CHARGE DISTRIBUTION WITHIN 1,2-DICARBA-*closo*-DODECABORANE: DIPOLE MOMENTS OF ITS PHENYL DERIVATIVES

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The dipole moment of 1,2-dicarba-*closo*-dodecaborane is oriented with the positive end towards the carbon atoms as follows from measurements on phenyl derivatives with variable substituents. Towards the phenyl group, the substituent $1,2\text{-}C_2B_{10}H_{11}$ behaves as a weak electron acceptor.

Keywords: Dipole moments; Carboranes; Boranes; Electronic structure; Charge distribution; *Ab initio* calculations.

Hofmann and Lipscomb proposed in their pioneer work[1] the experimental availability of three positional isomers of icosahedral clusters $C_2B_{10}H_{12}$. On the basis of LCAO-MO calculations, they argued that the atomic charge on carbon atoms is positive, although simple atomic concepts such as electronegativity would have implied the opposite. The dipole moment of $1,2\text{-}C_2B_{10}H_{12}$ (**1**) was determined[2] to be 4.53 D in agreement with our present measurement (4.50 D). It lies in the C_2 axis but the positions of the positive and negative ends are not evident. A comparison with the dipole moments of the bromo derivatives[3] $1,2\text{-}Br_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ and $9,12\text{-}Br_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ should confirm qualitatively the above proposal but there is an inherent weakness that the electron distribution can be affected by the immediately bonded substituents.

Our intention in this work was to gain more information about the electron distribution in the molecule of **1** by the method common in organic chemistry[4,5] – introducing, at a greater distance, non-interacting substituents with known partial dipole moments *viz.*, in the *para* position of the benzene ring. Our first task was thus confirming the direction of the vector

of **1**. Once the phenyl group was introduced, we could deal with the second problem, a possible interaction of the $C_2B_{10}H_{11}$ group with the benzene ring. For this purpose we prepared[6] 1-(4-substituted phenyl)-1,2-dicarba-*closo*-dodecaboranes **2a**–**2e** with variable *para* substituents (X = H, CH_3, Br, Cl, NO_2 for **2a**, **2b**, **2c**, **2d**, **2e**, respectively; see Fig. 1) and measured the

2	X
a	H
b	CH_3
c	Br
d	Cl
e	NO_2
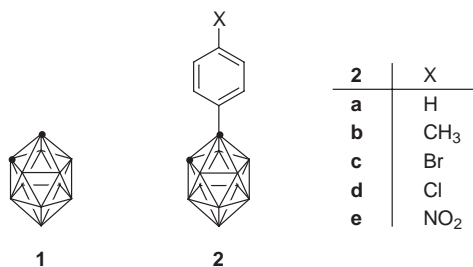
corresponding dipole moments[7]. Their vector analysis is presented in Fig. 1. The dipole moment of a given derivative, *e.g.* the vector **CIZ** for **2d**, can be represented with a very good approximation[4] as a sum of the two vectors: the unknown dipole moment of **2a** (**HZ**) and the known moment of the
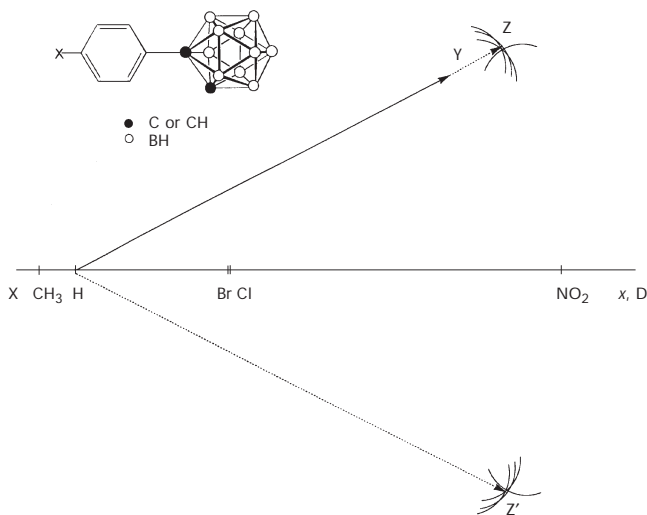

FIG. 1

Vector analysis of experimental dipole moments of **1**, **HY**, **2a**, **HZ** and **2b**–**2e** (points CH_3, Cl, Br, NO_2). The moments are shown by the arrows from the positive towards the negative end

substituent, vector **CIH**. In geometrical terms, the task is to construct a triangle given its three sides. This procedure was repeated for the four substituted compounds **2b**–**2e** and good agreement was reached in graphical representation, similar to that in standard examples[9] (see the arcs in Fig. 1 intersecting with a good precision in one point). Note that in principle two equivalent solutions are possible, points Z and Z′, of which Z is considered with respect to the choice of the carbaborane orientation towards the benzene ring in the molecular diagram in Fig. 1. The dipole moment of **2a** (vector **HZ** as a mean value) was determined to be 5.0 D at an angle of 28° to the exohedral C–C_{ar} bond, *i.e.*, practically in the symmetry axis of the carbaborane moiety. (An electron diffraction study of **2a** (ref.[10]) yielded an angle of 31° between this axis and the C–C_{ar} bond.)

