Structure and properties of 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaboranes(12): a quantum chemical study

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The molecular and electronic structures and thermodynamic parameters of 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane(12) molecules in the singlet ground state were calculated by the Hartree—Fock, DFT, and MP2 (including B3LYP/6-311G(2d,2p) and MP2/6-311+G(d,2p) methods). The energies and character of spatial localization of the frontier MOs in *o*-, *m*-, *p*-carboranes(12) correlate with the changes in the configuration stabilities and reactivities in the reactions of carboranes with electrophilic and nucleophilic agents and bases. The electrostatic potential distributions in the molecules and the atomic charge distribution of hydrogen atoms correlate with the known chemical properties of carboranes(12). The thermodynamic parameters of two isomerization reactions, $o\text{-}C_2B_{10}H_{12} \rightleftharpoons m\text{-}C_2B_{10}H_{12}$ and $m\text{-}C_2B_{10}H_{12} \rightleftharpoons p\text{-}C_2B_{10}H_{12}$, calculated for the temperature range 298—1000 K agree with experimental data within the limits of measuring error. The values of the electron density and the Laplacian of the electron density at the (3, −1) critical points of the B—H and C—H bonds correlate with the reactivities of the title compounds.

Key words: carboranes(12), quantum chemical calculations, frontier MOs, topology of total electron density, configuration stability, reactivity.

The electronic structures of *closo*-carboranes(12), $C_2B_{10}H_{12}$, and their derivatives has been studied by theoretical[1—8] and experimental[9] methods. In most cases the results of calculations of the molecular structures and relative stabilities of these compounds are compared with the experimental data. Only a few attempts to relate the electronic structure characteristics to the configuration stability, regularities of the electrophilic and nucleophilic reactions, and the acidities of carboranes were reported.[10—12] Usually, the Mulliken charges on the cage atoms are used as a criterion for assessment of the reactivity.[10,12] However, this is not always true when studying the title compounds.[1] Analysis of the electron density distribution function in the vicinity of reaction centers is of paramount importance;[12] however, the computational cost of such calculations is very high. Advances made in this field of chemistry of boranes and carboranes have been documented in a review.[8]

In this work we carried out the HF, DFT, and MP2 (including B3LYP/6-311G(2d,2p) and MP2/6-311+G(d,2p)) quantum chemical calculations and determined the thermodynamic characteristics of the isomers of carboranes(12) for the temperature range 298—1000 K and established parameters of their ground-state electronic structure, which correlate with the configuration stability and with characteristic features of electrophilic and nucleophilic reactions. These are the energies and the structures of the frontier MOs, the electrostatic potential, the atomic charges of hydrogens in the molecules under study, and the characteristics of the total electron density function at the (3, −1) critical points of the B—H and C—H bonds.

Calculation Procedure

Quantum chemical calculations of the molecules of *o*-, *m*-, and *p*-carboranes were carried out by the Hartree—Fock and density functional (B3LYP) methods, at the second-order Møller—Plesset level of perturbation theory (MP2), and by the multiconfiguration CASSCF method with the 6-31G(d,p), 6-31G(d,2p), 6-31G(2d,2p), 6-31G(df,p), 6-311G(d,p), 6-311+G(d,p), 6-311G(2d,2p), and 6-311+G(d,2p) basis sets using the GAUSSIAN-98 program complex.[13] Full optimization procedure was conducted until a value of 0.000015 hartree Bohr^{-1} for the "Maximum Force" parameter, 0.000010 hartree Bohr^{-1} for the "RMS Force" parameter, 0.00006 a.u. for the "Maximum Displacement" parameter, and 0.00004 a.u. for the "RMS Displacement" parameter. The calculated interatomic distances in the title molecules differ from experimental values[14] by 0.02—0.05 Å, the smallest deviation being provided by the MP2 method. The thermodynamic characteristics of carboranes(12) obtained from B3LYP/6-311G(2d,2p) calculations for the temperature range

