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Gas-Phase Brønsted Superacidity of Some Derivatives of Monocarba-*closo*-Borates: a Computational Study

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The structures and gas-phase acidities (GA) of several $CB_{11}H_{12}H$-based carborane acid derivatives (HA) have been calculated with DFT B3LYP method using 6-311+G**, 6-311++G** basis sets. In order to verify the obtained GA values, several systems were also studied at G3(MP2) level of theory. Inserted substituents (CF_3, F, Cl, Br, I, CN, CH_3, etc.) followed the "belts" of the monocarborane cage starting from the boron antipodal to the carbon. In general, the predicted intrinsic gas-phase acidities of the systems varied according to the substituents in the following order of decreasing strength: $CF_3 > F > Cl > Br > I > CN > CH_3$. Nevertheless, some inconsistencies occurred. F and CN derivatives with lower degree of substitution had weaker intrinsic acidities than the respective Cl derivatives, but the situation was reversed in the case of a larger number of substituents. To obtain better understanding how the substituents influence the basicity of the carborane anion, three hypothetical reaction series were investigated, in which the protonation center was fixed on the boron atom (B_{12}), antipodal to the carbon (C_1), and a single substituent replaced the hydrogens at the vertexes of the three remaining positions (C_1, B_2, and B_7). The intrinsic gas-phase acidities in these series of neutral carborane-based acids $CB_{11}X_1H_{11}H$ are found to clearly depend on the field-inductive and resonance effects of the substituent X. Some influence of the polarizability of X on the reaction center (B_{12}) could be detected only in the alpha position (B_7).

Introduction

For some time,[1−8] it has been accepted that carboranes present a new class of extremely inert, superweakly coordinating anions whose conjugate acids are Brønsted acids of unprecedented strength. These deductions are based on extensive and convincing but mostly qualitative and often indirect evidence of different origin.

Because of the fundamental challenges and interest of measuring the acidity of superstrong acids, several investigations were published that have concentrated on developing methods for ranking them. The first preliminary computational evidence[5,9,10] that the intrinsic (gas-phase) superacidity of conjugated acids of carboranes can exceed that of the "classical" strong inorganic acids by many powers of ten was published some time ago. The solution phase superacidity has been evaluated indirectly by Reed et al. using the NH stretching frequency shifts of Oct_3NH^+ in CCl_4 induced by H-bond formation between the latter proton donor and the superweak anionic base.[10,11] The protonation-induced ^{13}C NMR shifts of mesityl oxide in liquid SO_2 have been used for the ranking of the acid strength of some superacids[11] as well. Also, a theoretical approach was introduced that attempts to evaluate the intrinsic acidity order by means of analyzing molecular electrostatic potential surfaces.[12] Although, the solid and gas-phase structures of $CB_{11}Cl_{11}H_1H$ have been determined,[13] no direct measurements of Brønsted acidity of these acids neither in solution nor in the gas-phase have been performed so far. Nevertheless, an extensive research on finding even more weakly coordinating anions is going on,[2,3,5−10] and one of the main trends has been the introduction of suitable strong electron-acceptor substituents that are capable of extensive negative charge delocalization from the anionic protonation center. These results with some modern concepts[14] have been considered as a route of making less basic anions. Central in this paradigm is the design of a more or less well-defined anionic protonation site whose basicity reduction is carried out with the introduction of a limited number of substituents. As the carborane cage's many vertexes pose a possibility of introducing a large number of groups, the chemical properties of already inherently very weakly basic and chemically extremely stable carba-*closo*-borate anions could be significantly modified by substituents of different kind. Although this feature poses a great prospect of creating application-specific counterions in terms of solubility and reactivity,[15] the introduction of the substituents can change the location of the most basic site of the anion considerably.

In the present paper, we shall focus on the significant extension and study of the computational intrinsic gas-phase acidity scale using mostly high level density functional theory (DFT) and ab initio G3(MP2) calculations of monocarborane based superacid derivatives with a wide range of substituents of different nature. In order to obtain reliable results, different possible protonation geometries and the effects of substituents on the reaction site are compared.

Methods

The DFT calculations were carried out on $CB_{11}X_nH_{12\text{-}n}H$ (X = CN, F, Cl, CF_3, etc.; $n = 0, 1, 6, 11, 12$) cages mostly at B3LYP/6-311+G** level with Gaussian 03 system of programs.[16] The parent carborane acid $CB_{11}H_{12}H$ and several of its derivatives were calculated also with the ab initio G3(MP2) theory. For some species, where there was a possibility of a significant negative charge accumulation on hydrogen atoms, also the 6-311++G** basis set was used. As iodine is not

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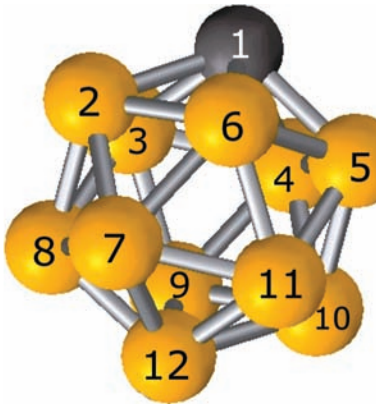

Figure 1. Numbering of the vertexes of the dodecaborate anion. The substituents have not been displayed.

parametrized in the 6-311G range of basis sets, SDD was used for this specific atom.

When modeling, the boron cluster was viewed as the belts of vertexes: 1:5:5:1 (Figure 1, no hydrogens displayed). Replacement of hydrogens with substituents was done systematically beltwise, starting from the vertex antipodal to carbon, that is, position 12.

For most of the compounds, several input geometries of different protonation sites were composed to determine the most basic one. Full geometry optimizations as well as vibrational analyses were carried out for all anions and their conjugated acids.

