Title

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Journal

Angewandte Chemie International Edition, 51(36)

ISSN

1433-7851

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Publication Date

2012-09-03

DOI

10.1002/anie.201203958

Peer reviewed

DOI: 10.1002/anie.201203958

Noncovalent Interactions

Evidence for C–H Hydrogen Bonding in Salts of *tert*-Butyl Cation[**]

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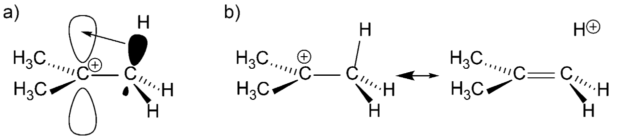
The *tert*-butyl cation[1] is an iconic intermediate in organic chemistry, with hyperconjugation being the textbook explanation for its stability. Positive charge is delocalized by donation of electron density from aligned C–H bonds into the formally empty $2p_z$ orbital on the cationic C atom, thereby giving partial double bond character to the C–C bonds, increasing the δ^+ charge on the H atoms, and lengthening the C–H bonds (Scheme 1).



Scheme 1. Two representations (a and b) of hyperconjugative delocalization of positive charge in the *tert*-butyl cation. In (a), a filled orbital is denoted in black.

The importance of hyperconjugation in isolated (i.e. gas-phase) *tert*-butyl cations has been thoroughly established by theory[2] and is substantiated by the outstanding agreement between the experimental gas-phase IR spectrum of argon-tagged $t\mathrm{Bu}^+$ ions obtained by photodissociation and that calculated for the C_s symmetrical structure.[3]

Hyperconjugation was invoked by Olah et al. in 1964 to explain the unusually low IR frequency of the C–H stretch (ν_{max} 2830 cm^{-1}) of $t\mathrm{Bu}^+$ ions in an SbF_5 superacid matrix.[4] Near coincidence with the ν_{max} value in the gas phase (2834 cm^{-1})[3] has left the impression that the same explanation solely rationalizes the stability of $t\mathrm{Bu}^+$ ions in condensed phases. We now show that this convergence of gas- and condensed-phase spectral data is fortuitous. The IR spectrum of $t\mathrm{Bu}^+$ ions in the solid state requires explanation not only in terms of hyperconjugation but also through hydrogen bonding, an idea first put forward by Hollenstein and Laube[5] when describing close contacts between methyl groups and the $Sb_2F_{11}^-$ counterion in the X-ray structure of a salt of a *tert*-butyl cation.

The *tert*-butyl cation is remarkably stable as the salt of an inert carborane anion.[6] Such salts are readily isolated either by abstraction of a hydride ion from butane with methyl carborane reagents[7] or by heating salts of diethylchloronium ions to 150 °C.[8] Figure 1 shows a representative solid-state IR spectrum of the $CHB_{11}Cl_{11}^-$ salt of $t\mathrm{Bu}^+$ with a νCH_{max} band at 2792 cm^{-1}. Comparison with the spectrum of the [D_9]-deuterated cation (dashed line) shows an H/D ratio of 1.366:1, thus confirming the essentially pure C–H stretching mode of this band.

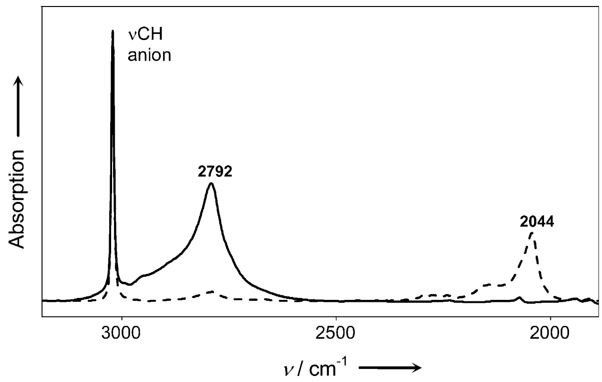


Figure 1. Solid-state IR spectrum of [$t\mathrm{Bu}^+$][$CHB_{11}Cl_{11}^-$] (solid line) and its deuterated cation analogue (dashed line).

The sensitivity of the $t\mathrm{Bu}^+$ ion to its environment differentiates stabilization by intermolecular hydrogen bonding from stabilization by intramolecular hyperconjugation. The νCH_{max} frequency of the $CHB_{11}Cl_{11}^-$ carborane salt is already 38 cm^{-1} lower than that in SbF_5 superacid media, and it moves even lower (as much as 88 cm^{-1}) as the carborane anion becomes more basic. A plot of the νCH_{max} value for $t\mathrm{Bu}^+$ salts versus anion basicity on the νNH scale[9] (Figure 2) shows a linear correlation. Since the νNH scale is based on a measure of hydrogen-bonding ability by IR spectroscopy, so too must the νCH value.