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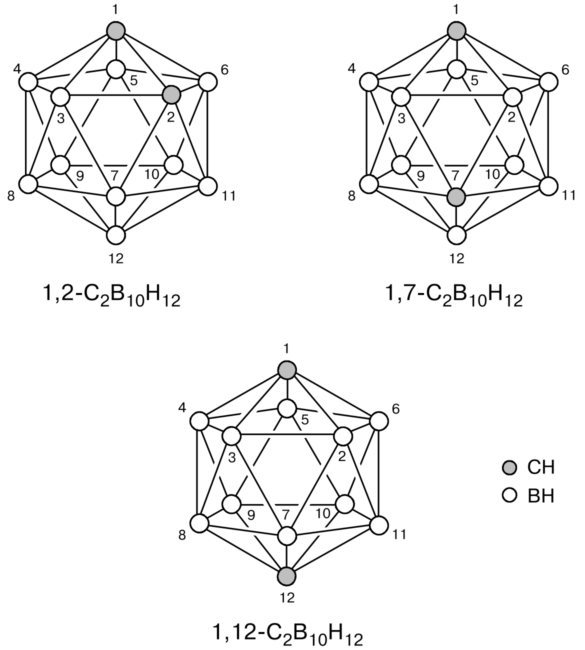
298—1000 K coincided with experimental data within the limits of measuring error. The electronic characteristics were obtained in different approximations. The results of the B3LYP/6-311G(2d,2p) and MP2/6-311+G(d,2p) calculations (see below) gave the best agreement with experimental data. Each level of theory correctly describes the electronic parameters of carboranes(12), *e.g.*, the dipole moment (μ) and the first ionization potential (*U*). For *o*-carborane, the experimental values of μ and *U* are respectively 4.31—4.53 D[14] and 9.0—10.62 eV[15—17] (*cf.* theoretical values 4.22—4.51 D and 8.77 (B3LYP)—11.13 (MP2) eV, respectively). The energies of the first excited states of the *o*-, *m*-, and *p*-carborane molecules were obtained from CASSCF/6-31G(d,p) calculations with the active space including four electrons and seven MOs. The topological parameters of the total electron density distribution function according to Bader[18] were determined by the MP2/6-311+G(d,2p) method using the "AIM" parameter (algorithm by J. Cioslowski) in the GAUSSIAN-98 program complex.[13]

Results and Discussion

A characteristic feature of carboranes(12) (Fig. 1) is the ability of their molecules to undergo cage rearrangements in the order *o*- → *m*- → *p*-isomer at 700—1000 K.[19] It was experimentally proved that *o*-isomer is completely converted into *m*-isomer, while the *m*- and *p*-isomers are equilibrated (free energy of the *m*- → *p*-carborane isomerization is[20] ~0.25 kcal mol^{-1} at 920—970 K).

Earlier,[12] the thermodynamic parameters of the isomers of carboranes(12) under standard conditions were calculated in small basis sets (at most 6-31G(d,p)) without inclusion of correlation corrections.



1,2-$C_2B_{10}H_{12}$ 1,7-$C_2B_{10}H_{12}$

1,12-$C_2B_{10}H_{12}$

Fig. 1. Molecular structures of 1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaboranes(12). Hydrogen atoms are not shown.

We calculated the thermodynamic parameters of isomerization reactions of carboranes(12)

$$o\text{-}C_2B_{10}H_{12} \rightleftharpoons m\text{-}C_2B_{10}H_{12}, \qquad (1)$$

$$m\text{-}C_2B_{10}H_{12} \rightleftharpoons p\text{-}C_2B_{10}H_{12} \qquad (2)$$

in the B3LYP/6-311G(2d,2p) approximation for the temperature range 298—1000 K and a pressure of 1 atm.

Analysis of the results obtained (Fig. 2) showed that reaction (1) is shifted to products in the temperature range under study (-15.9 kcal mol^{-1} < ΔG < -15.4 kcal mol^{-1}). Reaction (2) is characterized by establishment of equilibrium between *m*- and *p*-carborane under the isomerization conditions (800—1000 K, -0.35 kcal mol^{-1} < ΔG < < 0.25 kcal mol^{-1}). The content of *p*-carborane in the equilibrium mixture is 55—47% in this temperature range (calculated from the ΔG values). For T = 917 K, one has $\Delta G \approx 0.0$ kcal mol^{-1} and can expect equal concentrations of the *m*- and *p*-carboranes in the equilibrium mixture.

