

Why Are Carborane Acids so Acidic? An Electrostatic Interpretation of Brønsted Acid Strengths

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Acidity of Brønsted acids is explained in terms of the electrostatic potentials of the corresponding conjugate bases. The electrostatic potential distribution on the zero-flux surface of the *strongest isolable* carborane anions is seen to provide a good measure of their acidities. Increasing value of the lowest minimum in the electrostatic potential is observed to be a signature of increasing acidity.

The *strongest isolable acids*, as demonstrated via their stabilization of the benzenium ion in salts and the carbocation in dichloromethane, have been of recent interest.^{1–4} The acidities of the compounds of this class, viz., [CHB₁₁R₁₁]H, [CHB₁₁X₁₁]H, and [CHB₁₁R₅Cl₆]H (with R = H, CH₃ and X = Cl, Br, I), have been attributed to *their anions being exceptionally weak bases*. Inertness of these anions has been attributed to, quoting Reed and co-workers verbatim:¹ (i) *the large size of the anions*, (ii) *the delocalized nature of the negative charge of these anions*, and (iii) *the shield of the halide substituents*. Moreover, these compounds have been labeled as *the strongest acids that could be stored in glass*, alluding to the inertness of their bases derived from a σ aromaticity within the [CB₁₁][−] icosahedral cage.¹ The structures, free energies, and heats of formation of these acids have been calculated earlier, and they have been ranked high in scales of calculated gas-phase acidity.⁵ However, the question as to *why are they acidic* still needs an analysis and interpretation in terms of their fundamental electronic properties. In this Communication, we attempt to give a simple physical explanation and quantification for Brønsted acidity by analyzing the theoretically evaluated molecular electrostatic potential⁶ (MESP) of the respective conjugate bases/anions.

MESP is defined as the work done in bringing a unit test positive charge from infinity to a point of reference. For a

molecule with positive point charges {Z_A} at nuclear position vectors {R_A} and a negatively charged continuous charge density $\rho(\mathbf{r})$ at all points in space, the MESP, $V(\mathbf{r})$ (in au), is given by

$$V(\mathbf{r}) = \sum_A Z_A / |\mathbf{r} - \mathbf{R}_A| - \int \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d\mathbf{r}' \quad (1)$$

This classical definition of MESP itself suffices to show why it should be a good indicator of acidity. Negative regions of the potential generally are the sites preferred for electrophilic attack, and with the bare proton being a first-order approximation to a unit point positive charge, it would be indeed interesting to relate Brønsted acid strengths with MESP.

A simple way of analyzing the acidities of the carboranes would be to concentrate on the MESP of the corresponding conjugate bases. The MESP of any negatively charged molecule has certain interesting properties, as proven by Gadre and Pathak.⁹ Anions are characterized by the existence of a charge neutral surface from Gauss' theorem (in au) in classical electrostatics,^{6,9} which is as expressed by eq 2. Here,

$$\int \nabla V \cdot d\mathbf{S} = q \quad (2)$$

∇V is the gradient of the electrostatic potential V , $d\mathbf{S}$ is a surface element associated with a unit outward normal, which defines the orientation of the surface \mathbf{S} , and q is the charge enclosed. For all anions, there exists an outer surface covering it, enclosing zero charge, which is defined by the following equation.⁹

- (6) For a detailed review on molecular electrostatics, see: Gadre, S. R.; Shirsat, R. N. *Electrostatics of Atoms and Molecules*; Universities Press: Hyderabad, India, 2000.
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$$\nabla V \cdot dS = 0 \quad (3)$$

The net charge of the anion thus resides outside this surface, and the charge density outside integrates to the integral charge of the anion.⁹ This surface thus forms a natural boundary of an anion that is uniquely defined and is less arbitrary than the van der Waals surface or the 0.001/0.002 au-valued isosurface of the charge density. The surface is anisotropic and has a finite extent defining a proper shape.⁹ It is also characterized by being the one that includes all of the directional minima of the electrostatic potential.

The MESP of carborane anions has been calculated using the in-house developed property evaluation package IND-PROP⁷ from the corresponding wave functions obtained from *Gaussian 03*⁸ suite of programs at Hartree-Fock/6-311++G-(2d,2p) optimized geometries. All of the calculations reported here are in the gas phase. Zero-flux surfaces and isosurfaces for analyzing MESP were plotted using the in-house-developed graphics package UNIVIS-2000.⁷ MESP, $V(\mathbf{r})$, on this surface is analyzed for the conjugate bases, and the minimum values are reported in Table 1.