The intrinsic gas-phase acidity ($\Delta G_{\mathrm{acid}} \equiv \mathrm{GA}$) of a neutral acid HA was calculated according to the following thermodynamic heterolysis equilibrium:

$$\mathrm{HA} \rightleftarrows \mathrm{A}^- + \mathrm{H}^+ \qquad (1)$$

The ΔG_{acid} values (at 298 K) were calculated taking into account the zero-point energies, finite temperature (0 to 298 K) correction, and the pressure−volume work term pV. The absence of imaginary frequencies (Nimag = 0) was considered as the criterion of a true minimum.

By definition, the gas-phase Brønsted acidity of a neutral acid HA is equal to the gas-phase basicity of its conjugate base, A-. In cases where the thermodynamically most stable protonated system was partially decomposed (i.e., a substituent or part of it was abstracted by proton), the next stable protonated form was used.

Results

The computational results for ΔG_{acid} values of the conjugate acids of the carborane anions $\mathrm{CB}_{11}\mathrm{X}_n\mathrm{H}_{12\text{-}n}^-$ are given in Table 1. More detailed information about the results of the DFT calculations is available in Supporting Information or from the authors upon request.

For the unsubstituted (parent) compound $\mathrm{CB}_{11}\mathrm{H}_{12}\mathrm{H}$, the calculations at three different levels of theory (DFT B3LYP 6-311+G**, DFT B3LYP 6-311++G**, and ab initio G3(MP2)) yielded the structure which resembles that structure where the loosely bound H_2 molecule is attached to the B_{12} atom of the $\mathrm{CB}_{11}\mathrm{H}_{11}^-$ cage ($\mathrm{B}_{12}\mathrm{H}$ and H−H distances 1.35 and 0.82 Å, respectively) and provided the ΔG_{acid} values (266.5 (265.5 ref 5), 265.5, and 265.2 kcal·mol^{-1}, respectively). These are in a reasonable agreement with each other. The B_{12}−H bonds are relatively long compared with the remaining B−H distances in the cage ($\mathrm{B}_5\mathrm{H} = \mathrm{B}_7\mathrm{H} = 1.19$ Å). This implies that the protonated parent compound should rather be viewed as a complex between the $\mathrm{CB}_{11}\mathrm{H}_{11}$ cage (as a Lewis acid) and H_2 (as a Lewis base). Most certainly this complex is extremely reactive, because of the very low basicity H_2. This could be the reason why all attempts to synthesize the unsubstituted parent neutral acid $\mathrm{CB}_{11}\mathrm{H}_{12}\mathrm{H}$ have so far failed.[2]

The close agreement for the results using different levels of theory was also noticed for different mono- and multisubstituent systems for which DFT 6-311+G** (or 6-311++G**) and ab initio correlated G3(MP2) calculations were made for comparison. In all cases, the differences between GA values calculated at those levels of theory agreed within 1−3 kcal·mol^{-1}, except for the $\mathrm{CF}_3\mathrm{SO}_2$-substituted system ($\Delta\Delta G_{\mathrm{acid}} = 3.9$ kcal/mol).

As underlined by Michl et al.,[17] most of the calculated negative charge in the unsubstituted monocarba-*closo*-dodecaborate anion resides on the carbon vertex. Nevertheless, because of the anisotropy of the electrostatic potential in the unsubstituted acid, the most favorable center of protonation is the B_{12} atom. Introduction of substituents can change the charge distribution considerably. This brings up the necessity to evaluate and compare several local energetic minima throughout the structure. Henceforth, there will be an overview of the most probable predicted protonation sites of the derivatives and their gas-phase acidities.

Discussion

Monosubstituted Derivatives of $\mathbf{CB_{11}X_nH_{12\text{-}n}H}$ Where X = F, Cl, Br, I, CN, $\mathbf{CF_3SO_2}$, $\mathbf{NO_2}$, $\mathbf{NH_2}$, $\mathbf{NMe_2}$, $\mathbf{CH_3}$, and $\mathbf{CF_3}$, and *n* = 1. The results of the computational predictions of basicity of the carborate anion with a single substituent placed on the B_{12} vertex ranked the systems according to the increasing GA values (kcal·mol^{-1}, decreasing acidity): $\mathrm{CF}_3 \rightarrow \mathrm{Br} \approx \mathrm{Cl} \rightarrow \mathrm{I} \rightarrow \mathrm{F} \rightarrow \mathrm{CMe}_3 \approx \mathrm{CH}_3 \rightarrow \mathrm{H} \rightarrow \mathrm{CN} \rightarrow \mathrm{CF}_3\mathrm{SO}_2 \rightarrow \mathrm{NO}_2 \rightarrow \mathrm{NH}_2 \rightarrow \mathrm{NMe}_2$. The most stable protonated forms of monosubstituted F, Cl, CF_3, and CH_3 derivatives have very similar geometry. Both hydrogens attached to B_7 are equidistant from it and 0.831−0.834 Å from each other (Figure 2a). The small distance between the hydrogen nuclei supports the idea of some charge transfer[18−23] (covalent) character and could be viewed as an expression of a partial two electron three center bond in the BH_2 fragment. Their conjugate acids display the increasing acidity order (Table 1), CH_3 (261.2) → F (257.2) → Cl (255.3) → CF_3 (253.1), where the derivative with more electronegative fluorine substituent is less acidic than the chlorine counterpart. In the literature,[24−30] several approaches have been suggested to explain this type of effects of substituents.