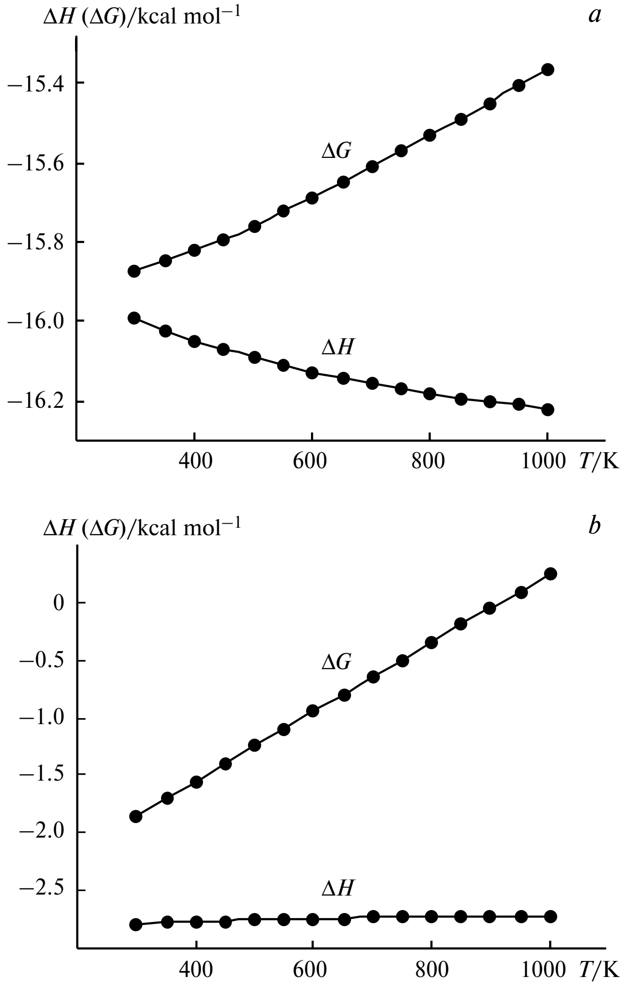


Fig. 2. Changes in enthalpies (ΔH) and Gibbs energies (ΔG) of reactions (1) (*a*) and (2) (*b*) plotted *vs.* temperature according to B3LYP/6-311G(2d,2p) calculations.

Table 1. Total energies (E_{tot}/a.u.^{a}), total energy differences (ΔE_{tot}/kcal mol^{-1}), the HOMO (E_{HOMO}/eV) and LUMO (E_{LUMO}/eV) energies, and the energy gaps (ΔE/eV) obtained from B3LYP/6-311G(2d,2p) (I) and MP2/6-311+G(d,2p) (II) calculations, and experimental ionization potentials (IP) of *o*-, *m*-, and *p*-carborane molecules

Parameter	$-E_{\text{tot}}$		ΔE_{tot}		$-E_{\text{HOMO}}$		E_{LUMO}		ΔE		IP	$\Delta E'^{b}$
	I	II	I	II	I	II	I	II	I	II		
o-$C_2B_{10}H_{12}$	332.1766314	331.0274385	+19.13	+18.66	8.79	11.19	–0.49	+0.80	8.30	11.99	10.13[15], 9.0[17]	8.75
m-$C_2B_{10}H_{13}$	332.2027971	331.0517885	+2.71	+3.38	8.82	11.06	–0.33	+0.95	8.50	12.01	10.14[15], 10.1[17]	8.88
p-$C_2B_{10}H_{12}$	332.2071174	331.0571812	0.00	0.00	8.86	11.02	–0.28	+1.14	8.58	12.16	10.3[16], 10.6[24]	8.97

[a] 1 a.u. = 627.5095 kcal mol^{-1}.

[b] Energy difference between the first excited state and the ground state molecules; obtained from CASSCF(4,7,NRoot=2)/6-31G(d,p) calculations.

The total energies of *m*- and *p*-carboranes (Table 1) obtained from DFT/6-311G(2d,2p) and MP2/6-311+G(d,2p) calculations are also similar.

The results obtained provide a correct explanation for the course of the rearrangements of the isomers of carboranes(12). The $\Delta H°$ value for reaction (1) calculated in this work, –16.0 kcal mol^{-1}, coincides, within the limits of measuring error, with the experimental $\Delta H°$ value (–18.0±3.5 kcal mol^{-1}) determined[21] from the heats of combustion of carboranes(12) (gas phase, normal conditions). The thermodynamic parameters calculated in this work are also in good agreement with the experimental values determined from the position of equilibrium (2) (ΔG_{calc} = +0.1 kcal mol^{-1} at 950 K, ΔG_{exp} = +0.25 kcal mol^{-1},[20] *cf.* ΔG_{calc} = –0.8 kcal mol^{-1} from Ref. 12).