The anion of the strongest acid $[\text{CHB}_{11}\text{Cl}_{11}]^-$ has the least-negative-valued minimum in MESP of value -0.131 au. The trend in V_{\min} follows the experimental trend as given by N-H stretching frequencies of the salts of the bases with tri-*n*-octylammonium.¹ The trend in the values is followed for all of the cases barring $[\text{CHB}_{11}\text{H}_3\text{Br}_6]^-$, with V_{\min} showing that the corresponding acid is stronger compared to the other carborane acids. This case, however, does fall in line with a scale of acidities from the ¹³C NMR measurements of protonated mesityl oxide¹ and even a previous PM3 characterization of acidities by heats of formation.⁵ The deviations, in general, could perhaps be attributed to volume/polarizability effects. Higher wavenumbers are indicative of higher acidity because the less stronger the binding of the conjugate base with N-H, the stronger the N-H bond and the higher the wavenumber and, hence, the less reactive is the conjugate base. V_{\min} values in Table 1 evidence the trend in acidity followed by the carborane acids, with low negative values being indicators of high acidity.

It is worthwhile wondering why the MESP is more negative in certain regions/for some species. The negativity of the MESP is an interplay between the nuclear potential and the potential due to the continuous charge density. It has been reported before by Suresh and Gadre¹⁰ how substituent effects, such as electron-withdrawing effects, inductive effects, electron-donating effects, and aromaticity, are manifested in the MESP. Electron-donating groups tend to make regions over the aromatic ring more negative, and electron-withdrawing groups make the potential more positive. A comparison of the anions $[\text{CHB}_{11}\text{Cl}_{11}]^-$ and $[\text{CHB}_{11}\text{F}_{11}]^-$ itself is an exemplification of the above statement. Fluorine, being more electronegative, renders the minima on the zero-flux surface much more negative as compared to the chlorine substituents, whose minima are less negative. The polarizability/polarizing power of the substit-

Table 1. V_{\min} , the Minimum of MESP on the Zero-Flux Surface, V_{av} , the Average on the Surface, V_{σ} , the Standard Deviation, and V_0 , the Volume of the Surface for the Conjugate Bases of Carborane Acids^a

conjugate base	V_{\min} (V_{av} , V_{σ})	V_0 (\AA^3)	$\nu_{\text{N-H}}^b$
$[\text{CHB}_{11}\text{Cl}_{11}]^-$	-0.131 (-0.107, 0.015)	301.4	3163
$[\text{CHB}_{11}\text{Me}_{11}]^-$	-0.131 (-0.110, 0.022)	410.5	3156
$[\text{CHB}_{11}\text{H}_3\text{Br}_6]^-$	-0.145 (-0.120, 0.027)	380.7	3125
$[\text{CHB}_{11}\text{H}_3\text{Cl}_6]^-$	-0.151 (-0.116, 0.025)	229.6	3148
$[\text{CH}_{11}\text{Me}_3\text{Cl}_6]^-$	-0.154 (-0.119, 0.028)	301.4	3143
$[\text{CHB}_{11}\text{F}_{11}]^-$	-0.154 (-0.125, 0.020)	173.5	
$[\text{CHB}_{11}\text{H}_{11}]^-$	-0.159 (-0.137, 0.017)	142.5	3129
$[\text{CHB}_{11}\text{H}_3\text{F}_6]^-$	-0.174 (-0.130, 0.030)	152.0	
$[\text{CF}_3\text{SO}_3]^-$	-0.233 (-0.210, 0.035)		
$[\text{NO}_3]^-$	-0.272 (-0.234, 0.024)		
$[\text{CH}_3\text{COO}]^-$	-0.314 (-0.294, 0.068)		

^a All of these values are in atomic units. ^b N-H frequencies (in cm^{-1}) of corresponding tri-*n*-octylammonium salts in CCl_4 as given in ref 1.

uents is also inherent in the continuous charge density (which is obtained from a quantum mechanical calculation), and hence the potential due to this density would show the effects as are evident in the V_{\min} values tabulated.