The proportions of the effects are system-dependent and complex; thus, it is reasonable to look at their influence from a qualitative point of view in the context of average acidity increase per substituent (Table 2): $\mathrm{CH}_3 \rightarrow \mathrm{F} \rightarrow \mathrm{I} \rightarrow \mathrm{Cl} \approx \mathrm{Br} \rightarrow \mathrm{CF}_3$. In the case of the single-atom halogen derivatives, the proton-affinity on the B_7 vertex decreases with the increasing size of the halogen substituent atom. But as the electronic polarizability of the substituent in this sequence increases, the most favorable protonation site does not remain on the B_7 vertex, but in the case of the Br- and I-derivatives, it shifts onto the substituent (0.7 and 2.2 kcal/mol lower in energy compared with B_7 vertex, respectively).

In the case of F, Cl, CMe_3, and CH_3 substituents that do not yield hydrogen bridges with proton, the acidity ranking follows somewhat the interplay of the field/inductive and polarizability terms of the substituents (vide infra). CF_3, in turn, shows rather large acidifying effect compared with what could be expected from the corresponding sigma parameters.[30−32]

TABLE 1: Results of Acidity Calculations with DFT B3LYP Method at 6-311+G and 6-311++G** Level and with G3(MP2) Method**

acid	protonation site[a]	ΔG_{acid}[b]	acid	protonation site[a]	ΔG_{acid}[b]
$CB_{11}H_{12}H$	B_{12}	266.5	$CB_{11}(CN)_6H_6H$	CN_{12}	250.0
$CB_{11}H_{12}H$	B_{12}	265.5[c]	$CB_{11}(CN)_{11}H_1H$	CN_{12}	228.3
$CB_{11}H_{12}H$	B_{12}	265.5[d]	$CB_{11}(CN)_{12}H$	CN_{12}	225.0
$CB_{11}H_{12}H$	B_{12}	265.2[e]	$CB_{11}(CF_3)_1H_{11}H$	B_7	253.1[g]
$CB_{11}(CH_3)_1H_{11}H$	B_7	261.2[d,g]	$CB_{11}(CF_3)_1H_{11}H$	B_7	251.3[e,g]
$CB_{11}(CH_3)_1H_{11}H$	B_7	259.3[e,g]	$CB_{11}(CF_3)_6H_6H$	B_2	211.7[g]
$CB_{11}(CH_3)_6H_6H$	7 - 8 - 12	263.2[d,g]	$CB_{11}(CF_3)_{11}H_1H$	7 - 8 - 12	172.7[g]
$CB_{11}(CH_3)_{11}H_1H$	7 - 8 - 12	266.2[d,g]	$CB_{11}Br_1H_{11}H$	Br_{12}	255.2
$CB_{11}(CH_3)_{12}H$	7 - 8 - 12	264.9[d,g]	$CB_{11}Br_6H_6H$	$Br_{12} \rightarrow Br_7$	245.9[f]
$CB_{11}F_1H_{11}H$	B_7	257.2	$CB_{11}Br_{11}H_1H$	$Br_{12} \rightarrow Br_7$	236.3
$CB_{11}F_1H_{11}H$	B_7	256.0[e]	$CB_{11}I_1H_{11}H$	I_{12}	255.8
$CB_{11}F_6H_6H$	7 - 8 - 12	232.6	$CB_{11}I_6H_6H$	$I_{12} \rightarrow I_7$	246.7
$CB_{11}F_6H_6H$	7 - 8 - 12	231.6[e]	$CB_{11}I_{11}H_1H$	$I_{12} \rightarrow I_7$	240.0
$CB_{11}F_6H_6H$	2 - 3 - 7	232.5	$CB_{11}F_{11}(CH_3)_1H$	$F_{12} \rightarrow F_7$	217.0
$CB_{11}F_6H_6H$	2 - 3 - 7	230.7[e]	$CB_{11}(CF_3SO_2)_1H_{11}H$	$O \rightarrow H_7$	273.0
$CB_{11}F_{11}H_1H$	$F_{12} \rightarrow F_7$	216.4[f]	$CB_{11}(CF_3SO_2)_1H_{11}H$	$O \rightarrow H_7$	269.1[e]
$CB_{11}F_{12}H$	$F_{12} \rightarrow F_7$	212.8	$CB_{11}(NO_2)_1H_{11}H$	$O \rightarrow H_7$	275.5
$CB_{11}Cl_1H_{11}H$	B_7	255.3	$CB_{11}(NO_2)_1H_{11}H$	$O \rightarrow H_7$	275.8[e]
$CB_{11}Cl_1H_{11}H$	B_7	254.2[e]	$CB_{11}(NH_2)_1H_{11}H$	N_{12}	309.0
$CB_{11}Cl_6H_6H$	$Cl_{12} \rightarrow Cl_7$	242.2[f]	$CB_{11}(NMe_2)_1H_{11}H$	N_{12}	312.2
$CB_{11}Cl_6H_6H$	$Cl_{12} \rightarrow Cl_7$	243.1[e]	$CB_{11}(CMe_3)_1H_{11}H$	B_7	261.0
$CB_{11}Cl_{11}H_1H$	$Cl_{12} \rightarrow Cl_7$	230.4[f]	$CB_{11}(CMe_3)_1H_{11}H$	B_7	258.0[e]
$CB_{11}Cl_{12}H$	$Cl_{12} \rightarrow Cl_7$	229.3	$CB_{21}H_{22}H$	B_{12}	257.0
$CB_{11}(CN)_1H_{11}H$	CN_{12}	274.0	$CB_{21}F_1H_{21}H$	B_7	246.5
$CB_{11}(CN)_1H_{11}H$	CN_{12}	271.4[e]	$CB_{21}Cl_1H_{21}H$	B_7	246.5

[a] The sites of protonation for the most stable forms. B_x denotes a boron vertex with proton arranged to it symmetrically with the substituent. X - Y- Z denotes a facet of the boron cage. $A_x \rightarrow C_y$ denotes a geometry where proton is on a substituent A in the position x having HB interaction with substituent B in the position y. CN_{12} denotes the substituent that has proton attached to it forming a linear system. [b] ΔG_{acid} values given in kcal/mol at 298 K, calculated at 6-311+G** level if not noted differently. [c] Reference 5. [d] Calculated at 6-311++G** level. [e] Calculated with G3(MP2) method. [f] Reference 10. [g] Thermodynamically most stable system was achieved, when HF, CF_3H, or CH_4 were eliminated. The most stable nondecomposed protonated form was used for calculations of ΔG_{acid} values. See text for comments.