Earlier,[22] it was reported that the second-order Jahn—Teller effect can influence the configuration stability of carboranes. The HOMO—LUMO gaps of *o*-, *m*-, *p*-carboranes(12) calculated in this work in all approximations including B3LYP/6-311G(2d,2p) and (to some extent) MP2/6-311+G(d,2p) (see Table 1) correlate with experimental data on the configuration stabilities of these molecules. The HOMO—LUMO gap width increases on going from *o*- to *p*-carborane and so do the stabilities of the isomers. Therefore, the parameters ΔE of *o*-, *m*-, and *p*-carboranes(12) can serve as an "orbital" criterion for their configuration stabilities. Analysis of the energies of the first excited singlet states and the ground singlet states of the molecules of *o*-, *m*-, *p*-carboranes(12) obtained from CASSCF/6-31G(d,p) calculations revealed a similar trend (see Table 1). Thus, changes in the energy differences between the ground and excited states of the molecules in question are in good agreement with the changes in the width of the corresponding HOMO—LUMO gaps.

According to our data, parameters of the frontier MOs can serve as a basis for analysis and prediction of trends of changes in not only the configuration stabilities, but also the reactivities of carboranes. A correct description of the reactivities of different isomers of the carboranes in question and pathways of electrophilic and nucleophilic reactions can be made based on analysis of the spatial distributions and energies of the frontier and nearest-energy MOs in terms of Fukui´s frontier MO approach.

The HOMO energies obtained from DFT calculations with inclusion of correlation corrections in all the basis sets used (results of B3LYP/6-311G(2d,2p) computations are listed as an example in Table 1) regularly decrease on going from *o*- through *m*- to *p*-carborane(12), which is in agreement with the decrease in the reactivities of these isomers in electrophilic substitution reactions. Note that the MP2/6-311+G(d,2p) approximation provides an incorrect order of the HOMO energies of carboranes(12) (see Table 1), namely, they increase on going from *o*- through *m*- to *p*-carborane, although experiments showed an increase in ionization potential of the isomers of carboranes(12) in the same order (see Table 1) and weakening of the electron-donor properties of carboranes(12).

Analysis of reaction pathways requires inclusion of the spatial distribution of the frontier and nearest-energy MOs (provided similar energies of these orbitals). Information on localization of these MOs was obtained from corresponding MO LCAO expansion coefficients and by analyzing the spatial distribution of the corresponding orbital wave functions. In the *o*-carborane molecule, the HOMO is mainly localized on the B(9) and B(12) atoms that are the most distant from carbon atoms and to a lesser extent on the B(8) and B(10) atoms, which makes these centers the most nucleophilic in character (Fig. 3).

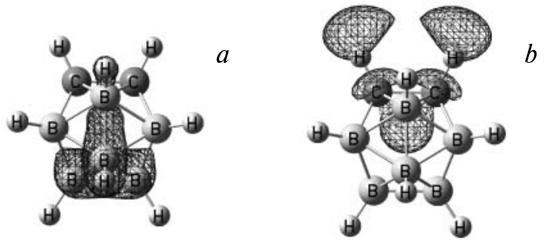


Fig. 3. Spatial distributions of HOMO (*a*) and LUMO + 1 (*b*) in *o*-carborane molecule from B3LYP/6-311G(2d,2p) calculations.

A similar electron density distribution was also obtained for the *m*-carborane HOMO. The B(9) and B(10) atoms are the most distant from carbon atoms, being also nucleophilic centers of this molecule. In the *p*-carborane molecule, all boron atoms are equivalent and each of them can act as the nucleophilic center.

All computational methods employed in this work predict that the LUMOs of the isomers of carboranes(12), which are responsible for the electrophilic properties of the molecules (in terms of the frontier MO theory), are localized on the nearest environment of carbon atoms. The electrophilic properties of carboranes(12) also manifest themselves in that these compounds possess the acidic properties, that is, *o*-, *m*-, *p*-carboranes are CH-acids characterized by experimental pK_a values of 23.3, 27.9, and 30.0, respectively.[23] The MOs governing the acidic properties of carboranes and localized on hydrogen atoms of C—H bonds are not necessary the LUMOs; rather, this depends on the approximation employed. For instance, B3LYP/6-311G(2d,2p) calculations of *o*-carborane molecule showed that the vacant orbital is the LUMO + 1 (see Fig. 3). The energies of the vacant MOs localized on hydrogen atoms of the C—H bonds are −0.159 (LUMO + 1), +0.145 (LUMO + 3), and +0.166 eV (LUMO + 2) for *o*-, *m*-, and *p*-carborane, respectively, which is consistent with the experimental order of decreasing acidity. The energy of the LUMO, which is localized on boron atoms in the nearest environment of carbon atoms, also shows a regular increase (see Table 1). This is in agreement with the decrease in the reactivities of these compounds in the reactions with nucleophilic agents (*e.g.*, cleavage of the carborane(12) cages under the action of amines of alkali metal alcoholates).