This result allows answering the two above questions. First, directions of the dipole moments of **1** (vector **HY** in the symmetry axis) and **2a** (vector **HZ**), coincide within the experimental errors: also their absolute values are very close. There is no doubt that even the dipole moment of **1** as well as that of **2a**, is oriented with the positive end towards the carbon atoms and with the negative end inside the carbaborane skeleton, in agreement with the assumptions[1,2,+].

Second, a more detailed analysis is possible, comparing the dipole moment of **1** (vector **HY**, Fig. 1) and that of **2a** (vector **HZ**). Their difference in the absolute value is 0.5 D. Generally, this difference is called a mesomeric dipole moment[12] and interpreted as an electron shift from the benzene ring into the carbaborane skeleton. If the group $C_2B_{10}H_{11}$ is considered as an organic substituent, it is classified as a weak acceptor. This is in agreement with the substituent constants[13] σ_m and σ_p, 0.47 and 0.49, respectively; as expected $\sigma_p > \sigma_m$ but the difference is minute. For common simple organic substituents X, the mesomeric dipole moment was defined[14] as the vector difference between the dipole moments of compounds C_6H_5X and CH_3X. However, the mesomeric dipole moments of acceptors need not be inter-

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+ The RMP2(fc)/6-31G* geometry optimisation of **1** with the C_{2v} symmetry restriction (NIMAG = 0 at RHF/6-31G*) using the Gaussian94 program package[11] provided the total Mulliken charge on C(1,2) of –0.51 (Note that μ of **1** was calculated to be 4.53 D at this correlated level and, according to Gaussian convention, it points away from the negatively charged part of **1**.) Because of the well-known drawbacks of the Mulliken approach[12a], we also employed the natural population analysis (NPA) of Weinhold, Reed and Weinstock[12] to get the charge distribution of **1** in a more sophisticated manner. However, these calculations yielded the total charge on carbons of –0.57, *i.e.*, a value very close to that provided by the Mulliken scheme.

preted[15] on the basis of resonance or conjugation: the enhanced dipole moment can be also due to electron shifts within the benzene ring (polarisation) without giving a double bond character to the bond C–X. Indeed, the length of the C–C$_{Ar}$ exoskeletal linkage in **2a** was determined to be 150.0(8), 150.3(4) and 151.6 pm as followed from the electron diffraction, X-ray diffraction and RHF/6-31G* studies, respectively[10]. In any case, the acceptor character of the group C$_2$B$_{10}$H$_{11}$ is in agreement with the NMR (ref.[16]) and MCD (ref.[17]) studies. Note that most aromatic acceptor substituents possess dipole moments oriented out from the benzene ring but there is not a strict relationship[18].

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 6. Compounds **2a**, **2b**, **2c** and **2d** were prepared by allowing to react 6,9-bis(ligand)decaborane(12), 6,9-L$_2$B$_{10}$H$_{12}$, where L was CH$_3$CN, with a substituted phenylacetylene, 4-X-C$_6$H$_4$CCH (X = H, CH$_3$, Br, Cl). See, *e.g.*, Heying T. L., Ager J. W., Jr., Clark S. L., Mangold D. J., Goldstein H. L., Hillman M., Polak R. J., Szymanski J. W.: *Inorg. Chem*. **1963**, *2*, 1089. Compound **2d** was obtained by nitration of **2a**: Hawthorne M. F., Berry E. T., Wegner A. P.: *J. Am. Chem. Soc*. **1965**, *87*, 4746. The purity of all compounds was checked by analytical TLC and the structures of the molecules were confirmed on the basis of ^{1}H{^{11}B} and ^{11}B{^{1}H} NMR spectra recorded on a Varian Unity-500 instrument in CDCl$_3$ solution. Example: NMR spectrum of **2a** (in ppm, see also ref.[10] for a comparison): B(3,6) –12.2, B(4,5) –11.7, B(7,11) –13.7, B(8,10) –9.9, B(9) –3.0, B(12) –5.0. The corresponding boron atoms in **2b**–**2d** resonated at about the same frequencies as in **2a**.
 7. Dipole moments were measured at 25 °C in benzene (five solutions, weight fraction $1.8 \cdot 10^{-4}$ to $1.1 \cdot 10^{-3}$) by the method of Guggenheim and Smith[8]. Relative permittivities were measured at 6 MHz on a home-made DK-meter with direct frequency reading. Refractive indices were measured on an Aerograph refractive index detector (Varian). The following dipole moments were obtained: **1** 4.50, **2a** 4.94, **2b** 5.32, **2c** 3.66, **2d** 3.64 and **2e** 2.26 D; the estimated uncertainty was 0.05 D. For constructing Fig. 1, the following

standard bond moments were used: H–C$_{al}$ 0.3, H–C$_{ar}$ 0, C$_{ar}$–Cl 1.6, C$_{ar}$–Br 1.57 and C$_{ar}$–NO$_2$ 4.0 D.

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