Journal of Molecular Structure 978 (2010) 246–249

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

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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ARTICLE INFO

Article history:
Received 15 December 2009
Received in revised form 9 February 2010
Accepted 9 February 2010
Available online 18 February 2010

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

Keywords:
Halogens
Carboranes
Dipole moments

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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doi:10.1016/j.molstruc.2010.02.027

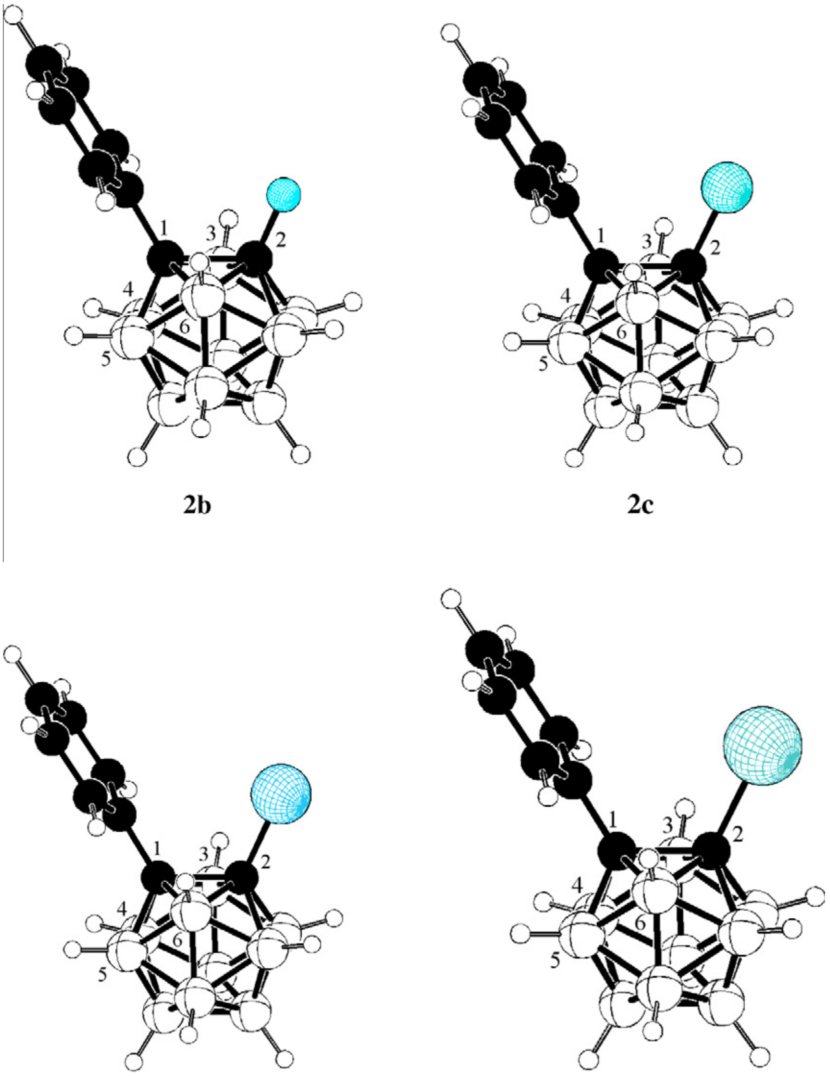

Fig. 1. 1-Ph-2-X-1,2-dicarba-*closo*-dodecaboranes, (X = F **2b**, Cl **2c**, Br **2d**, I **2e**).

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 $^1H\{^{11}B\}$ and $^{11}B\{^1H\}$ 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.

2.3. Computational details

Structure optimizations (no symmetry constraints), harmonic vibrational frequency analyses, calculations of NMR chemical shifts (without spin–orbit corrections to them), and dipole moments employed the Gaussian 03 suite of programs [16]. Structures were optimized both at B3LYP [17,18] and at the frozen-core MP2 [MP2(fc)] levels, using the 6-31G* [19] basis for F and Cl, and quasi-relativistic energy-consistent pseudopotentials [20] with DZP valence basis sets for Br and I. NMR chemical shift calculations were done with gauge-including atomic orbitals (GIAO) [21] at B3LYP level, at the MP2/6-31* (F, Cl) and DZP (Br, I) level. These calculations used the same ECPs for Br and I as the optimizations and IGLO-II all-electron basis sets [22] for all atoms, the latter being well-designed for magnetic properties calculations.