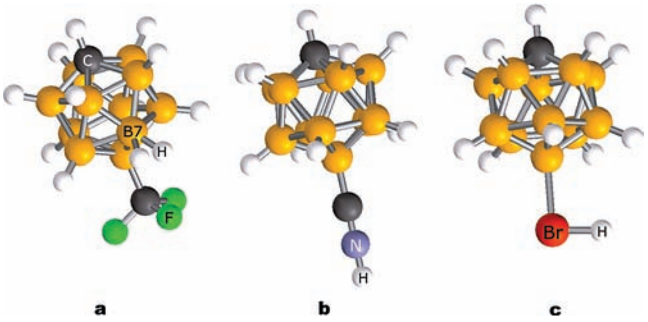

Figure 2. Protonation sites for some single-substituted derivatives of monocarba-*closo*-dodecaborane acids.

Although, NO_2, CN, and CF_3SO_2 have been considered extremely potent in reducing anion basicity, attractive protonation sites on sp^2 oxygen or nitrogen atoms make the monotriflyl-, -nitro-, and -cyano-derivatives less acidic than the unsubstituted compound. Also, the NH_2 and NMe_2 derivatives protonate on the substituent and have predicted gas-phase acidities far lower than any other derivatives in this investigation.

Hexasubstituted Derivatives of $CB_{11}X_nH_{12\text{-}n}H$ Where X = F, Cl, Br, I, CN, CH_3, and CF_3 and $n = 6$. Diverse protonation site geometries were observed with these derivatives. In the Cl-, Br-, and I-substituted systems, proton interacts with the substituent in the position 12 and is chelated by the substituent in the position 7 (Figure 3e). In terms of negative charge distribution, the hexafluoro carborane acid $CB_{11}F_6H_6H$ represents a unique system. Although, the one-atom halogen substituents, in general, appear to be the most favorable protonation sites in the form of intramolecular hydrogen bridge between two substituents and H, lower polarizability makes the proton interaction with the fluorine-shield somewhat less stable. Preferred protonation sites with rather insignificant 0.5 kcal·mol^{-1} difference in energies can be found near the boron cage above the facets 7-8-12 and 2-3-7. The protonation site on the B_{2-6} vertex is only by 1 kcal·mol^{-1} less favorable, that is, practically indistinguishable from that for two previous sites. Although the hexa-CH_3 carborane has a similar protonation geometry (Figure 3d), with the exception of about 6 kcal·mol^{-1} difference between the energies of 7-8-12 and the next most basic site on the 2-7-8 facet, increasing the number of CH_3-covered vertexes increases the anion basicity.

In the hexakis-CF_3 derivative, the most favorable protonation site (which does not lead to the possible eliminations) is on the B_{2-6} vertex that is probably "as near as it gets" to C_1, yielding the GA of 211.7 kcal·mol^{-1} (Figure 3f).

The next most favorable protonation site on B_{2-6} vertex of the fluorine derivative was by 1.1 kcal·mol^{-1} more acidic. The hexakis-CF_3-substituted carborane, protonated in the similar way, was the most stable one.

On the scale of the intrinsic acidities, the clusters with six F and Cl substituents, respectively, switched their places: $CF_3 > F > Cl > Br \approx I > CN > CH_3 > H$. Also, different from the singly substituted acids, the $(CN)_6$ derivative is more acidic than the $(CH_3)_6$ derivative or the unsubstituted carborane. The Cl_6 derivative was estimated to be about 3.8 kcal·mol^{-1} more acidic than the Br_6 derivative (Figure 4).

Derivatives of $CB_{11}X_nH_{12\text{-}n}H$ Where X = CN, F, Cl, and CH_3 and $n = 11$ and 12. As the protonation geometries of the systems calculated with 12 substituents had no significant difference from their 11-substituent counterparts, there is a reason to expect that all uniformly substituted undeca- and dodeca-derivatives have similar protonation geometry.

TABLE 2: Average[a] Acidity Increase (ΔG_{acid} Value in kcal·mol^{-1} Decrease) Per Substituent Compared to $CB_{11}H_{12}H$ in Some $CB_{11}X_{12}H$ Based Systems[b]

acid	$n^c = 1$	protonation site	$n^c = 6$	protonation site	$n^c = 11$	protonation site	$n^c = 12^e$
$CB_{11}F_nH_{12-n}H$	−8.3	B_7	−5.5	7 - 8 - 12[d]	−4.5	$F_{12} \rightarrow F_7$	−4.4
$CB_{11}Cl_nH_{12-n}H$	−10.2	B_7	−3.9	$Cl_{12} \rightarrow Cl_7$	−3.2	$Cl_{12} \rightarrow Cl_7$	−3.0
$CB_{11}Br_nH_{12-n}H$	−10.3	Br_{12}	−3.3	$Br_{12} \rightarrow Br_7$	−2.7	$Br_{12} \rightarrow Br_7$	
$CB_{11}I_nH_{12-n}H$	−9.7	I_{12}	−3.1	$I_{12} \rightarrow I_7$	−2.3	$I_{12} \rightarrow I_7$	
$CB_{11}(CF_3)_nH_{12-n}H$	−12.4	B_7	−9.0	B_2	−8.4	7 - 8 - 12	
$CB_{11}(CH_3)_nH_{12-n}H$	−4.3	B_7	−0.4	7 - 8 - 12	0.1	7 - 8 - 12	0.1
$CB_{11}CN_nH_{12-n}H$	8.5	CN_{12}	−2.6	CN_{12}	−3.4	CN_{12}	−3.4
$CB_{11}CF_3SO_2H_{11}H$	7.5	$O \rightarrow H_7$					
$CB_{11}NO_2H_{11}H$	10.0	$O \rightarrow H_7$					
$CB_{11}NH_2H_{11}H$	43.5	N_{12}					
$CB_{11}NMe_2H_{11}H$	46.7	N_{12}					

