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The Structure of the Strongest Brønsted Acid: The Carborane Acid $H(CHB_{11}Cl_{11})$

Evgenii S. Stoyanov, Stephan P. Hoffmann, Mark Juhasz, and Christopher A. Reed*

Center for S and P Block Chemistry, Department of Chemistry, University of California, Riverside, California 92521

Received December 19, 2005; E-mail: chris.reed@ucr.edu

Carborane acids are a new class of protic acids notable for their "strong yet gentle" properties that allow the isolation of reactive cations (e.g., HC_{60}^+, $C_6H_7^+$, *t*-butyl cation, H_3O^+, $H_5O_2^+$).[1,2] As a class, they are stronger than previously known Lewis-free Brønsted acids (CF_3SO_3H, FSO_3H, etc.), and the carborane acid having 11 chlorine substituents on the boron cluster, $H(CHB_{11}Cl_{11})$, is presently the strongest and most robust.[3] Until now, their structures have been unknown. Herein, we report IR and X-ray data that establish their gas and solid phase structures.

Anhydrous carborane acids are sublimable solids. When $H(CHB_{11}Cl_{11})$ is heated under vacuum in an IR gas cell, the spectrum of the gaseous acid begins appearing at ca. 170 °C (initial pressure 10^{-5} Torr), and its intensity increases progressively without changes in band frequencies up to 230 °C (Figure 1). A broad, asymmetric band with a maximum at 2332 cm^{-1} is assigned to νHCl vibrations. Weak superimposed bands at 2065, 1955, and 1909 cm^{-1} are overtones of anion vibrations. The broadness and lower frequency of the νHCl absorption compared to the sharp νHCl band of gaseous HCl (2886 cm^{-1}) indicates involvement of the proton in intramolecular Cl−H···Cl-type H-bonding. The asymmetric contour can be deconvoluted into two components at 2357 and 2066 cm^{-1} with ca. 6:5 abundance ratio, suggesting the presence of two distinct isomers of the gaseous acid, labeled **A** and **B**, respectively. When normalized to unit intensity, the band contour does not change measurably within the temperature range of 180−230 °C, so **A** and **B**, if in equilibrium, differ little in energy.

Earlier[4] and present DFT calculations yield monomer structures that are consistent with these data. There are two low energy structures (Figure 2), one having the acidic proton bound to Cl at the 12 position with significant secondary H-bonding to Cl at the 7 position (assigned to **A**), the other having a more equally shared proton at the 7,8-Cl positions (assigned to **B**). The slightly greater basicity of Cl at the 12 position compared to that at the 7,8 positions results in greater inequivalence in the Cl−H···Cl bonding in **A** relative to **B**, consistent with the higher frequency and smaller bandwidth of νHCl in **A**. Isomer **A** is calculated to be 1.3 kcal mol^{-1} lower in Gibbs energy than **B**, consistent with its higher observed abundance. A 2,7 isomer is calculated to be 2.9 kcal mol^{-1} higher in energy than **B** and may also be present. The existence of related 7 and 12 isomers of alkyl carboranes with a low barrier to interchange has recently been established by NMR spectroscopy.[5]

Upon cooling the IR cell, the gas phase acid condenses onto the windows. In the νHCl frequency range, the spectrum of the freshly condensed acid (Figure 3b) is very similar to that for the gas phase, indicating that monomeric structures **A** and **B** are retained. A νCH band of the solid acid at 3023 cm^{-1} replaces that from the gas phase at 3034 cm^{-1} (Figure 3, left inset). The small red shifts of νCH and νHCl ($\Delta_{HCl} = 63$ cm^{-1} for both **A** and **B**) are consistent with the phase change. The spectrum of the $CHB_{11}Cl_{11}^-$ anion is very similar in both phases (Figure 3, right inset).

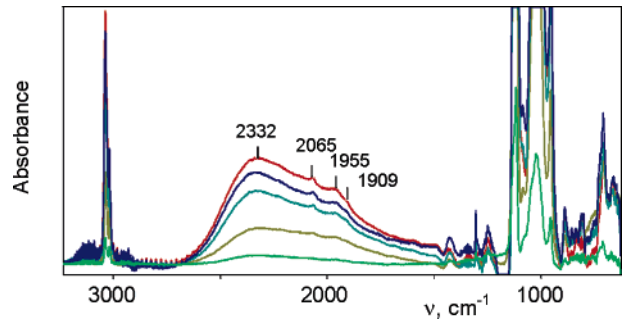

Figure 1. IR spectrum of $H(CHB_{11}Cl_{11})$ in the gas phase with increasing partial pressure and temperature, ca. 180 °C (green) to 230 °C (red).