3. Results and discussion

The electron deficiency of the *o*-carborane cage brings about its behavior both towards alkyl and aryl groups: the dipole moments are: *o*-carborane, 4.50 D [7], 1-methyl-*o*-carborane, 4.75 D [23], and 1-phenyl-*o*-carborane, 4.93 D [7]. From these values the carborane acts as an electron acceptor. The direction of the dipole in the latter was experimentally determined and, in essence of this approach, coincides within experimental error with that in *o*-carborane [7] and the same direction may be anticipated in the case of 1-methyl-*o*-carborane.

In organic chemistry, there are two sets of the so-called bond moments [8]that mainly incorporate electronic interaction between a substituent and a substrate: i.e. one for a bond between a substituent and methyl carbon, the other for a bond between a substituent and phenyl carbon, [8] as exemplified for halogens: $X{-}C_{methyl}$, F = 1.79, Cl = 1.87, Br = 1.82, I = 1.65 D, $X{-}C_{phenyl}$ the corresponding values are 1.47 D, 1.59 D, 1.57 D, 1.40 D, respectively. These vectors turned out to be very helpful in structural analyses of organic substances.

Dipole moments of **2b**–**e** indicate that neither of these bond moments can be associated with μ of a X–C bond in 1-phenyl-2-X-*o*-carboranes (see Table 2). In other words, we are unable to verify experimental dipole moments of **2b**–**e** by a simple vector addition of that for **2a** [μ(**2a**), a substrate] and a bond moment applied for C(2)–X (a substituent), which is an usual approach in organic chemistry used e.g. in conformational analysis and feasible e.g. for a series of 12-X-1-$SB_{11}H_{11}$ (X = Cl, Br, I) where X–B bond dipole moments were found to be very close to $\mu(X{-}C_{phenyl})$ [24]. In the present study, the corresponding $\Delta\mu$'s differ from either set of group moments in their absolute values, for X = F and Cl to a lesser extend (see Table 2).

It is very likely that the opposite direction of "μ(C(2)–X)" in relation to μ(**2a**), mainly due to their electron-withdrawing effect, reduces the value of μ(**2a**). However, for X = Br and predominantly for X = I this tendency is compensated by an "internal" attraction directing from I (i.e. from its positively charged outer shell, see [12], note also that NPA [25] charge of I in **2e** is 0.3e at MP2/DZP) towards the negative "region" of the benzene quadrupole moment [26]. This "vector" (Fig. 2, dashed and full arrows within the cage correspond to the direction of the dipole moments in **2a** and **2e**, respectively) roughly lies at an angle of ca. 120°–140° with respect to the direction of μ(**2a**) (the angle X–C(2)–I is ca. 80° at MP2/DZP, where X is the centre of the phenyl ring) This is also partly true for Br in **2d** (NPA = 0.19) and far from being true for Cl and mainly for F (NPA = 0.1 and −0.31, respectively). That bromine and iodine are involved in this intramolecular halogen bonding can be demonstrated in terms of HOMO's as compared with HOMO's for **2b** and **2c**: there is no contribution to this orbital for F and Cl (Fig. 3). Note that the both sets of calculations (Table 2) follow the experimental trend but DFT values perform slightly better in terms of comparison with experimental data.

Table 2
Dipole moments (in D) of **1** and **2a**–**e**.

	μ	$\Delta\mu$[a]	μ(MP2)[d]	μ(B3LYP)[d]
1[b]	4.50	–	4.53	4.28
2a[c]	4.93	0.00	5.62	5.49
2b	3.67	1.26	4.68	4.58
2c	3.61	1.32	4.72	4.70
2d	4.13	0.80	4.88	4.84
2e	4.72	0.21	5.23	5.09

[a] [μ(**2a**) − μ(**2x**)], **x** = **b**–**e**.

[b] [μ(**2a**) − μ(**1**)] is considered to be so-called mesomeric dipole moment and is interpreted as an electron shift from the benzene ring into the carborane skeleton [7].

[c] See Ref. [10].

[d] For the basis set used, see Section 2.

