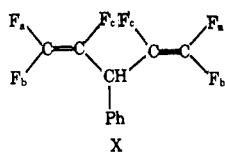


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 (19) X: bp 41–42 °C (5 mm);  $^{19}\text{F}$  NMR  $\phi^\circ$  102.6 ( $F_a$ , d, d,  $J_{F_a, F_b} = 77.5$ ,  $J_{F_a, F_c} = 35.8$  Hz), 120.4 ( $F_b$ , d, d, d,  $J_{F_b, F_c} = 114.4$ ,  $J_{F_b, H} = 6.3$  Hz $^{(2)}$ ), 177.9 ppm ( $F_c$ , d, d, d,  $J_{F_c, H} = 25.0$  Hz); mass spectrum  $m/e$  calcd 252.1684, found 252.0373.



- (20) Mixtures of the mono- and diphosphonium salt were obtained with less than a 2:1 ratio of 1 to initial olefin.

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## The Hydronium Ion ( $\text{H}_3\text{O}^+$ ), Pyramidal or Planar?

Sir:

The ion  $\text{H}_3\text{O}^+$  is a simple species of fundamental importance in chemistry. It is, therefore, a matter of great importance that, as a result of a most interesting  $^{17}\text{O}$  NMR study, the conclusion was drawn that this cation is "practically planar".<sup>1</sup> This is certainly an unexpected result, since the isoelectronic molecule,  $\text{NH}_3$ , has a bond angle of  $\sim 107^\circ$ . However, it seems that there is strong *ab initio* theoretical support for a planar geometry<sup>2</sup> and, possibly, some support from infrared spectroscopy.<sup>3</sup>

I therefore wish to examine the NMR evidence for this contention and then to turn to other arguments which, I believe, show that a pyramidal structure for  $\text{H}_3\text{O}^+$  is most probable, the mean  $\angle\text{HOH}$  angle being  $\sim 111^\circ$ .

The argument in favor of planarity is as follows:<sup>1</sup>  $\text{H}_2\text{O}$  is  $\text{sp}^3$  hybridized and has  $J_{\text{O-H}} = 79.9$  Hz;  $\text{H}_3\text{O}^+$  has  $J_{\text{O-H}} = 106$  Hz, which is an increase of 33%. On the reasonable assumption that there is a linear relation between  $J_{\text{O-H}}$  and the  $s$  character of the oxygen  $\sigma$  orbitals,<sup>4</sup> this requires *ca.*  $\text{sp}^2$  hybridization for  $\text{H}_3\text{O}^+$ , which suggests that it is planar.

However, the bond angle for  $\text{H}_2\text{O}$  is  $\sim 104.5^\circ$ ,<sup>5</sup> and, assuming orbital following, which is tacitly assumed in all these arguments, this leads to a  $\sigma$ -orbital hybridization at oxygen of *ca.*  $\text{sp}^4$ , i.e.  $\lambda^2 = 4$ . Using the same argument, that the  $s$  character increases by 33% on going from  $\text{H}_2\text{O}$  to  $\text{H}_3\text{O}^+$ , I find that the  $s$  character for  $\text{H}_3\text{O}^+$  should be  $\sim 26.6\%$ , giving  $\lambda^2 = 2.76$ . Then, using Coulson's equation<sup>5</sup> relating bond angle to hybridization (eq 1), I find the bond angle to be  $\phi = 111.3^\circ$ . This line of reasoning is supported by  $J(^{15}\text{N-H})$  data for  $\text{NH}_3$  and  $\text{NH}_4^+$ .<sup>6</sup> The coupling constant for  $\text{NH}_4^+$  is 73.7 Hz, and  $\lambda^2 = 3.0$ . The coupling for  $\text{NH}_3$  of 64 Hz leads to a predicted value for  $\lambda^2$  of 3.6, whereas the experimental bond angle of  $\sim 107^\circ$  leads to  $\lambda^2 = 3.5$ .