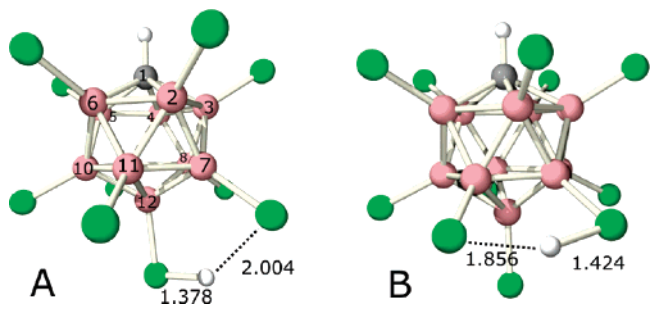

Figure 2. Carborane atom numbering scheme and DFT calculated structures of the 7,12 isomer (**A**) and the 7,8 isomer (**B**) of $H(CB_{11}Cl_{11})$ at the B3LYP/6-311+G(d,p) level. H−Cl distances in Å.

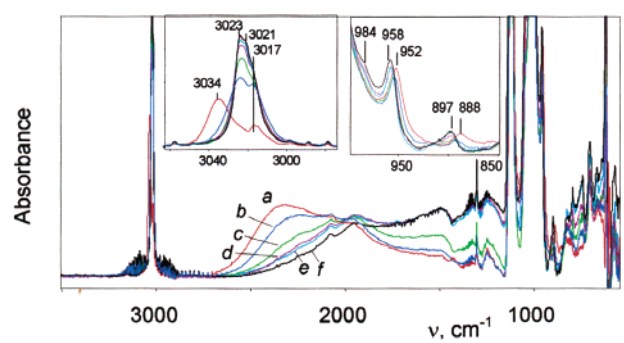

Figure 3. Dependence of IR spectra of $H(CHB_{11}Cl_{11})$ in the gas (*a*, red) and solid phases (*b*−*f*) on temperature (°C) and cumulative cooling time (min): (*b*) 230 (0), (*c*) 160 (2), (*d*) 130 (4), (*e*) 100 (7), (*f*) 55 (15).

The condensed phase monomeric structures are metastable, and upon aging of the acid film and decreasing the temperature, the IR spectrum in the νHCl region quickly decays with concomitant development of a strong continuous absorption in the range of 2200−1100 cm^{-1} (Figure 3c−f). This absorption is characteristic of acid dimers. Acids having polydentate oxyanions commonly dimerize, being stabilized by complementary pairs of strong H-bonds of the inequivalent O−H···O-type (e.g. in carboxylic,

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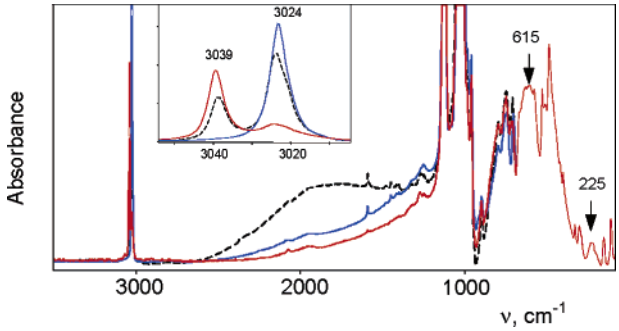

Figure 4. IR spectra of different sublimed films of $H(CHB_{11}Cl_{11})$: (a) the dimeric form (black, dashed) and two polymeric forms (b) with νCH at 3039 cm^{-1} (red, studied by X-ray) and (c) at 3024 cm^{-1} (blue).

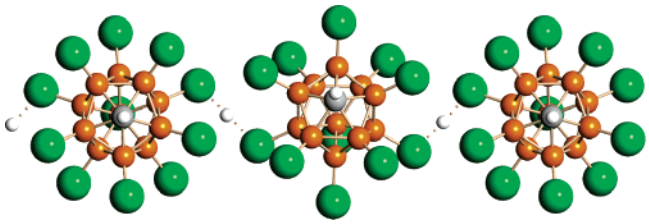

Figure 5. Perspective view of the proton-bridged X-ray crystal structure of $H(CHB_{11}Cl_{11})$ looking down the C−H bonds of the carborane anions (green = Cl, orange = B, gray = C, white = H).

dialkylphosphoric, dialkylphosphinic,[6] and nitric[7] acids). The low barrier to proton transfer between two minima of a double-well potential function is responsible for the appearance of a broad absorption for O−H···O stretching, for example, in the 3000−1500 cm^{-1} range for strong phosphoric acid dimers.[7] In the present case of Cl−H···Cl bonding, with a stronger acid and heavier atoms, the absorption lies at lower frequency, in the 2200−1100 cm^{-1} range. The dimeric form of $H(CHB_{11}Cl_{11})$ can be obtained directly by rapid sublimation using high sublimation temperatures (200−260 °C) and immediate condensation onto cold cell windows (Figure 4a).

