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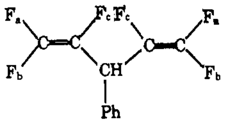
(19) X: bp 41–42 °C (5 mm); ^{19}F NMR ϕ^* 102.6 (F_a, d, d, $J_{F_a,F_b} = 77.5$, $J_{F_a,F_c} = 35.8$ Hz), 120.4 (F_b, d, d, d, $J_{F_b,F_c} = 114.4$, $J_{F_b,H} = 6.3$ Hz[12]), 177.9 ppm (F_c, d, d, d, $J_{F_c,H} = 25.0$ Hz); mass spectrum *m/e* calcd 252.1684, found 252.0373.



X

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

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The Hydronium Ion (H_3O^+), Pyramidal or Planar?

Sir:

The ion H_3O^+ 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}O NMR study, the conclusion was drawn that this cation is "practically planar".[1] This is certainly an unexpected result, since the isoelectronic molecule, NH_3, has a bond angle of ~107°. However, it seems that there is strong ab initio theoretical support for a planar geometry[2] and, possibly, some support from infrared spectroscopy.[3]

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 H_3O^+ is most probable, the mean $\angle$HOH angle being ~111°.

The argument in favor of planarity is as follows:[1] H_2O is sp^3 hybridized and has $J_{O-H} = 79.9$ Hz; H_3O has $J_{O-H} = 106$ Hz, which is an increase of 33%. On the reasonable assumption that there is a linear relation between J_{O-H} and the s character of the oxygen σ orbitals,[4] this requires ca. sp^2 hybridization for H_3O^+, which suggests that it is planar.

However, the bond angle for H_2O is ~104.5°,[5] and, assuming orbital following, which is tacitly assumed in all these arguments, this leads to a σ-orbital hydridization at oxygen of ca. sp^4, i.e. $\lambda^2 = 4$. Using the same argument, that the s character increases by 33% on going from H_2O to H_3O^+, I find that the s character for H_3O_+ should be ~26.6%, giving $\lambda^2 = 2.76$. Then, using Coulson's equation[5] relating bond angle to hybridization (eq 1), I find the bond angle to be $\phi = 111.3°$. This line of reasoning is supported by $J(^{15}N-H)$ data for NH_3 and NH_4^+.[6] The coupling constant for NH_4^+ is 73.7 Hz, and $\lambda^2 = 3.0$. The coupling for NH_3 of 64 Hz leads to a predicted value for λ^2 of 3.6, whereas the experimental bond angle of ~107° leads to $\lambda^2 = 3.5$.

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

This value is supported by solid-state studies. Early NMR data suggested that H_3O^+ was nearly planar, but subsequent X-ray diffraction studies on a wide range of salts containing H_3O^+[7] gave an average bond angle between the central oxygen and three hydrogen-bonded neighbor atoms of 109.3 ± 5°. Since strong hydrogen bonds are usually nearly linear, this strongly supports the concept that, in the solid-state, H_3O^+ 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 H_3O^+ is pyramidal in the solid state.[7,8] Thus for p-$CH_3C_6H_4SO_3^-H_3O^+$, the mean bond angle is 110.4° (110.7, 111.2, 109.2°) while for $F_3CSO_3^-H_3O^+$ it is 112.7° (111.1, 115.5, 111.6°). 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 H_3O^+. Furthermore, since the liquid-phase studies were for H_3O^+ in liquid 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 NH_3 (107°) to H_3O^+ (111.3°). This may result in part from hydrogen bonding, but probably largely reflects the change in electronegativity.[9] The same trend is observed, for example, for the isoelectronic hydrides $\cdot AlH_3^-$, $\cdot SiH_3$, and $\cdot PH_3^+$.[10]

I conclude that the important new ^{17}O NMR data reported by Mateescu and Benedikt suggest that H_3O^+ is pyramidal in solution with a bond angle of ~111.3°.

Acknowledgment. I thank a referee for helpful comments.