Traditionally, the reactivity is assessed from the Mulliken atomic charges. However, the atomic charges of borons calculated in all the approximations used in this work are inconsistent with the experimentally established order of electrophilic substitution and nucleophilic addition in the carborane polyhedron (Table 2).

At the same time we found that the atomic charges of hydrogens calculated by the HF and DFT (*e.g.*, B3LYP/6-311G(2d,2p), see Table 3) methods correlate with the order of electrophilic substitution and nucleophilic addition and characterize a decrease in the reactivity in the order *o*-, *m*-, *p*-carborane.

A decrease in the atomic charges of the hydrogens participating in the C—H bonds in the order *o*-, *m*-, *p*-carborane in all the approximations used, *e.g.*, B3LYP/6-311G(2d,2p) (see Table 3) is in agreement with the experimentally observed order of reduction of the acidity of these compounds. Similarly to calculations of the frontier MO parameters (MO energies and spatial distribution of the wave functions), the exception are the MP2/6-311+G(d,2p) calculated atomic charges of the hydrogens involved in the C—H bonds (see Table 3).

Table 2. Mulliken atomic charges (q) for carborane cage atoms and electrostatic potentials on atoms (φ) in *o*-, *m*-, and *p*-carborane molecules

Atom	B3LYP /6-311G(2d,2p)		MP2 /6-311+G(d,2p)	
	q/e	$-\varphi$/a.u.*	q/e	$-\varphi$/a.u.*
	o-Carborane (C_{2v})			
B(9) (B(12))	+0.0842	11.4635	+0.0747	11.4373
B(8) (B(10))	+0.0118	11.4591	+0.1097	11.4344
B(4) (B(5), B(7), B(11))	+0.0605	11.4345	−0.1876	11.4072
B(3) (B(6))	+0.0911	11.4100	−0.1734	11.3796
C(1) (C(2))	−0.1229	14.6632	−0.1193	14.6175
	m-Carborane (C_{2v})			
B(9) (B(10))	+0.0256	11.4600	+0.1109	11.4359
B(5) (B(12))	+0.1170	11.4398	−0.1824	11.4110
B(4) (B(6), B(8), B(11))	+0.0440	11.4354	+0.0132	11.4083
B(2) (B(3))	+0.1198	11.4107	−0.4566	11.3803
C(1) (C(7))	−0.1735	14.6910	+0.0204	14.6487
	p-Carborane (D_{5d})			
B	+0.0571	11.4357	−0.0663	11.4088
C	−0.1069	14.6959	−0.1675	14.6542

* 1 a.u. = $3.0277 \cdot 10^{-9}$ C m^{-1}.

Table 3. Mulliken atomic charges (q) for hydrogen atoms and electrostatic potential on atoms (φ) in *o*-, *m*-, and *p*-carborane molecules

Atom	B3LYP /6-311G(2d,2p)		MP2 /6-311+G(d,2p)	
	q/e	$-\varphi$/a.u.*	q/e	$-\varphi$/a.u.*
	o-Carborane			
H(9) (H(12))	−0.0726	1.1658	+0.0552	1.1645
H(8) (H(10))	−0.0668	1.1591	+0.0529	1.1585
H(4) (H(5), H(7), H(11))	−0.0405	1.1423	+0.0562	1.1399
H(3) (H(6))	−0.0252	1.1270	+0.0604	1.1227
H_{C-H}	+0.0605	1.0345	+0.2024	1.0289
	m-Carborane			
H(9) (H(10))	−0.0661	1.1597	+0.0537	1.1593
H(5) (H(12))	−0.0516	1.1503	+0.0603	1.1473
H(4) (H(6), H(8), H(11))	−0.0437	1.1435	+0.0546	1.1414
H(2) (H(3))	−0.0266	1.1274	+0.0748	1.1228
H_{C-H}	+0.0550	1.0538	+0.1830	1.0504
	p-Carborane			
H_{B-H}	−0.0464	1.1438	+0.0609	1.1417
H_{C-H}	+0.0535	1.0611	+0.1880	1.0589

* 1 a.u. = $3.0277 \cdot 10^{-9}$ C m^{-1}.

The electrostatic potential (φ) on the boron (see Table 2) and hydrogen atoms (see Table 3) in the isomers of the title molecules correlates with the reactivities of these compounds and with the order of electrophilic substitution and nucleophilic addition reactions. Both B3LYP/6-311G(2d,2p) and MP2/6-311+G(d,2p) methods give a similar description of the potential φ for different positions of reaction centers in a particular isomer and in different isomers.