With more gradual sublimation over longer time periods (≥1 h) at lower temperatures (180−200 °C), a new IR spectrum of a visibly crystalline solid phase is observed (Figure 4b,c). The appearance of sharp νCH bands from the carborane anion at 3039 and 3024 cm^{-1} (Figure 4 inset) indicates the presence of two different crystalline phases. The relative intensity of these two bands varies according to the sublimation conditions with the 3039 cm^{-1} band typically being more abundant, although occasionally absent (Figure 4c). The Cl−H···Cl vibrations do not differ significantly between the two phases, indicating they have very similar structures. The carborane cluster bands (right inset of Figure 2) only distinguish between monomer and dimer/polymer structures.

A fragment of the crystalline phase (having νCH at 3039 cm^{-1}) was used for single-crystal X-ray determination. As shown in Figure 5, the structure contains linear polymeric chains with proton bridges between Cl atoms at the 7−11 positions of the carborane anions. These are indicated by short inter-anion Cl···Cl contacts and lengthening of the associated B−Cl bonds. The Cl···Cl distances involved in the two crystallographically independent Cl···H···Cl bridges are 3.171(3) and 3.209(3) Å, whereas all other Cl···Cl nonbonding contacts are >3.36 Å. The B−Cl bond lengths of unprotonated Cl atoms lie in the range of 1.745(10)−1.796(10) Å, whereas those associated with proton bridges are 1.831(10)−1.845(10) Å. The binding of the carborane anions to the acidic proton via Cl atoms from the 7−11 pentagonal belt rather than the slightly more basic 12 position (see monomer **A**, Figure 2) is probably a consequence of packing efficiency and statistical advantage. The same bias in the crystalline state toward the 7 rather than the 12 position was seen in the X-ray structure of *i*-$Pr(CHB_{11}Me_5Br_6)$.[5] The H atoms were located in the X-ray refinement of $[H(CHB_{11}Cl_{11})]_n$ with the following dimensions: for one Cl−H−Cl bridge, Cl−H = 1.28(9) and 1.92(10) Å, ∠Cl−H−Cl = 166(7)°; and for the other, Cl−H = 1.74(11) and 1.47(11) Å, ∠Cl−H−Cl = 179(8)°. While not conclusive, these data are consistent with somewhat unsymmetrical H-bonding and easy displacement of H along the trajectory between the Cl atoms.

If the Cl−H−Cl groups in the polymeric acid were symmetric with local $D_{\infty h}$ symmetry, only the doubly degenerate bend (ν_2) and the antisymmetric Cl−H−Cl stretch (ν_3) would be IR active. Bands corresponding to these vibrations are observed in the IR spectrum of the bichloride ion, HCl_2^-, which is a good structural model for the polymeric (and dimeric) carborane acid. In the solid state, the bichloride ion can be asymmetric or symmetric depending upon the cation,[8,9] and when asymmetric, the ν_1 symmetric Cl···Cl stretch becomes weakly IR active (~200 cm^{-1}). The polymeric acid has quite similar bands (Figure 4). Thus, the very broad and distorted band with maximum at ~1100 cm^{-1} is assigned to ν_3, the high intensity, broad band at ~615 cm^{-1} whose shape is distorted by Evans holes[10] is assigned to ν_2, and a weak low-frequency band at 225 cm^{-1} can be attributed to ν_1. The IR activity of ν_1 is consistent with the X-ray structure which indicates two types of ClHCl groups with different degrees of asymmetry. Together, the IR and X-ray data indicate strong, low-barrier, nearly symmetric H-bonding.

In summary, the gas and solid phase structures of $H(CHB_{11}Cl_{11})$ have been determined. Related data for $H(CHB_{11}H_5Br_6)$ (see Table in Supporting Information) indicate that these structures are general for carborane acids. The different structures have implications for acidity. With the highest νHCl frequency and the smallest Cl−H···Cl angle reflecting bond strain, the monomeric acid should show the highest acidity. Upon thermodynamically favored dimerization, angle strain in the Cl−H···Cl group is presumably relieved, the strength of the H···Cl bond increases, and the acid should express diminished acidity. In the polymeric crystalline phases, the Cl−H−Cl bonding is more nearly symmetrical and somewhat stronger than the dimer, so acidity will be further diminished. These differences may be important considerations when using gas and solid phase carborane acids to protonate the weakest bases.

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Supporting Information Available: Experimental details, IR spectra, DFT calculations, and X-ray structure details. This material is available free of charge via the Internet at http://pubs.acs.org.

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