[a] ΔG_{acid} difference between the given and parent $CB_{11}H_{12}H$ molecule divided by the number of substituents. [b] Based on data from Table 1. [c] n is the number of substituents. [d] The anions protonated on the 7 - 8 - 12 and 2 - 3 - 7 facets had about the same acidity. [e] The 12- and 11-substituent systems had similar geometry.

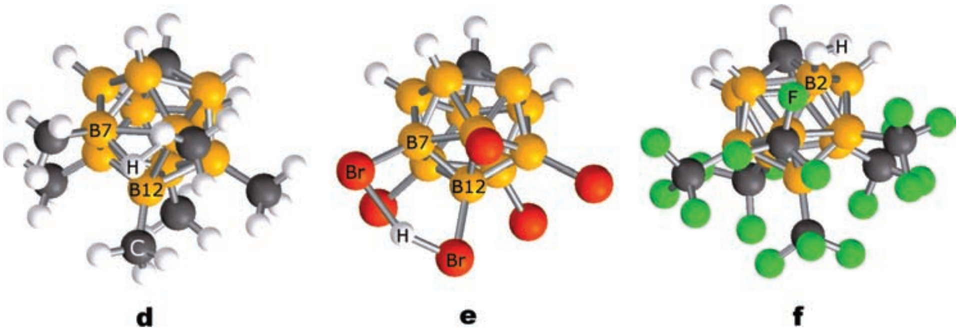

Figure 3. Protonation sites for some polysubstituted derivatives of monocarba-*closo*-dodecaborane acids.

Undeca-Br- and -I-, undeca- and dodeca-Cl-derivatives, and the corresponding fluoro systems each have several protonation sites of very close energetic values, all of them with a proton forming a hydrogen bridge between the substituents on the antipodal polyhedron ($HCB_{11}X_{11}H$, X ≡ F; Cl: F_{12}−H···F 0.974/1.781 Å; Cl_{12}−H···Cl 1.379/2.000 Å). Although the undeca- and dodeca-fluorocarboranes have several orders of magnitude stronger acidity compared with the rest of the corresponding halide systems, it is accompanied also with a greater degree of distortion that is expressed by 16.5° tilt of the F_{12}- and about 12° tilt of the F_7-substituent toward proton, compared with the respective angles in the nonprotonated systems. Thus, a large number of "hard" electron-withdrawing groups attached directly to the cage vertexes weaken the bonding between the boron atoms, making the whole molecule more susceptible to distortions and fragmentation.[35] The distortions, though on a smaller scale, are also visible in Cl, Br, and I systems.

The $(CF_3)_{11}$ system had the most stable protonation site (characterized by $N_{imag} = 0$) above the 7-8-12 facet of the boron cage which resembled the polysubstituted CH_3 derivatives (Figure 3d). The calculated basicity of the protonation site was 172.7 kcal·mol^{-1} (Figure 4), which would make the system about 70 powers of ten more acidic than the parent compound. Several attempts were made to find a stable protonation center near or between the CF_3 and CH_3 substituents. However, all initial geometries where proton was on or between the CF_3 or CH_3 substituents proved unviable and, during the geometry optimization, led to the elimination of HF or CH_4, respectively. The resulting $CB_{11}(CH_3)_{10}CH_4$ was about 6 kcal·mol^{-1} and $CB_{11}(CF_3)_{10}CF_2HF$ up to 56 kcal·mol^{-1} lower in energy relative to the most stable intact protonated form; thus, the abstraction of hydrogen fluoride, HF, could be a favorable reaction path. This also means that the actual reversible Brønsted equilibrium will probably not be observable experimentally, and the acidity value around 173 kcal·mol^{-1} has to be regarded as hypothetical. The same is true for the hexakis- and monotrifluoromethyl derivatives.

The successive substitution with poorly polarizable and low electronegativity CH_3 group appears to rather shield more attractive protonation sites than have a significant effect on the electron distribution of the cage. It yields about 2 kcal·mol^{-1} stabilization for $CB_{11}(CH_3)_6H_6H$ and further 3 kcal·mol^{-1} for $CB_{11}(CH_3)_{11}H_1H$ compared with the singly substituted derivative. Nevertheless, substituting the H at C_1 brought the acidity again slightly above the unsubstituted system.

Interesting results are displayed by the CN derivatives. With a protonated lone pair of electrons on the nitrogen, the monosubstituted acid is by 8.5 kcal·mol^{-1} weaker than $CB_{11}H_{12}H$. With 6, 11, and 12 substituents, the acidity increases considerably reaching 225 kcal·mol^{-1} making $CB_{11}(CN)_{12}H$ by 4.3 kcal·mol^{-1} more acidic, than $CB_{11}Cl_{12}H$. Distinctively, introducing electron-withdrawing groups does not alter the location of the most favorable protonation site on the CN-substituted carborane derivatives; thus, the increase of the acidity is achieved in the similar way as with "common" Brønsted acids, by reducing the electron density of a well-defined protonation center.

Effects of Substituents. The primary characteristic that directly affects the location of the protonation site, and thus the intrinsic acidities of the systems, is the presence or lack of a lone pair of electrons. Anions of most of the known Brønsted acid molecules contain a well-defined and easily accessible protonation center that carborane anions generally lack. This is the main reason of their inherently enormous acidity.