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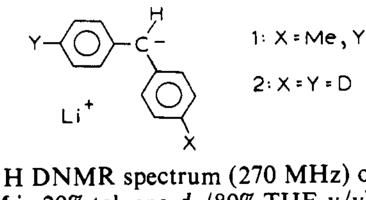
Stabilization of Carbanions by Silicon. Restricted Aryl Rotation in the 4-Methyl-4′-trimethylsilyldiphenylmethyl Anion

Sir:

It is well known that groups containing silicon (e.g., $SiMe_3$) stabilize negative charge on an *adjacent* carbon atom.[1] Much current research centers on identification of the origin of this stabilization.[2] 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 ^1H 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

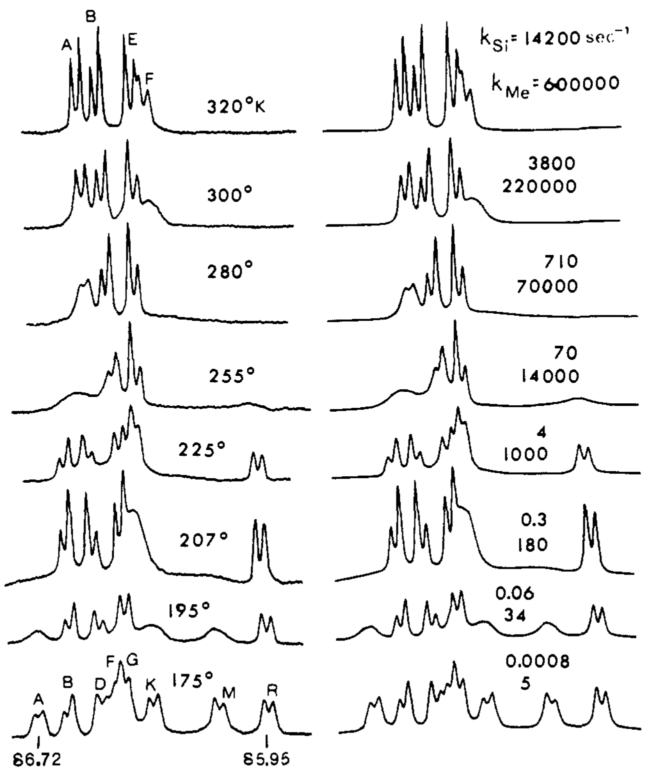


Figure 1. The experimental ^{1}H DNMR spectra (270 MHz, left column) of the aryl protons of the lithium salt of the 4-methyl-4′-trimethylsilyldiphenylmethyl anion (**1**, 0.4 M in 20% toluene-d_8/80% THF) and theoretical spectra (right column) computed as a function of k_{Me} and k_{Si} which are the first-order rate constants for rotation of the methylated and silylated rings, respectively.

of an apparent AF spectrum [δ_A 6.63, δ_F 6.40 ($^3J_{AF}$ = 8.1 Hz)] and a BE spectrum [δ_B 6.57, δ_E 6.45 ($^3J_{BE}$ = 8.1 Hz)] consistent with the presence of two different rings (Figure 1).[3] The observation of just two types of proton for each ring at 320 K speaks for rapid aryl rotation on the ^{1}H DNMR time scale. However, the higher field doublet of the AF spectrum (δ_F) is partially collapsed because of the onset of a DNMR effect. Indeed, at lower temperatures (Figure 1), the spectrum of **1** undergoes complex changes and at 175 K is sharpened into an AFKM spectrum [δ_A 6.72, δ_F 6.46, δ_K 6.34, δ_M 6.11 ($^3J_{AF}$ = $^3J_{KM}$ = 8.1 Hz)] and a BDGR spectrum (δ_B 6.62, δ_D 6.51, δ_G 6.43, δ_R 5.95 ($^3J_{BD}$ = $^3J_{GR}$ = 8.1 Hz)]. The observation of four different protons for each ring is consistent with slow rotation of *both* aryl groups in an essentially coplanar delocalized anion.[4] Based on a previous study, the AFKM spectrum observed for **1** at 175 K is assigned to the 4-methylphenyl group.[5] As the temperature is raised above 175 K (e.g., 195 K and 207 K, Figure 1), the AFKM spectrum collapses before the BDGR spectrum. *Thus, the 4-methylphenyl group is rotating faster than the 4′-trimethylsilylphenyl moiety.* Indeed, accurate DNMR line shape simulations were achieved using an AFKM to MKFA spin exchange model for 4-methylphenyl rotation which is superimposed on a BDGR to GRBD spin exchange model for the 4-trimethylsilylphenyl rotation (Figure 1). Indeed, at 255 K, the rate constant for 4-methylphenyl rotation (k_{Me} = 14 000 s^{-1}; $\Delta G^{\ddagger}$ = 10.0 ± 0.1 kcal/mol) is *200 times greater* than that for 4′-trimethylsilylphenyl rotation (k_{Si} = 70 s^{-1}; $\Delta G^{\ddagger}$ = 12.7 ± 0.1 kcal/mol).