$$\phi = \cos^{-1} \left[ \frac{1.5}{2\lambda^2 + 3} - \frac{1}{2} \right] \quad (1)$$

This value is supported by solid-state studies. Early NMR data suggested that  $\text{H}_3\text{O}^+$  was nearly planar, but subsequent X-ray diffraction studies on a wide range of salts containing  $\text{H}_3\text{O}^+$ <sup>7</sup> gave an average bond angle between the central oxygen and three hydrogen-bonded neighbor atoms of  $109.3 \pm 5^\circ$ . Since strong hydrogen bonds are usually nearly linear, this strongly supports the concept that, in the solid-state,  $\text{H}_3\text{O}^+$  is pyramidal. Indeed, if it were to be planar, it would be a quite extraordinary coincidence that the neighboring anions should always adopt this pyramidal arrangement. More recent neutron diffraction studies confirm conclusively that  $\text{H}_3\text{O}^+$  is pyramidal in the solid state.<sup>7,8</sup> Thus for  $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$

$\text{H}_3\text{O}^+$ , the mean bond angle is  $110.4^\circ$  (110.7, 111.2,  $109.2^\circ$ ) while for  $\text{F}_3\text{CSO}_3^- \text{H}_3\text{O}^+$  it is  $112.7^\circ$  (111.1, 115.5,  $111.6^\circ$ ). These angles are very close to those formed with the hydrogen bond acceptor atoms, showing that the hydrogen bonds are nearly linear.

These values are remarkably close to that deduced from the NMR data. This is an important result since it establishes that the constraints imposed by the crystal packing do not exert a major influence on the structure of  $\text{H}_3\text{O}^+$ . Furthermore, since the liquid-phase studies were for  $\text{H}_3\text{O}^+$  in liquid  $\text{SO}_2$ , which is only weakly basic, they show that the bond angle is not strongly dependent upon the extent of hydrogen bonding.

It is interesting to note that there is an increase in average bond angle on going from  $\text{NH}_3$  ( $107^\circ$ ) to  $\text{H}_3\text{O}^+$  ( $111.3^\circ$ ). This may result in part from hydrogen bonding, but probably largely reflects the change in electronegativity.<sup>9</sup> The same trend is observed, for example, for the isoelectronic hydrides  $\cdot\text{AlH}_3^-$ ,  $\cdot\text{SiH}_3$ , and  $\cdot\text{PH}_3^+$ .<sup>10</sup>

I conclude that the important new  $^{17}\text{O}$  NMR data reported by Mateescu and Benedikt suggest that  $\text{H}_3\text{O}^+$  is pyramidal in solution with a bond angle of  $\sim 111.3^\circ$ .

**Acknowledgment.** I thank a referee for helpful comments.

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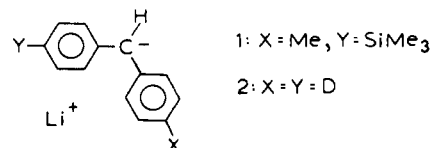
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## Stabilization of Carbanions by Silicon. Restricted Aryl Rotation in the 4-Methyl-4'-trimethylsilyldiphenylmethyl Anion

Sir:

It is well known that groups containing silicon (e.g.,  $\text{SiMe}_3$ ) stabilize negative charge on an *adjacent* carbon atom.<sup>1</sup> Much current research centers on identification of the origin of this stabilization.<sup>2</sup> This report concerns dynamic NMR (DNMR) studies of restricted aryl rotation in the lithium salt of the 4-methyl-4'-trimethylsilyldiphenylmethyl anion (**1**) and extended Hückel calculations for more simple related systems. These results allow a quantitative assessment of the effect of a para trimethylsilyl group on the stability of a diphenylmethyl anion.



The  $^1\text{H}$  DNMR spectrum (270 MHz) of the aryl rings of **1** (0.4 M in 20% toluene- $d_8$ /80% THF, v/v) at 320 K consists