In the literature, the substituent effects have been mainly differentiated as field-inductive, resonance, and polarizability[30−38]

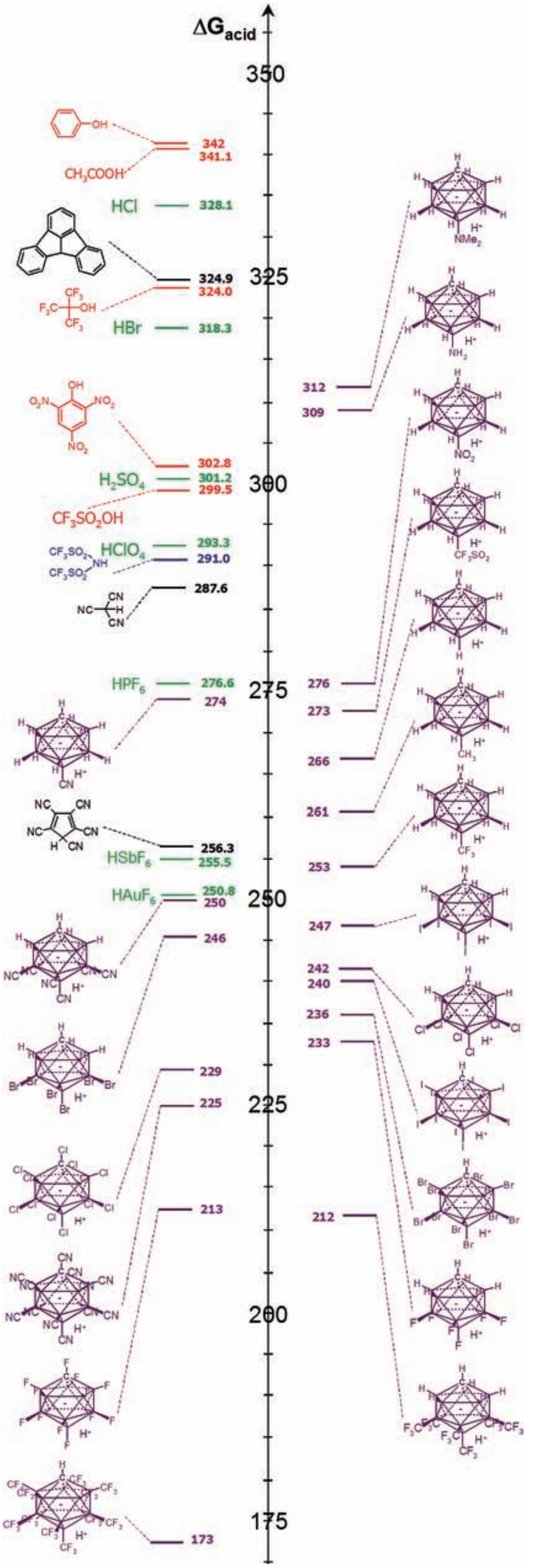

Figure 4. GA (kcal/mol, DFT B3LYP 6-311+G**) of some monocarba-*closo*-dodecaborate acid derivatives (Table 1) compared to a selection of Brønsted acids (refs 5, 33, 34).

effect. In addition, also simple protonation site shielding[11,12] has been suggested.

The interplay of the substituent effects is complex because of the strong dependence on the molecular structure. In this light, we have made DFT calculations to estimate the influence of the effects of the substituents on the reaction site by comparing the acidities of hypothetical monosubstituted carborane acids in isostructural series in which a single substituent is in the position 1, 2, or 7 and the protonation site is fixed at the same position as in the case of the unsubstituted carborane acid (B_{12}). The $\Delta\Delta G_{acid}$ values for these hypothetical derivatives, where $\Delta\Delta G_{acid} = \Delta G_{acid}(CB_{11}H_{11}X_1H) - \Delta G_{acid}(CB_{11}H_{12}H)$, are presented in Table 3. The energies of the individual compounds are listed in Supporting Information.

TABLE 3: $\Delta\Delta G_{acid}$ Values (kcal·mol^{-1}) of Some Hypothetical Monocarba-*Closo*-Dodecaborate Acid Derivatives Protonated on B_{12} Relative to the Unsubstituted $CB_{11}H_{12}H$

substituent	C1[a]	B2[a]	B7[a]
CH_3	0.5	0.7	−0.1
NMe_2	0.2	0.3	−0.3
t-Bu	0.0	−0.7	−1.0
NH_2	−0.9	0.7	1.2
F	−4.7	−3.0	−4.2
Br	−5.3	−6.1	−7.4
Cl	−5.9	−6.6	−6.7
CF_3	−7.6	−8.1	−9.6
CN	−10.1	−9.9	−11.9
NO_2	−11.4	−11.9	–[b]
CF_3SO_2	−14.1	−10.3	–[b]

[a] Location of the substituent on the carborane cage (see Figure 1). [b] During the geometry optimization proton drifted onto oxygen.

Within this isostructural series $-CH_3$ and $-NMe_2$ had only marginal influence on the acidity, and the *t*-Bu-substituent attached to B_2 and B_7 vertexes made the system 0.7 and 1.0 kcal·mol^{-1} more acidic, respectively. When bound to C_1, no change was noticed. The $-NH_2$, when placed on the C_1, reduced the basicity of the protonation site, but on the boron vertexes, the result was opposite. From the halogen-containing substituents, CF_3SO_2 had the strongest acidifying effect followed by $-CF_3$. By their effect on the anions' gas-phase basicity $-Cl$ and $-Br$ were similar and substitution with $-F$ had at least an order of magnitude smaller effect than the latter two. Because of the distal oxygen atoms, the results of NO_2- and CF_3SO_2-substituted derivatives were not usable in the data set of B_7 since during the geometry optimization proton drifted away from its initial location on B_{12} to the oxygen atoms of the substituents.