Volume of the zero-flux surface, designated as V_0 is a measure of the size of the anions, which is one of the factors determining their acidity. The trend in the volumes also follows, as expected, with highly acidic carboranes having larger volumes. However, V_0 does not appear to be the only criterion for acidity, as may be noticed from Table 1. A further detail on the nature of the potential is brought out by the average values of MESP on the zero-flux surface (V_{av}) and the standard deviation (V_{σ}), with V_{av} generally decreasing with increasing acidity. The V_{σ} values show that the variation in MESP on the zero-flux surface generally decreases with increasing acidity.

The conjugate bases of the protic acids HNO_3 and CH_3COOH and the strong acid HCF_3SO_3 have also been examined for the sake of comparison of the acidic strengths from MESP minima on the zero-flux surface. All of these acids are deemed much weaker than the carborane acids, and within themselves, they show an ordering of $\text{HCF}_3\text{SO}_3 > \text{HNO}_3 > \text{CH}_3\text{COOH}$.

Figure 1 exhibits the electrostatic potential maps of some of the conjugate bases, including those corresponding to the strongest one. The MESP maps are interpreted in terms of isosurfaces, and in the present context, -0.125 au isosurfaces have been plotted. Generally, negative-valued isosurfaces enclosing high-negative-valued regions would be larger in extent. In Figure 1, $[\text{CHB}_{11}\text{H}_{11}]^-$ is almost covered completely by the isosurface, while the least negative and most acidic $[\text{CHB}_{11}\text{Cl}_{11}]^-$ just has a small region opposite to the CH, the lower end of the skeleton. In addition, it is evident that the minimum of MESP is between the two chlorines at the lower end of the boron cage and the minima are considerably less negative than those of the fluorine-substituted systems. The difference in binding of the proton for the chlorine-substituted anions and the fluorine-substituted ones is also qualitatively and quantitatively brought out by the MESP maps. For the chlorine-substituted ones, it is more likely that the proton is shared between the chlorines, as has been observed previously.⁵ A common feature of all of the

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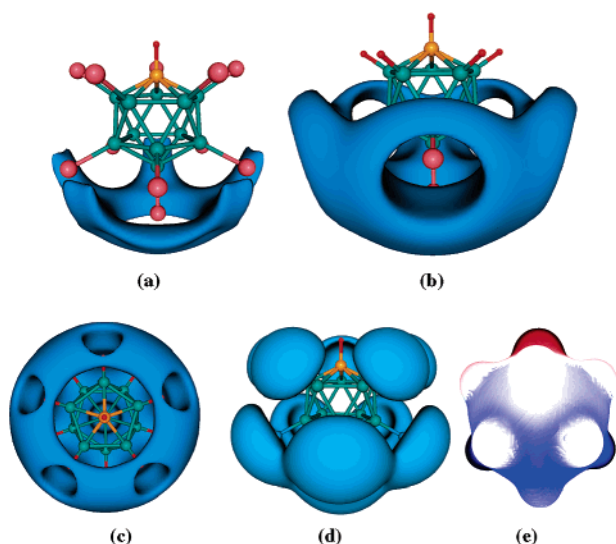


Figure 1. Depiction of -0.125 au MESP isosurfaces for (a) $[\text{CHB}_{11}\text{Cl}_{11}]^{-}$, (b) $[\text{CHB}_{11}\text{H}_5\text{Cl}_6]^{-}$, (c) $[\text{CHB}_{11}\text{H}_{11}]^{-}$ (viewed from the top, with HC pointing out of the plane of the paper), and (d) $[\text{CHB}_{11}\text{F}_{11}]^{-}$. Part e shows the charge neutral outer surface for $[\text{CHB}_{11}\text{H}_{11}]^{-}$, with the MESP being textured as red for low negative values, blue for high negative values, and white for intermediate values.

carborane acids is the nature of the potential, with its variation starting from the CH hydrogen to the diametrically opposite substituents. The textured zero-flux surfaces for all of the anions are qualitatively similar, with the most negative region being around the substituents diametrically opposite to CH.

