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^{13}C Chemical Shift Tensor of the Isopropyl Cation

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Recent developments in theoretical and experimental methodologies have led to renewed interest in the structure and spectra of carbenium ions.[1,2] Reliable NMR chemical shift calculations are now possible with a variety of means, including the IGLO,[3] LORG,[4] GIAO[5] approaches, and with the inclusion of electron correlation.[6] Thus, Sieber, Schleyer, and Gauss were able to confirm the C_{2v} structure of the benzenonium carbenium ion and reproduce the experimentally determined isotropic chemical shifts using GIAO-MP2/tzp/dz calculations.[7]

A characteristic common to all carbenium shift calculations reported thus far is that they have discussed only the isotropic chemical shift which is observable in solution. We have recently reported measurements of the principal components, δ_{11}, δ_{22}, and δ_{33}, of the ^{13}C shift tensors for various carbenium ions synthesized on solid acids including zeolites and metal halide powders.[8,9] As demonstrated by the work of Facelli and Grant,[10] agreement between calculated and experimental values of all three principal components is a more stringent test of methodology than agreement of the averages.

We prepared the isopropyl cation by the adsorption of 2-bromopropane-*2*-^{13}*C* onto frozen SbF$_5$ at 223 K using methods similar to our previous work.[9] Figure 1 shows a ^{13}C CP/MAS spectrum of the isopropyl cation acquired at 83 K using a slow spinning speed to generate at least four orders of spinning sidebands. Analysis of these features using the method of Herzfeld and Berger[11] yields the experimental values $\delta_{11} = 497$ ppm, $\delta_{22} = 385$ ppm, and $\delta_{33} = 77$ ppm. The isotropic ^{13}C shift in Figure 1, 320 ppm, is within 1 ppm of the value in magic acid solution.[12] Other NMR evidence including dipolar dephasing experiments (not shown) and observation at higher temperature of a scalar doublet ($^1J_{\mathrm{C-H}} = 165$ Hz) proves that the species we observed is a secondary carbenium ion and not the tertiary cations that we obtain at higher temperatures by oligomerization and rearrangement (not shown) or directly from other precursors. Myhre and Yannoni used somewhat different methodology to observe the isotropic shifts of the *sec*-butyl cation in frozen SbF$_5$.[13] Those workers also concluded that the frozen SbF$_5$ matrix greatly restricts the dynamics of this cation, even at 213 K, and our experience with the isopropyl cation and other cations in this medium near 77 K is that large amplitude motions of the carbons can be discounted as a possible mechanism for averaging the chemical shift tensor.

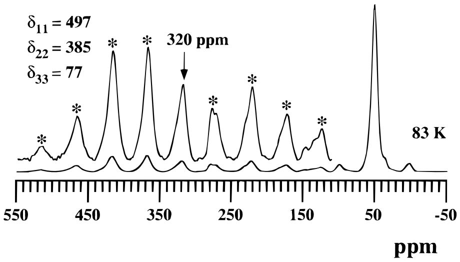

Figure 1. 75.4 MHz ^{13}C CP/MAS spectrum of the isopropyl cation in SbF$_5$ acquired at 83 K. The spinning speed for this experiment was 3681 Hz. Asterisks indicate spinning sidebands. The isotropic peak at 320 ppm is assigned to the center carbon for the isopropyl cation and at 51 ppm to the methyl carbons of the cation.

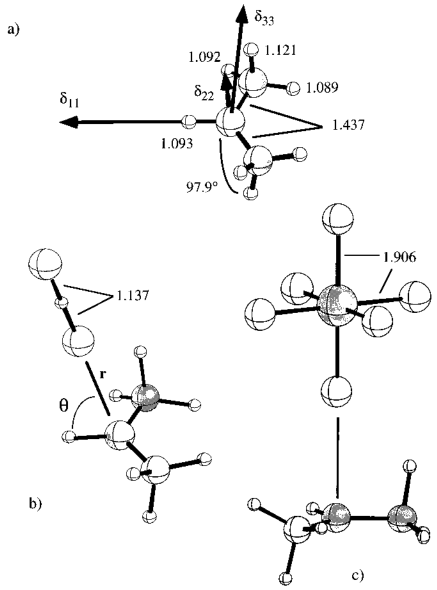

Figure 2. (a) MP2/6-311++G** optimized geometry of the C_2 isopropyl cation with selected bond distances in angstroms. The orientation of the chemical shift tensor for C_2 is indicated. (b) Isopropyl cation complexed with FHF$^-$; the values of **r** and θ are given in Table 1. (c) Isopropyl cation complexed with SbF$_6^-$.

Schleyer and co-workers performed MP2/6-311G(d,p) calculations of various geometries of the isopropyl cation, including single-point MP4 energies and zero-point energies, and predicted that the point group configuration of the lowest energy is C_2.[14] Our MP2/6-311++G**[15] optimizations confirm the important features of Schleyer's findings, and our C_2 structure is shown as Figure 2a.