The $\Delta\Delta G_{acid}$ values from Table 3 for the gas-phase proton transfer equilibria were statistically analyzed in the framework of the multilinear correlation equation:

$$\Delta\Delta G_{acid} = a_0 + b_1\sigma_F + b_2\sigma_\alpha + b_3\sigma_{R^-} \qquad (2)$$

The single or two parameter special cases using correlations of the gas-phase acidities of the above-mentioned hypothetical derivatives with the field-inductive (σ_F), polarizability (σ_α), and resonance (σ_{R^-}) constants[30,32] are given in Table 4.

When the substituents were positioned on C_1, that is, antipodal position to the reaction center, the basicity of the anion was best described by σ_F and σ_{R^-} terms. The exclusion of more deviating points gave no improvement, and there was no notable and statistically reliable dependence of $\Delta\Delta G$ on polarizability effect as measured by σ_α. When the set of B_2-substituted derivatives' gas-phase acidities were set against the σ_F and σ_{R^-} parameters, the exclusion of CF_3SO_2 and CH_3 derivatives improved the correlation coefficient up to $R = 0.99$. The σ_α parameter, again, had no notable influence on the result. In the case of the series of B_7-positioned substituents (i.e., in the α

TABLE 4: Results of Data (Table 3) Processing According to Multilinear Correlation Eq 2

	a_0	b_1	b_2	b_3	R^a	s^b	$n/n_0{}^c$	t^d
C_1	1.23 ± 0.60	−17.7 ± 1.3			0.973	1.15	11/11	0.99
	1.88 ± 0.89	−17.8 ± 1.3	1.66 ± 1.20		0.974	1.14	11/11	0.999
	0.10 ± 0.37	−15.4 ± 0.7		−6.74 ± 1.11	0.995	0.517	11/11	0.99
B_2	0.97 ± 1.00	−16.0 ± 2.2			0.971	1.91	11/11	0.99
	−0.45 ± 1.06	−13.1 ± 2.0		−8.48 ± 3.16	0.952	1.47	11/11	0.999
	−0.15 ± 0.59	−15.2 ± 1.2		−10.3 ± 1.9	0.984	0.84	10/11[e]	0.99
B_7	0.96 ± 1.19	−18.6 ± 3.3			0.891	2.12	9/9	0.99
	3.30 ± 1.46	−19.9 ± 2.7	5.31 ± 2.45		0.93	1.72	9/9	0.999
	0.46 ± 0.77	−17.7 ± 1.2	2.02 ± 1.2	−11.0 ± 2.0	0.988	0.724	9/9	0.999
	−0.66 ± 0.58	−17.0 ± 1.3		−12.7 ± 2.0	0.984	0.827	9/9	0.99
	−0.40 ± 0.44	−17.6 ± 1.0		−14.4 ± 1.6	0.992	0.591	8/9[f]	0.95

[a] *R* - correlation coefficient. [b] *s* - standard deviation. [c] n_0 - total number of points involved in the correlation, *n* - the number of points remaining after the exclusion of significantly deviating points. [d] *t* - confidence level. [e] The CF_3SO_2-derivative was excluded. [f] The $(CH_3)_2N$-derivative was excluded.

position to the reaction center on the B_{12} vertex) besides the field-inductive and resonance effects also the inclusion of σ_α, polarizability constants somewhat improved the overall correlation. It is evident that the contribution of the field-inductive effect into the overall substituent effect is dominant for all three series of positions, B_7, B_2, and C_1. The share of the $b_1\sigma_F$ term for the substituents with significant σ_F values was 7 to 36 times larger than the corresponding $b_2\sigma_\alpha$ and 3 to 16 times larger than $b_3\sigma_{R^-}$. Statistically important contribution belongs also to the resonance-effect term, whereas it is difficult to find similar proof for the polarizability effect for the positions B_2 and C_1. With some probability, the polarizability effect could be present in the case of B_7-positioned substituents; thus, one could recognize a pattern similar to the correlation of gas-phase acidities of 4-substituted benzoic acids,[39] where the contributions of the field-inductive and resonance effect were found to be dominant. In confirmation of these findings, the NBO second order perturbation theory analysis of the derivatives showed very strong stabilizing (LP−LP*) interactions between the lone pairs and empty nonbonding orbitals of the neighboring boron atoms (the electron pair can be on two different LP-type orbitals with close energetic values), and the NBO analysis found the occupation of the valence non-Lewis orbitals 13% and more. A feature that should attract attention is the smaller than expected change in the acidities, when the distance between protonation and substitution sites is varied. That, together with the significance of the σ_R term in the intrinsic gas phase acidity correlations (Table 4), could be considered as the indications of aromaticy[40] of carboranes.

Carborane Acids of Different Size. If the computational results for carborane-based systems with different sizes of the boron cage [$CB_4X_nH_{5-n}H$, $CB_5X_nH_{6-n}$ (X = F, Cl, or CF_3)[9] and $CB_{21}H_{22}H$[41] (Table 1)] are set against each other, it is possible to bring out the following trends. With the increasing volume of the anion, the basicity-reducing effect of larger surface area decreases. The monocarba-*closo*-dodecaborane derivatives stand on a kind of borderline where single-substituent systems still have the acidity ranking similar to the monocarba-*closo*-penta- and -hexa-boranes[9] (Figure 5): F → Cl → CF_3. But in the case of the corresponding 22-vertex F and Cl derivatives, the intrinsic gas-phase acidities are already nearly equal.