The νCH_{max} value for the *tert*-butyl cation in SbF_5 superacid media[4] cannot be added to this graph with certainty because the exact nature of the counterion (SbF_6^-, $Sb_2F_{11}^-$, $Sb_3F_{16}^-$ etc.) is unknown. Only the νNH value for SbF_6^- is known (88 cm^{-1}),[9] and the corresponding point for this counterion has been added to Figure 2. Since higher oligomeric $[SbF_6 \cdot n SbF_5]^-$ ions will have νNH values somewhat lower than that of SbF_6^-, we estimate that the correct datum point will lie quite close to the linear correlation line (arrow in Figure 2).

Also plotted in Figure 2 are νCH data for another iconic intermediate of organic chemistry, namely the $C_6H_7^+$ (arenium) ion. Stable salts of the benzenium ion are readily

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[**] This work was supported by the National Science Foundation (CHE-1144838) and the National Institutes of Health (GM 23851).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201203958.

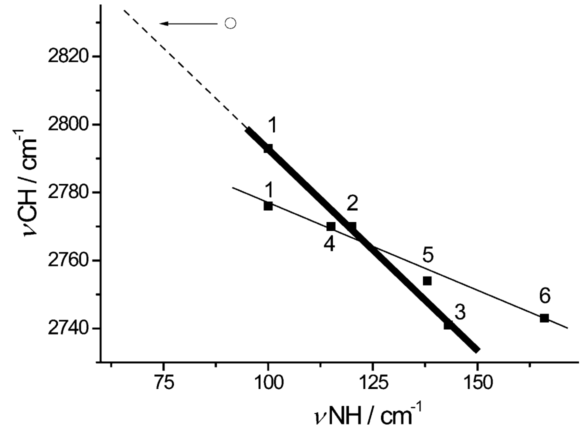


Figure 2. Correlation of νCH with anion basicity on the νNH scale for tBu$^+$ (bold line) and $C_6H_7^+$ (thin line) ions with $CHB_{11}Cl_{11}^-$ (1), $CHB_{11}Me_5Cl_6^-$ (2), $CHB_{11}Me_5Br_6^-$ (3), $CHB_{11}H_5Cl_6^-$ (4), $CHB_{11}H_5Br_6^-$ (5), and $CHB_{11}H_5I_6^-$ (6) counterions. ○ denotes SbF_6^-.

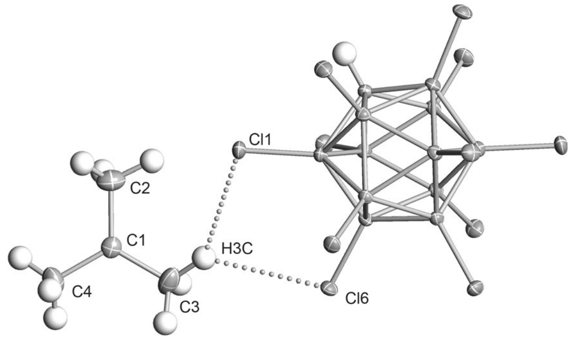
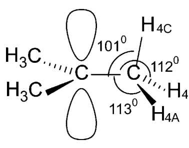


Figure 3. X-ray structure of [tC_4H_9][$CHB_{11}Cl_{11}$] showing a representative C–H···Cl asymmetric bifurcated hydrogen bond. Selected bond distances [Å]: C1-C2 1.452(1), C1-C3 1.443(1), C1-C4 1.451(1), C3-H3C 1.01(2), H3C-Cl1 2.98(2), H3C-Cl6 3.23(2). Angles [°]: C2-C1-C3 120.7(1), C2-C1-C4 119.4(1), C3-C1-C4 119.9(1), C3-H3C-Cl1 146(2), C3-H3C-Cl6 137(2).

prepared by protonation of benzene with carborane acids,[10] and [C_6H_7][$CHB_{11}Me_5Br_6$] has been characterized by X-ray crystallography.[11] Low-frequency νCH bands were noted in its IR spectrum and ascribed to ion pair C–H···Br interactions at the protonated C atom. The linearity of the plot of νCH versus anion basicity on the νNH scale further validates the importance of hydrogen bonding in carbocations. The flatter slope observed for the benzenium ion relative to that of the *tert*-butyl cation indicates weaker hydrogen bonding by the $C_6H_7^+$ ion. This can be readily understood in terms of efficient π delocalization of positive charge in the larger ion.

