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Charge distribution within hypercarbon-halogenated 1-Ph-2-X-1,2-dicarba-*closo*-dodecaboranes, (X = F, Cl, Br, I): A dipole moment and computational study

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Dedicated to Professor Heinz Oberhammer on the occasion of his 70th birthday.

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ABSTRACT

Vector analyses of experimental dipole moments of a series of halogenated 1-Ph-2-X-1,2-dicarba-*closo*-dodecaboranes, (X = F, Cl, Br, I) combined with theoretical calculations show that there are intramolecular contacts between heavy halogens (Br and I) and the benzene ring, whereas this attraction is absent for F and Cl.

1. Introduction

The *o*-, *m*- and *p*-carboranes (1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaboranes, 1,2-, 1,7-, 1,12-*closo*-$C_2B_{10}H_{10}$) represent relatively large, very symmetrical and remarkably stable molecules. Such high stabilities of these icosahedral systems have led to their use in such diverse fields as medicine (neutron capture therapy [1], molecular scaffolding (rigid building units [2]) and material science [3]), *m*-carboranes (1,7-) attracting much less attention in contrast to *o*- and *p*-carboranes. This is also valid in terms of researching these distorted icosahedra with an aim at their potential applications in nanotechnology [4].

Interest in capacity of these carboranes, regarded as three-dimensional aromatic systems [5], to communicate electronically with substituents resulted in our interest in acquiring data that describe both charge distribution within them and their ability to serve as models for simple electronic devices on the molecular level: the dipole moments and computational study of the *p*-carborane system with various substituents bonded to both carbon ends of the icosahedron [6] has revealed that the *p*-carborane cage behaves as a moderate conduit for electronic effects. The direction of the dipole moment in *o*-carborane [7], **1**, was unambiguously confirmed by a well-established graphical method [8], based on geometrical solution of triangles, on a series of 1-(4-substituted-phenyl)-*o*-carboranes with the orientation of the positive end of the dipole towards the carbon atoms. As a consequence, the dipole moment vector of 1-Ph-*o*-carborane, **2a**, lies at an angle of 28° with respect to the exohedral C–C_{ar} bond, i.e. practically in the symmetry axis of the carborane structure (an electron diffraction study of **2a** yielded this angle to be 31° [9]).

The knowledge of the dipole moment value of *o*-carborane cage and its direction helps us to understand electronic interactions between substituents on carbon atoms and the *o*-carborane cage. Halogens are relatively easily bonded to the *o*-carborane carbons experimentally and fluorine was found to act as a weaker π-electron donor in 1-Ph-2-X-1,2-*closo*-$C_2B_{10}H_{10}$ (**2b**, Fig. 1a) as revealed by NMR and computational data [10]. Interaction of halogens with benzene has been computed elsewhere [11] and it would therefore be interesting to know how such an interaction proceeds if halogen and benzene ring are attached to the two neighbouring cage carbons of *o*-carborane. Halogens are also prone to the so-called "halogen bonding" in terms of σ-hole (bonding towards nucleophiles with a region of positive electrostatic potential on the outermost portion of the surfaces of halogens [12]).

In order to understand this phenomenon further, we prepared a series of 1-Ph-2-X-1,2-*closo*-$C_2B_{10}H_{10}$ (X = F, Cl, Br, I, **2b**, **2c**, **2d**, **2e**, respectively, Fig. 1a–d) and measured their dipole moments for quantifying the corresponding electron distribution. We also carried out theoretical calculations of these systems.