Carborane Acids and the Infrared νNH Scale.[10] Several attempts to evaluate the Brønsted acidities of very strong acids in different indirect ways[10−12] have been made recently. The most intriguing of them is the measurement[10,42] of NH stretching frequency shifts of Oct_3NH^+ in CCl_4, induced by H-bond formation between this proton donor and a superweak anionic base. We have extended the $\Delta\nu$NH plot of carborane acids versus the gas-phase acidities given in ref 10. The undecahalogeno and hexaiodo derivatives give a very good linear correlation ($y = 0.2388x + 206.45$; $R^2 = 0.997$; Figure 6).

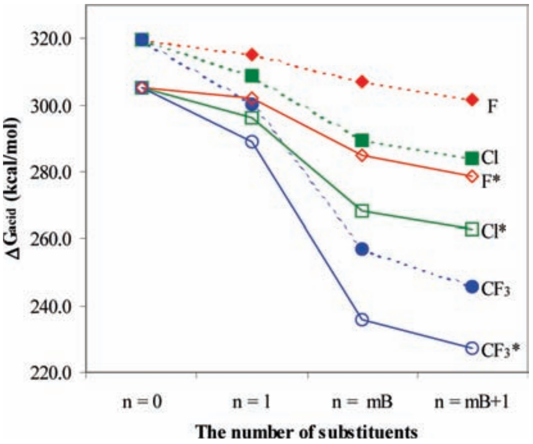

Figure 5. Ranking of intrinsic acidities of $CB_4X_nH_{5-n}H$ (X = F, Cl, CF_3) and $CB_5Y_nH_{6-n}H$ (Y = F*, Cl*, CF_3*) derivatives based on the substitution degree where *n* is the number of substituents and *m*B is the number of boron vertexes (4 or 5 depending on the system) in the carborane clusters.

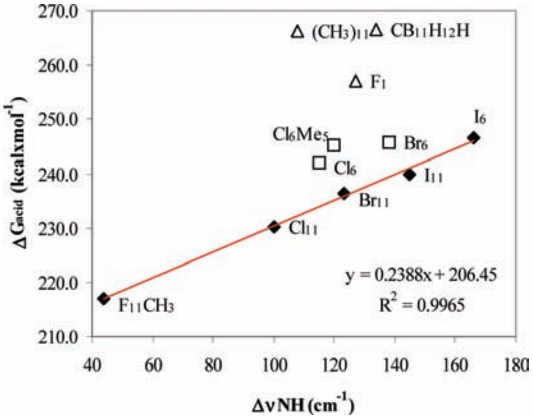

Figure 6. $\Delta\nu$NH values of some carborane superacids plotted against their calculated intrinsic gas-phase acidities. The acids corresponding to the substituents on the labels can be found in Table 5.

Although, the hexa-iodo carborane anion is isostructural to $CB_{11}Br_6H_6^-$, $CB_{11}Cl_6H_6^-$, and $CB_{11}Cl_6(CH_3)_5^-$, its conjugate GA fits better with the linear relationship of carborane acids with higher degree of substitution. Nevertheless, if all presented polysubstituted derivatives (Table 5) are included in the plot, the R^2 value is significantly reduced. As the protonation site of

TABLE 5: ΔG_{acid} Values (kcal·mol^{-1}) of Some Carborane Acid Derivatives and Their Corresponding $\Delta\nu$NH Values[a] (cm^{-1})

acid	$\Delta\nu$NH	$\Delta G_{\mathrm{acid}}^{\mathrm{calc}}$
$CB_{11}H_{12}H$	134	266.5
$CB_{11}(CH_3)_{11}H_1H$	108	266.2
$CB_{11}F_1H_{11}H$	127	257.2
$CB_{11}Br_6H_6H$	138	245.8
$CHB_{11}Cl_6Me_5H$	120	245.2
$CB_{11}Cl_6H_6H$	115	242.0
$CB_{11}I_6H_6H$	166	246.7
$CB_{11}I_{11}H_1H$	145	240.0
$CB_{11}Br_{11}H_1H$	123	236.3
$CB_{11}Cl_{11}H_1H$	100	230.3
$CB_{11}F_{11}CH_3H_{11}H$	44	217.0

[a] The acidities are acquired from ref 5 and present calculations; $\Delta\nu$NH values originate from ref 10.

$CB_{11}(CH_3)_{11}H_1^-$ is very near to the boron cage, in the case of $HCB_{11}H_{12}$ and in protonated $CB_{11}F_1H_{11}^-$, the H−H hydrogen bond distance refers to significant covalent character. It is possible that it makes it difficult for the rather bulky Oct_3NH^+ probe to adequately model all (including steric) interactions.

Conclusions

The protonation geometries and acidities of 32 monocarba-*closo*-dodecaborate acid derivatives with different degrees of substitution were investigated with DFT B3LYP method at 6-311+G** and 6-311++G** levels and with the high-level G3(MP2) approach. The protonation sites and thus the GA values were found to be highly dependent on the properties of the substituents. The most acidic systems were the ones that had vertexes filled with CF_3 and F substituents.

To obtain a better understanding how the substituents affect the basicity of the carborane anion, three hypothetical reaction series were investigated, in which the protonation center was fixed on the boron atom (B_{12}) and a single substituent replaced the hydrogens at the vertexes of the three different remaining positions (C_1, B_2, and B_7). The intrinsic GA values in these series of neutral carborane-based acids, $CB_{11}H_{12}X$, clearly depend on the field-inductive and resonance effects of the substituent X. Some polarizability effect of X on the reaction center (B_{12}) could be detected only in the alpha position (B_7).

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Supporting Information Available: Full details of quantum chemical calculations of Table 1 (Tables S1−S76); HF, ΔH, and ΔG values of the species in Table 3 (Tables S77−S79); the results from Table 3 set against the σ_I, σ_α, and σ_R parameters and the resulting correlation data (Table S80); complete ref 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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