The φ values for the H atoms of the C—H bonds also correlate with the changes in the acidic properties in the order *o*-, *m*-, *p*-carborane.

Analysis of theoretical values of the electron density (ρ) and the Laplacian of the electron density ($\nabla^2\rho$) at critical points of B—H and C—H bonds in the molecules under study showed regular changes in these parameters (Table 4).

One can also conclude that in all isomers these bonds have a covalent character.[18] The B—H bonds approach the intermediate type of bonds.[18] Table 4 shows that the ρ and $\nabla^2\rho$ values at the critical points of the H—B(9) (H—B(12)) and H—B(8) (H—B(10)) bonds of *o*-carborane are almost equal to each other, whereas the same parameters at the critical points of the H—B(9) (H—B(10)) and H—B(5) (H—B(12)) bonds of *m*-carborane differ to a greater extent. This is in qualitative agreement with experimental data on electrophilic substitution reactions of carboranes(12), namely, the reactions of *m*-carborane are much more selective than those of *o*-carborane.[19]

Note that the ρ and $\nabla^2\rho$ values at the (3, –1) critical points of C—H bonds in the *m*- and *p*-carborane molecules are similar to the corresponding values for ethane molecule (for *o*-carborane, they are similar to the ρ and $\nabla^2\rho$ values for ethylene and acetylene molecules). Thus, for both hydrocarbons and carboranes the $\nabla^2\rho$ values change in the same order, namely, they decrease on going from a less to a more acidic compound.

A much smaller $\nabla^2\rho$ value of the C—H bond compared to that of the B—H bond is due to a larger value of the "perpendicular contraction" of the electron density for the C—H bonds compared to the B—H bonds (Table 5). The parameters λ_{1-3} of the H—B(9) (H—B(12)) and H—B(8) (H—B(10)) bonds of *o*-carborane are nearly equal. The λ_1 parameters of the H—B(9) (H—B(10)) and H—B(5) (H—B(12)) bonds in *m*-carborane differ to a much greater extent.

The smaller $\nabla^2\rho$ value for the C—H bond in *o*-carborane molecule is due to smaller λ_{1-3} parameters of this bond compared to the corresponding values in *m*- and *p*-carborane molecules. This suggests that the electron density of the C—H bond in *o*-carborane is localized in a more compact spatial domain about the bond line compared to other isomers. Greater extent of compactness and localization of the electron density in the C—H

Table 4. MP2/6-311+G(d,2p) calculated ρ and $\nabla^2\rho$ values at the (3, –1) critical points of B—H and C—H bonds in *o*-, *m*-, and *p*-carborane molecules and (for comparison) of C—H bonds in ethane, ethylene, and acetylene molecules

Bond	ρ/e Å^{-3}	$-\nabla^2\rho$/e Å^{-5}
	o-Carborane (C_{2v})	
H—B(9) (H—B(12))	0.1790	0.1181
H—B(8) (H—B(10))	0.1789	0.1146
H—B(4) (H—B(5), H—B(7), H—B(11))	0.1818	0.1383
H—B(3) (H—B(6))	0.1847	0.1640
H—C(1) (H—C(2))	0.2983	1.1760
	m-Carborane (C_{2v})	
H—B(9) (H—B(10))	0.1783	0.1856
H—B(5) (H—B(12))	0.1804	0.1996
H—B(4) (H—B(6), H—B(8), H—B(11))	0.1806	0.2008
H—B(2) (H—B(3))	0.1829	0.2138
H—C(1) (H—C(7))	0.2872	1.0670
	p-Carborane (D_{5d})	
H—B	0.1808	0.2012
H—C	0.2870	1.0650
	Hydrocarbons	
C—H (ethane)	0.2845	1.0690
C—H (ethylene)	0.2929	1.1471
C—H (acethylene)	0.3007	1.2402

Table 5. Eigenvalues of the Hessian obtained from MP2/6-311+G(d,2p) calculations at the (3, –1) critical points of B—H and C—H bonds for *o*-, *m*-, and *p*-carboranes and (for comparison) of C—H bonds in ethane, ethylene, and acetylene molecules: "perpendicular contraction" values (λ_1, λ_2) and "parallel expansion" values (λ_3) of the electron density