We calculated the chemical shift tensor of the isolated cation using the GIAO-MP2 implementation of Gauss,[6,16] with tzp (C) and dz (H) basis sets,[17] using Cartesian functions under general

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Table 1. Theoretical and Experimental Principal Components (δ_{11}, δ_{22}, and δ_{33}) and Isotropic Chemical Shift[a] (δ_{iso}) of the ^{13}C Chemical Shift Tensor for the Isopropyl Cation[b]

system	method	**r**, θ (Å, deg)	δ_{iso} (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
C_2	RHF		341	562	443	19
C_2	MP2		328	545	409	30
C_2	MP2/RA		328	545	406	34
C_2	DFT		335	543	434	28
C_2	DFT/RA		335	543	431	30
C_2/FHF^-	MP2	2.8, 90	316	527	392	30
C_2/FHF^-	MP2	2.8, 70	316	516	403	28
C_2/FHF^-	MP2	3.0, 90	320	532	397	30
C_2/FHF^-	MP2	3.0, 70	320	524	408	28
C_2/SbF_6^-	DFT	2.8, 90	317	528	395	27
C_2/SbF_6^-	DFT	2.8, 70	316	521	402	26
	exptl[c]		320	497	385	77

[a] Chemical shift values are reported relative to TMS optimized at the corresponding level of theory. The absolute shieldings (in ppm) of TMS are RHF, 191.5; MP2, 198.9; DFT, 183.5. [b] All values reported for the MP2/6-311++G** geometry. MP2 indicates GIAO-MP2/tzp/dz calculations. DFT indicates GIAO-B3LYP calculations with tzp (C), dz (H), and dzvp[24] (F, Sb) basis sets. RHF indicates a GIAO-RHF/tzp/dz calculation. [c] The estimated uncertainty in the isotropic shift is ca. 1 ppm and is 6 ppm or less for the principal components.

contraction. The principal components and isotropic shifts for the central carbon are shown in Table 1. The calculated isotropic shift for the C_2 structure is 8 ppm larger than that from experiment, but treatment of correlation is clearly essential as can be seen by comparison with the RHF result. The moderate discrepancy at the MP2 level in the isotropic shift actually belies larger and partially offsetting discrepancies in the principal components. For example, δ_{11} was calculated to be 545 ppm, but the experimentally measured value was only 497 ppm. The predicted orientation of the chemical shift tensor for the C_2 structure (Figure 2a) has δ_{11} coincident with the C−H bond along the C_2 axis, δ_{22} slightly (5°) out of the plane of the carbons, leaning away from the enlongated C−H bond, and δ_{33} at 85°, nearly perpendicular to the plane of the carbons. Schleyer et al. obtained an isotropic shift of 325 ppm[14] for the C_2 structure using the IGLO method, but this agreement was probably fortuitous. We carried out additional calculations using the GIAO approach and density functional theory (DFT) method[18] at the B3LYP[19]/tzp/dz level, and these give values close to those obtained at GIAO-MP2 (Table 1).

We investigated the sensitivity of the shift calculations to reasonable variations in bond distances and angles and found no remarkable sensitivity. At the suggestion of a referee, we also considered pyramidalization of the cation. We optimized the structure of its water adduct (i.e., protonated 2-propanol) at MP2/6-311++G**, froze the geometry, and removed H_2O. The isotropic ^{13}C shift of the pyramidally distorted center so generated was 431 ppm. We therefore investigated possibilities other than relaxation of the geometry.

As expected for C_2 symmetry, the cation is formally chiral and can racemize by methyl group rotation, passing through a C_s transition state.[14] Our calculated barrier for this process is ca. 0.7 kcal/mol, so this process is rapid on the NMR time scale, even at temperatures well below 77 K. Although the *isotropic* ^{13}C shift of the central carbon is unaffected by racemization, this dynamic process causes changes in sign of several of the off-diagonal elements of the chemical shift tensor.[20] We accounted for racemization by generating and symmetrizing the tensors for the two enantiomers in the same reference frame and then averaging the respective components. We then obtained the principal components by diagonalizing the averaged tensor. As shown in Table 1 for both the MP2 and DFT methods, "racemic averaging" changes each principal component by no more than 4 ppm, and this effect was considered no further.

There is already some evidence that the accurate calculation of isotropic shifts for simple cations with localized charge requires the inclusion of an approximate model of the medium. Thus, Olsson, Ottosson, and Cremer reported isotropic shift calculations for $(CH_3)_3C(Sol)_2^+$, Sol = H_2O, HCN, or NH_3.[21] Inclusion of H_2O (assumed to model the superacid solution component SO_2) improved agreement with the experimental isotropic shift for the *tert*-butyl cation in solution. Hollenstein and Laube recently reported the crystal structure of $(CH_3)_3C^+Sb_2F_{11}^-$.[22] The closest fluorines were positioned very close to the axis of the empty orbital on carbon; the closest F−C contacts were 2.9−3.1 Å.

As reasonable approximates to the effect of medium, we chose the models defined in Figure 2b,c. The geometries of the individual cation and anion were frozen, and their orientation was fixed by values of **r** and θ, suggested by the $(CH_3)_3C^+Sb_2F_{11}^-$ crystal structure. Due to program limitations, GIAO-MP2 calculations were not possible using SbF_6^- as a counterion. Thus, a single FHF^- was chosen as a substitute. A few representative MP2 results are shown in Table 1 to demonstrate that treatment of the anion can change the calculated isotropic shift and principal components. The DFT methodology allowed us to include the much larger SbF_6^- ion, and again we obtained upfield corrections in the isotropic shift, appreciable corrections to δ_{11}, and modest improvements in δ_{22}. δ_{33} was little improved by inclusion of the anion.

The principal components of a heteroatom-substituted secondary cation were recently reported.[23] In this communication we have reported the first such measurement for a nonsubstituted secondary carbenium ion. Furthermore, we have shown how the calculated values are affected by a simple treatment of the medium. A more exact agreement between theoretical and experimental values may require consideration of the full three-dimensional environment of the cation.

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