Not only is νCH_{max} for a tBu$^+$ salt unusually low, but the band is unusually broad compared to those of related cations such as the dimethylchloronium ion[8] or protonated methanol.[12] This broadening is an additional indicator of hydrogen bonding, and can be understood in terms of the variety of specific C–H···Cl interactions seen in the X-ray crystal structure of [tC_4H_9][$CHB_{11}Cl_{11}$].[13] The previous X-ray structures of *tert*-butyl cations[5,7] were obtained at lower resolution, whereas in the present structure the H atoms were located with reasonable certainty. As illustrated by a representative cation/anion interaction in Figure 3, most of the interactions of the C–H groups of the cation with the Cl atoms of the anion involve asymmetric bifurcated hydrogen bonding. All nine C–H groups have at least one H···Cl distance in the range 2.91(2)–3.29(2) Å, which is consistent with some degree of cation/anion interaction. Two of the C–H groups involve normal (monofurcated) hydrogen bonds with C–H···Cl angles near 163° and relatively short H···Cl distances in the range 2.91–2.95 Å. All nine C–H bonds in the cation are crystallographically independent, so each adds to the broadness of the νCH band.

As discussed for earlier X-ray structures,[5,7] the average 0.06 Å shortening of the C–C bond lengths compared to normal C(sp^2)–C(sp^3) bonds is widely taken as evidence for hyperconjugation. The higher resolution of the present structure enables further evidence for hyperconjugation to be found in the angles associated with the locations of the H atoms.[14] Perhaps remarkably, given its flat potential energy surface,[2] the planar view in Figure 3 reveals that the methyl groups of the cation in the solid-state structure sustain only minor rotational distortions from the idealized gas-phase C_s symmetry. Three C–H bonds are within 5–10° of optimal alignment with the vacant p_z orbital on the central C atom, which is consistent with near optimal hyperconjugative stabilization. As illustrated in Scheme 2 for a representative methyl group (C4), the C-C-H angle of the aligned C–H bond (101°) is about 10° more acute than the non-aligned ones, and is very close to the calculated gas-phase value (102°).[2a]



Scheme 2. Bond angle evidence for C–H(4C) bond hyperconjugation in the C4 methyl group.

Thus, both hyperconjugation *and* hydrogen bonding are present in solid-state salts of tBu$^+$ ions. Hydrogen-bonding interactions presumably also apply to the liquid phase, where anions and solvent molecules can act as hydrogen-bond acceptors. Only in the gas phase is hyperconjugation necessarily the sole mechanism for the dispersal of positive charge. Since nearly all practical reactions on hydrocarbons are carried out in condensed phases, the reality of hydrogen-bonding possibilities in carbocations deserves wider appreciation. For example, theory indicates that nonclassical carbocations are competent C–H bond donors to bases relevant to enzyme-catalyzed terpenoid synthesis.[15]

Traditionally, hydrogen bonding has been the province of hydrogen atoms bonded to elements more electronegative than carbon, typically oxygen and nitrogen. However, in the present age of weak interactions, hydrogen bonding involving intrinsically less polar bonds such as C–H and heavier acceptor atoms such as Cl has become more widely discussed.[16] In particular, C–H hydrogen bonding is favored as C–H bonds become acidic (e.g. in alkynes)[17] and when Cl is negatively charged.[18] It is evident in the present study that the hyperconjugatively delocalized positive charge on *tert*-butyl cations significantly enhances the ability of C–H bonds to engage in hydrogen bonding. In future work we will attempt to partition hyperconjugation from hydrogen-bonding effects and explore the extent of hydrogen bonding in other carbocations. Preliminary indications are that the phenomenon extends in alkyl cations only to CH groups that are α to the site of formal positive charge.

Experimental Section

Reactions and sample handling were carried out in Vacuum Atmospheres dry boxes (O_2, H_2O <1 ppm). The tBu$^+$ and [D_9]-tBu$^+$ salts of $CHB_{11}Cl_{11}^-$ were obtained by thermal decomposition of the corresponding protio- and deuterated diethylchloronium salts at 150 °C, as previously described.[8] The tBu$^+$ salts of $CHB_{11}Me_5Cl_6^-$ and $CHB_{11}Me_5Br_6^-$ ions were prepared as previously described in the Supporting Information.[7] Benzenium ion salts with $CHB_{11}Cl_{11}^-$, $CHB_{11}H_5Cl_6^-$, $CHB_{11}H_5Br_6^-$, and $CHB_{11}H_5I_6^-$ ions were prepared by wetting the corresponding carborane acids with liquid benzene and evaporating the excess benzene.[11]

IR spectra were recorded on a PerkinElmer Spectrum-100 spectrometer inside a dry box in transmission or ATR mode (4000–400 cm^{-1}), and the data manipulated using GRAMS/AI (7.00) software from Thermo Scientific.

Received: May 22, 2012

Keywords: carborane anions · hydrogen bonding · hyperconjugation · infrared spectroscopy · *tert*-butyl cations

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[13] CCDC 874494 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See Supporting Information for details.

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