Compound	Bond	$-\lambda_1$	$-\lambda_2$	λ_3
			e Å^{-5}	
o-Carborane	H—B(9) (H—B(12))	0.3708	0.3693	0.6220
	H—B(8) (H—B(10))	0.3691	0.3677	0.6222
	H—B(4) (H—B(5), H—B(7), H—B(11))	0.3888	0.3709	0.6214
	H—B(3) (H—B(6))	0.3965	0.3895	0.6219
	H—C(1) (H—C(2))	0.8157	0.8001	0.4400
m-Carborane	H—B(9) (H—B(10))	0.3530	0.3529	0.5203
	H—B(5) (H—B(12))	0.3696	0.3541	0.5241
	H—B(4) (H—B(6), H—B(8), H—B(11))	0.3696	0.3537	0.5225
	H—B(2) (H—B(3))	0.3790	0.3581	0.5233
	H—C(1) (H—C(7))	0.7766	0.7762	0.4857
p-Carborane	H—B	0.3691	0.3546	0.5225
	H—C	0.7749	0.7749	0.4848
Ethane	H—C	0.7120	0.7037	0.3463
Ethylene	H—C	0.7678	0.7594	0.3801
Acetylene	H—C	0.8435	0.8435	0.4470

interatomic space in *o*-carborane molecule (and therefore a decrease in the electron density on the corresponding H atom) facilitate the approach of the base compared to other isomers; this is probably responsible for the higher acidity of *o*-carborane. Table 5 shows that the λ_{1-3} parameters of the C—H bond in *o*-carborane molecule are similar to those of acetylene molecule characterized by the highest acidity among the hydrocarbons considered here. This can suggest that the acidities of carboranes and hydrocarbon molecules are governed by some common topological factors. For the *m*- and *p*-carboranes only the "perpendicular contraction" of the electron density of the C—H bond is similar to the corresponding value for ethylene molecule, whereas the "parallel expansion" of the electron density in carboranes is higher.

The distance from the C—H bond proton to the bond critical point is on the average 0.37 Å for different isomers (*cf.* 0.65 Å for B—H bonds). This corresponds to a strong effect of carbon atoms on the electron density in the region of the C—H bond, which is responsible for the acid character of this bond. As to the B—H bond, attractors have the opposite effect on the electron density; therefore, H atoms of these bonds are hydridic in character. Positions of the critical point of the C—H bonds in the molecules of carboranes(12) and in acetylene molecule are similar (0.37 and 0.35 Å, respectively).

The B—H bonds in *o*- and *m*-carborane molecules are the most distant from carbon atoms. They are characterized by maximum $\nabla^2\rho$ values at the critical points; according to Bader,[18] this indicates the greatest diffusivity of the electron density of these bonds. The Laplacian of the electron density, $\nabla^2\rho$, at the critical points of the B—H bonds in *p*-carborane molecule has a very low value, which corresponds to low (compared to other carboranes) diffusivity and high contraction of the electron density in the interatomic space. This can provide an explanation for low reactivity of *p*-carborane in electrophilic substitution reactions.

The smallest $\nabla^2\rho$ values at the critical points of the B—H bonds in positions 3, 6 and 2, 3 for *o*- and *m*-carboranes, respectively, are indications of "compact' electron density distribution for these bonds compared to other positions. Probably, in this case the interaction of nucleophilic species and boron atoms in the positions mentioned above is facilitated.

Thus, we revealed correlations between changes in the reactivities of *o*-, *m*-, and *p*-carboranes(12) and parameters of three basic levels of description of their electronic structure, based on analysis of the charge distribution of hydrogen atoms (not the cage atoms!) and the electrostatic potential on the cage atoms and on hydrogen atoms, the energies and spatial distribution of the frontier and nearest-energy MOs, and the topological characteristics of the critical points of the B—H and C—H bonds.

The results obtained may suggest that reactions of carboranes(12) with electrophilic agents (E) involve the B—H bonds rather than boron atoms (bonds within the polyhedral cage) of the molecule. This seems to be a reason for the observed correlation between the electronic parameters of these bonds and the atomic charges of hydrogens and reactivities. Here, the decisive role is probably played by the intermediate stage, where the electrophilic agent is coordinated to H atoms with the formation of a three-center two-electron bond B—H—E. Subsequent stages should involve a rearrangement of the B—H—E fragment and formation of the B—E bond and abstraction of a proton upon nucleophilic assistance by the solvent or a nucleophile conjugated with the electrophilic species.

