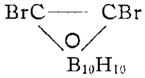
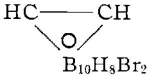
TABLE I

THE DIPOLE MOMENTS OF UNSUBSTITUTED AND DIBROMINATED *o*- AND *m*-CARBORANE

Compound	Slopes and intercepts of straight-line equations[a] obtained from data				
	a_ϵ	ϵ_1	a_n	n_1^2	μ, D[b]
 $\mathrm{HC{-}CH}$, $\mathrm{B_{10}H_{10}}$	11.3 ± 0.4	2.0161 ± 0.0008	0.3 ± 0.03	2.02718 ± 0.00005	4.31 ± 0.08
 $\mathrm{BrC{-}CBr}$, $\mathrm{B_{10}H_{10}}$	2.47 ± 0.09	2.0135 ± 0.0002	0.24 ± 0.01	2.02705 ± 0.00012	2.82 ± 0.06
 $\mathrm{HC{-}CH}$, $\mathrm{B_{10}H_8Br_2}$	14.8 ± 0.3	$2.0144 + 0.0005$	0.21 ± 0.06	2.02712 ± 0.00012	7.21 ± 0.13
$\mathrm{HCB_{10}H_{10}CH}$	4.84 ± 0.03	2.0145 ± 0.0002	0.29 ± 0.02	2.02706 ± 0.00010	2.78 ± 0.09
$\mathrm{BrCB_{10}H_{10}CBr}$	0.973 ± 0.097	2.0139 ± 0.0003	0.22 ± 0.02	2.02707 ± 0.00009	1.64 ± 0.40
$\mathrm{HCB_{10}H_8Br_2CH}$	7.83 ± 0.07	2.0152 ± 0.0002	0.39 ± 0.07	2.02676 ± 0.00017	5.14 ± 0.05

[a] The slopes and intercepts are for the following equations: $\epsilon_{12} = a_\epsilon(\omega_2) + \epsilon_1$ and $n_{12}^2 = a_n(\omega_2) + n_1^2$, where ϵ_{12} is the dielectric constant of the dilute solutions of the carboranes, n_{12}^2 is the square of the refractive index of the solutions, and ω_2 is the weight fraction of solute. ϵ_1 and n_1 are the dielectric constant and refractive index, respectively, of the solvent. They were obtained by extrapolating the above equations to $\omega_2 = 0$. a_ϵ and a_n are the slopes of the respective straight lines. The experimental data [R. E. Maruca, Thesis, Cornell University, Ithaca, N. Y., 1966] were fitted to these equations using a least-squares regression analysis on a Control Data Corporation Computer No. 1604 (program taken from Cornell Computing Center Write-up for Multiple Regression Analysis (MUREG), March 1965). [b] The dipole moments were calculated using the equation

$$\mu^2 = (\text{constant})\left(\frac{1}{d_1(\epsilon_1 + 2)}\right)(a_\epsilon - a_n)M_2$$

where (constant) = 1.47×10^{-1} at 25°, d_1 is the density of the solvent, and M_2 is the molecular weight of solute.

than benzene[21] and also to provide further checks on the dipole moments of *o*- and *m*-carborane previously reported in benzene solution.[14] Dielectric constant measurements were made on seven to ten independent samples of each compound and conducted as described previously.[14] Refractive indices of the solutions were measured to ±0.00002 unit with a dipping refractometer. All measurements were made at 25°.

Results

The dipole moments given in Table I were calculated using a modification of the Guggenheim method.[21] The errors indicated are experimental. There are errors up to 10% inherent in the method of calculation.

Discussion

The dipole moments of *o*- and *m*-carborane reported by Laubengayer and Rysz[14] had been measured in benzene solution. This determination has now been repeated using cyclohexane as solvent. When the values obtained in both solvents are compared, those in benzene are slightly higher but the discrepancy is within the limit of errors of the method used.

An analysis of the established series of moments in Table I shows that in the case of boron-bonded bromine the dipole moments are greater than in the unsubstituted parent compounds, whereas carbon-bonded bromine causes the opposite effect. These results can be explained by assigning the electron density in the carborane cage such that it is concentrated opposite the carbon atoms, which are therefore at the positive end of the cage dipole. The boron–bromine and carbon–bromine bond moments are required to be negative in the direction of the bromine atoms by this assignment.

Hoffman and Lipscomb's[15] molecular orbital calculations led to assignment of a partial positive charge on the two carbon atoms and the boron atoms in the 3 and 6 positions of the *o*-carborane nucleus. We further know from an X-ray diffraction study[12,13] on *o*-$\mathrm{B_{10}H_2Cl_8C_2H_2}$[8] that electrophilic substitution occurs last at $\mathrm{B_3}$ and $\mathrm{B_6}$, the boron atoms in closest proximity to the two carbon atoms, which renders them less electronegative than the other boron atoms. Our findings further reconcile theoretical considerations and experimental evidence.

In *m*-carborane the same authors[15] showed a partial positive charge on the two carbon atoms and the adjacent boron atoms in the 2 and 3 positions. Therefore, our experimental findings with *m*-carborane, 9,10-dibromo-*m*-carborane,[22] and *m*-$\mathrm{B_{10}H_{10}C_2Br_2}$ agree with the molecular orbital calculations.

The requirement that the carbon–bromine and boron–bromine bond moments be negative in the direction of bromine is quite reasonable. Even though the boron atoms opposite the carbon atoms in the electron-deficient cage appear to be more electronegative than the carbon atoms, the bromine atoms could very likely be more electronegative than both. This is particularly true since bromine is bonded to the cage by external, two-centered bonds while boron and carbon are in a delocalized system.

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