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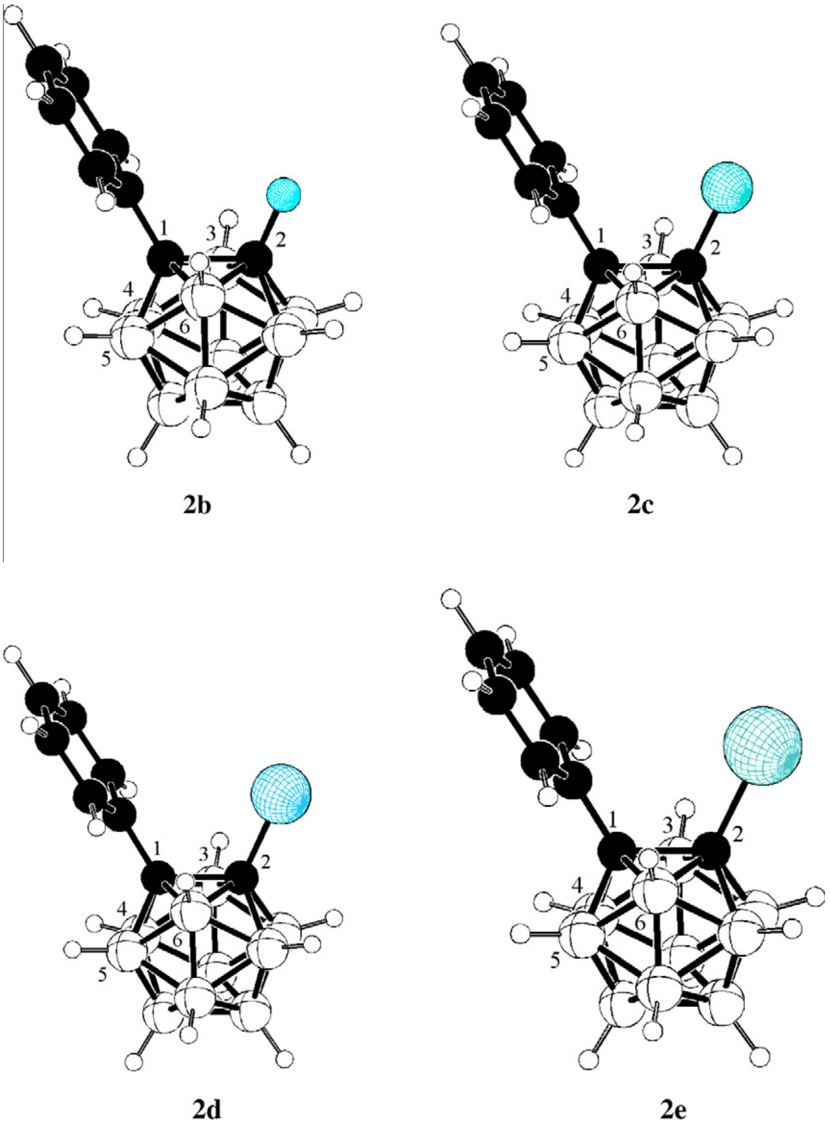

2b **2c** **2d** **2e**

Fig. 1. 1-Ph-2-X-1,2-dicarba-*closo*-dodecaboranes, (X = F **2b**, Cl **2c**, Br **2d**, I **2e**).

2. Experimental and computational details

2.1. Syntheses

Compounds **2b**, **2c**, **2d**, and **2e** were prepared by allowing to halogenate phenyl-*ortho*-carborane or lithiated **2a** with *N*-fluorobenzenesulfonimide/benzene, Cl_2/P_4O_{10}, Br_2/toluene, and I_2/tetrahydrofuran, respectively, according to known or slightly modified literature procedures [13]. 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. Table 1 provides ^{11}B chemical shifts and their comparison with computed values at GIAO-B3LYP, for basis sets and geometries used (see below).

2.2. Dipole moments

Dipole moments were measured at 25 °C in benzene (five solutions, weight fraction 1.8×10^{-4}–1.1×10^{-3}) by the method of Guggenheim and Smith [14,15]. 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: **2b** 3.67 D, **2c** 3.61 D, **2d** 4.13 D, **2e** 4.72, the estimated uncertainty was 0.05 D.

Table 1
^{11}B chemical shifts (in ppm) for 1-Ph-2-X-1,2-dicarba-*closo*-dodecaboranes, (X = H **2a**, F **2b**, Cl **2c**, Br **2d**, I **2e**) with respect to $BF_3 \cdot OEt_2$.

X	B(9)	B(12)	B(4,5)	B(7,11)	B(3,6)	B(8,10)
H[a]	−2.8	−4.8	−10.9	−12.8	−10.9	−9.1
Calc.[a]	0.0	−3.7	−10.5	−13.3	−15.2	−9.6
F	−3.8	−6.6	−11.3	−12.6	−13.5	−14.5
Calc.[b]	−7.1	−11.3	14.0	−15.6	−16.1	−16.4
Cl	−4.5	−6.4	−9.8	−10.8	−10.8	−11.8
Calc.[b]	−5.1	−6.8	−11.6	−11.6	−12.3	−13.5
Br	−4.2	−5.3	−9.1	−9.2	−10.9	−10.9
Calc.[b]	−4.8	−6.0	−11.2	−12.0	−12.8	−13.1
I	−3.2	−3.8	−7.3	−9.4	−9.4	−10.3
Calc.[b]	−4.4	−4.5	−11.2	−11.6	−12.6	−12.8

[a] Ref. [10] in which **2a** calculated at GIAO-B3LYP/6-311G*//MP2/6-31G*. There are a few minima of **2a** but only that of the same molecular shape as **2b–e** (i.e. phenyl group perpendicular to the C1–C2 plane) was considered in magnetic properties calculations.

[b] Calculated at the GIAO-B3LYP/II//MP2/basis set level, for the basis set used see Section 2.