Apart from these general characteristics of acidity, it is necessary to examine the stated reasons¹ for the acidity of the carborane acids and the inertness of their conjugate bases. An important factor is the size of these anions, which is quantified in terms of the volume of the zero-flux surface (cf. Table 1). The volumes of these anions are considerable, and they do indeed have an effect on the acidity, although the volume is *not* the sole determining factor. The second factor remarked upon in ref 1 is the *delocalized* negative charge of the conjugate bases. This is quantified in terms of the standard deviation of the MESP on the zero-flux surface. From Table 1, it is seen that these values do indeed show the same trend in acidity, with V_σ generally being lower with increased acidity. Why does a low variation in MESP contribute to the acidity? The low variation of MESP implies that the probability of a proton binding to different sites is now geometrically smeared without a localized deep negative region that is favored, hence the increase in acidity. The third factor as stated previously has been discussed in detail before, with shielding of the halide substituents being reflected in the values of MESP.

The chemical inertness of their conjugate bases has been one of the most remarkable features of these acids. This has been attributed to the rigidity of the icosahedral boron skeleton and a delocalization of the σ -bonding electrons resulting in a σ aromaticity. The topographical features⁷ of MESP and electron density reminiscent of bonding do give an intuitive picture of this, with the average values of MESP at the bond critical points (BCPs) and ring critical points decreasing with increasing acidity. In a comparison of

$[\text{CHB}_{11}\text{H}_{11}]^{-}$ and $[\text{CHB}_{11}\text{Cl}_{11}]^{-}$, the potential is lower at the BCPs for the latter. In addition, it is seen that the electron density at BCP increases for $[\text{CHB}_{11}\text{Cl}_{11}]^{-}$. Yet another noteworthy feature of the bonding topography is the slight displacement of the BCPs from the internuclear lines, with the angle deviation of the BCPs being an average of 2° . This feature is generally observed in strained systems, but considering the rigidity of the structure involved, this angle deviation could be attributed to a delocalization of the bonding density. The σ aromaticity in these structures is indeed interesting, and a quantification of this in terms of the topography of its properties requires an in-depth study.

A comparison of the acidity of the carboranes in terms of the features presented does indicate a general scale of acidities from electrostatics. In a comparison with standard monoprotic acids such as HNO_3 and CH_3COOH and strong acids such as triflic acid, the carborane acids are on a scale of higher acidity (in electrostatic terms). Within themselves, the carborane acids show a trend of $[\text{CHB}_{11}\text{Cl}_{11}]^{-} > [\text{CHB}_{11}(\text{CH}_3)_{11}]^{-} > [\text{CHB}_{11}\text{H}_5\text{Br}_6]^{-} > [\text{CHB}_{11}\text{H}_5\text{Cl}_6]^{-} > [\text{CHB}_{11}(\text{CH}_3)_5\text{Cl}_6]^{-} > [\text{CHB}_{11}\text{F}_{11}]^{-} > [\text{CHB}_{11}\text{H}_{11}]^{-} > [\text{CHB}_{11}\text{H}_5\text{F}_6]^{-}$ with respect to the minimum values of the electrostatic potentials of the anions. The scale of acidity presented here shows good agreement with the experimental observations (N–H stretching frequencies of the corresponding trioctylammonium salts), barring possibly the case of $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^{-}$. This case, however, falls in line with other results^{1,5} as mentioned before. Perhaps, the inclusion of a polarization correction to MESP¹¹ would be able bring out subtleties in the scale. However, this would result in a loss of simplicity in the proposed model, which utilizes just the scalar field of MESP. The scale proposed in this work predicts the fluorine-substituted carborane acid to be less acidic than the chlorine-substituted ones. This is in contrast to the expectations put forth by Reed and co-workers,¹² who have stated that the fluorine-substituted carborane acids would be more acidic. It would be very interesting to check the predictive nature of the electrostatic effects as and when the fluorine-substituted carborane acids are experimentally viable. Yet, another consideration is a comparison of the electrostatic scale with the calculated gas-phase ΔG_{acid} values given by Koppel et al.⁵ The scale given falls in line with the only exception of the fluorine-substituted ones.

The general reasons for strong Brønsted acidity have always been given in terms of chemical concepts such as resonance stabilization of the conjugate base and conjugative, hyperconjugative, and aromatic effects, all of which manifest intuitively in the electrostatic potential, a direct measure of reactivity.

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Supporting Information Available: Complete ref 8 and structures and energies of the carborane anions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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