Apparently, the reactions of carboranes(12) with bases occur in a similar fashion from the standpoint of structural transformations. The base (N) reacts with the C—H bond to form a three-center four-electron bond C—H—N in the transition state. Proton transfer to the base and solvation of the anionic center with the solvent molecule or cation completes the process.

On the contrary, the reactions of carboranes(12) with nucleophilic agents result in the addition and are followed by cleavage of the polyhedron, involve the cage bonds formed by the boron atoms if the nearest environment of carbon atoms. As a consequence, the polyhedral cage is opened, being stabilized in subsequent stages in the form of dicarba-*nido*-undecaborate(1−) anions.

Further quantum chemical reactivity studies of carboranes(12) will make it possible to obtain quantitative, structural, and thermodynamic parameters of these reactions.

References

1. D. A. Dixon, D. A. Kleier, T. A. Halgren, J. A. Hall, and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1977, **99**, 6226.
2. R. B. King and D. H. Rouvray, *J. Am. Chem. Soc.*, 1977, **99**, 7834.
3. E. D. Jemmis, *J. Am. Chem. Soc.*, 1982, **104**, 7017.
4. J. J. Ott and B. M. Gimarc, *J. Comput. Chem.*, 1986, **7**, 673.
5. M. Zhang and Y. Zhao, *J. Mol. Struct., THEOCHEM*, 2001, **545**, 105.
6. A. V. Okotrub, L. G. Bulusheva, and V. V. Volkov, *J. Mol. Struct., THEOCHEM*, 2000, **520**, 33.
7. A. Salam, M. S. Deleuze, and J.-P. Francois, *Chem. Phys.*, 2003, **286**, 45.
8. R. B. King, *Chem. Rev.*, 2001, **101**, 1119.
9. M. Yu. Antipin, A. V. Polyakov, V. G. Tsirel´son, M. Kappkhan, V. V. Grushin, and Yu. T. Struchkov, *Metalloorg. Khim.*, 1990, **3**, 831 [*Organomet. Chem. USSR*, 1990, **3**, 421 (Engl. Transl.)].
10. J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. A. Schroeder, *J. Am. Chem. Soc.*, 1966, **88**, 628.

11. M. L. McKee, *J. Am. Chem. Soc.*, 1992, **114**, 879.
12. K. Hermansson, M. Wojcik, and S. Sjoberg, *Inorg. Chem.*, 1999, **38**, 6039.
13. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *GAUSSIAN-98, Revision A.7*, Gaussian, Inc., Pittsburgh (PA), 1998.
14. V. I. Stanko, V. V. Khrapov, and T. A. Babushkina, *Usp. Khim.*, 1974, **43**, 1359 [*Russ. Chem. Rev.*, 1974, **43** (Engl. Transl.)].
15. V. M. Orlov, V. N. Pustobaev, T. Yu. Poroshina, V. A. Ol´shevskaya, L. I. Zakharkin, and G. L. Gal´chenko, *Dokl. Akad. Nauk SSSR*, 1989, **309**, 892 [*Dokl. Phys. Chem.*, 1989, **309**, 968 (Engl. Transl.)].
16. V. M. Orlov, V. N. Pustobaev, V. A. Ol´shevskaya, L. I. Zakharkin, and G. L. Gal´chenko, *Dokl. Akad. Nauk SSSR*, 1988, **300**, 898 [*Dokl. Phys. Chem.*, 1988, **300**, 518 (Engl. Transl.)].
17. T. Vondrak, *Tetrahedron*, 1987, **6**, 1559 (Engl. Transl.)].
18. R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, 1994, 458 pp.
19. R. N. Grimes, *Carboranes*, Acad. Press, New York—London, 1970, 272 pp.
20. L. I. Zakharkin, *Pure Appl. Chem.*, 1972, **29**, 513.
21. G. L. Gal´chenko, L. N. Martynovskaya, Yu. V. Gol´tyapin, and V. I. Stanko, *Zh. Obshch. Khim.*, 1971, **41**, 141 [*J. Gen. Chem. USSR*, 1971, **41** (Engl. Transl.)].
22. V. I. Stanko, V. A. Brattsev, and S. P. Knyazev, *Usp. Khim.*, 1979, **48**, 241 [*Russ. Chem. Rev.*, 1979, **48** (Engl. Transl.)].
23. O. A. Reutov, I. P. Beletskaya, and K. P. Butin, *CH-Acids*, Pergamon Press, Oxford, 1978, 228 pp.
24. T. P. Fehlner, M. Wu, B. J. Meneghelli, and R. W. Rudolf, *Inorg. Chem.*, 1980, **19**, 49.

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