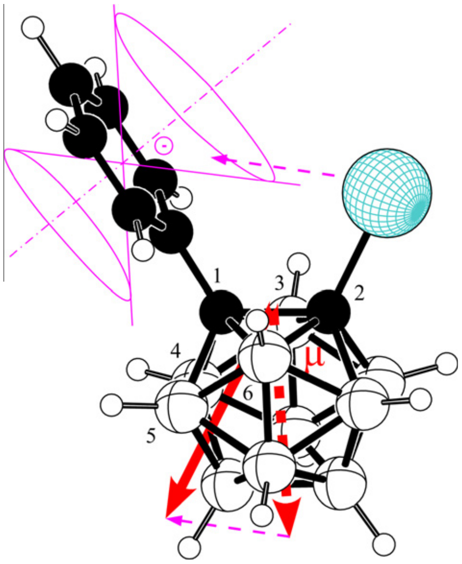

Fig. 2. Possible explanation of the dipole moment of **2e**.

Due to overlaps of many peaks in experimental ^{11}B NMR spectra of **2b**–**e**, the assignments provided in Table 1 are mainly based on the "best-fit" with the calculated values. The correct assignment of

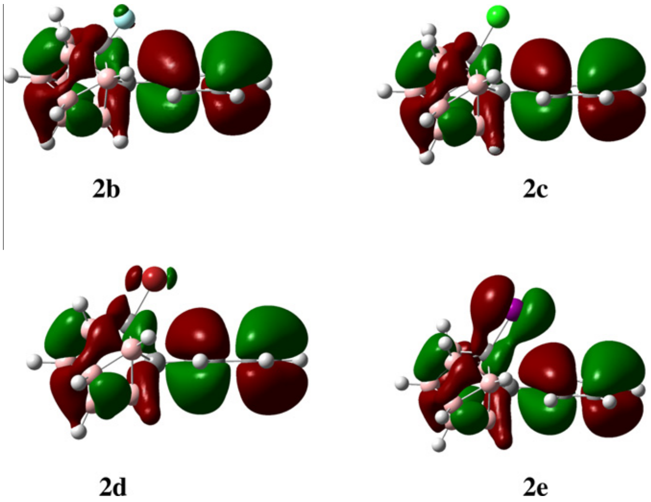
2b **2c**
2d **2e**

Fig. 3. HOMO for **2b**–**e** at HF level (for geometry used see Section 2).

Table 3
MP2 geometries (in Å, for the basis set used see Section 2) of **2a**–**e**.

X	C1–C2	C1–X	C2–B3/6	C1–B4/5	C1–B3/6	B3/4–B6/5	B4–B5
H[a]	1.659	1.088	1.701	1.705	1.731	1.769	1.773
F[a]	1.674 1.606(12)[b]	1.352 1.373(5)	1.703	1.704	1.734	1.768	1.781
Cl	1.692	1.758	1.707	1.702	1.734	1.770	1.780
Br	1.695 1.692(8)[c]	1.911 1.888(6)	1.706	1.700	1.735	1.775	1.780
I	1.695 1.696(8)[b]	2.143 2.107(6)	1.707	1.703	1.734	1.774	1.780

[a] For **2b** see also Ref. [10]. There are a few minima of **2a**, the less stable one with phenyl ring perpendicular to C1–C2 is listed for direct comparison with **2b**–**e**. The more stable form has phenyl group in the C1–C2 plane.

[b] Further nearest-neighbour separations in this X-ray structure also compare quite well with the theoretical geometry, see Ref. [13].

[c] Further nearest-neighbour separations in this X-ray structure also compare quite well with the theoretical geometry, see Ref. [27].

δ(^{11}B) for **2a** have also been helpful in assigning individual signals. Comparison of the spectra of **2b**–**e** reveals that the corresponding signals do not differ so much. This observation indicates that the cage geometries are not heavily influenced by individual X when relating them to the geometry of parent **2a** [10]. This finding is supported by their calculated geometries (Table 3): there is no significant influence of X on the cage geometry. Although no symmetry constraints have been applied in optimizations of these systems, the final structures obtained look like as if they had a symmetry of C_s.

The only differences between individual geometries consists in C–X bond lengths and it is obvious that the long C–Br (I) distances offer further support for accounting for the intramolecular contact of Br (I) with the benzene ring.

Acknowledgements

Financial support from the Ministry of Education of the Czech Republic (Project LC523) is greatly appreciated. We thank Dr. M.A. Fox (University of Durham, UK) for providing MP2 geometries and helpful comments and Dr. Jan Macháček of the Institute of Inorganic Chemistry of the ASCR, v.v.i for technical assistance.

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