The ^{13}C[^{1}H] DNMR spectra (22.64 MHz) of the 2,6,2′,6′ carbons of **1** (0.4 M in THF) also reflect two different barriers to aryl rotation (Figure 2). The asterisked peak at 350 K (Figure 2) collapses first at lower temperatures and is separated into two sharp singlets (δ 111.5, 120.6) at 220 K. However, the other resonance (δ 119.3 at 350 K) is highly exchange broadened at 220 K and is not separated into two singlets (δ 114.0, 122.6) until 180 K. The observation of four separate ^{13}C[^{1}H] signals at 180 K is of course consistent with a static coplanar anion. The asterisked peaks in Figure 2 are assigned to the silylated ring which is rotating at a slower rate than the methylated ring. A ^{13}C[^{1}H] DNMR line shape analysis at 250 K reveals the barriers for 4-methylphenyl rotation ($\Delta G^{\ddagger}$ = 10.0 ± 0.4 kcal/mol) and 4′-trimethylsilylphenyl rotation ($\Delta G^{\ddagger}$ = 12.6 ± 0.4 kcal/mol) to be in good agreement with the ^{1}H DNMR data.

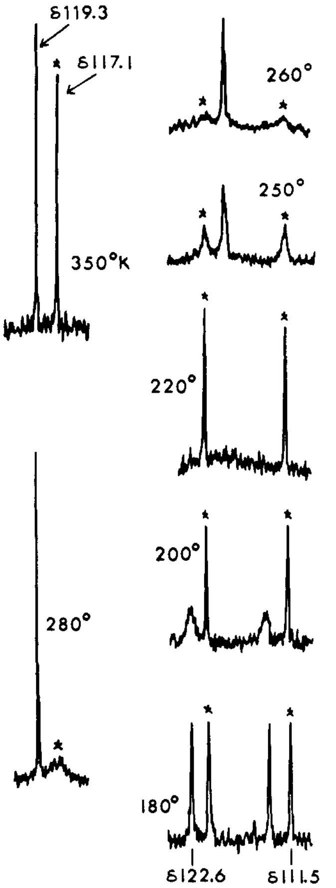


Figure 2. The ^{13}C[^{1}H] DNMR spectra (22.64 MHz) of the 2,6,2′,6′ carbons of **1** (0.4 M in THF).

The difference between the two barriers to aryl rotation ($\Delta\Delta G^{\ddagger}$ = 2.7 kcal/mol) in **1** is remarkable if one considers that each barrier is determined essentially exclusively by the strength of π bonding to the benzylic carbon. By comparison with the phenyl rotational barrier for anion **2** ($\Delta G^{\ddagger}$ = 11.2 ± 0.3 kcal/mol at 225 K),[6] it is clear that the 4-methyl group of **1** weakens π bonding of the 4-methylphenyl group to the benzylic carbon ($\Delta G^{\ddagger}$ = 10.0 kcal/mol) and the 4′-trimethylsilyl group strengthens the corresponding π bond ($\Delta G^{\ddagger}$ = 12.7 kcal/mol). Although it is virtually certain that there is an electronic "push-pull" effect which accentuates the barrier differential in **1**, there is no question that the *remote* 4′-trimethylsilyl group is quite effective at stabilizing negative charge. These observations are inconsistent with a simple inductive effect since methyl (σ_I = −0.07) and trimethylsilyl (σ_I = −0.09) are comparable electron donors in an inductive sense.[7] However, our data are qualitatively consistent with hyperconjugative substituent parameters which indicate methyl to be an electron donor (σ_{R° = −0.11) and trimethylsilyl to be an electron acceptor (σ_{R° = +0.07).[8]

To provide more insight into the nature of anion stabilization by silicon, we performed extended Hückel calculations[9] of the energy difference between a planar *4-substituted benzyl anion* and that geometry in which the methylene group is perpendicular to the plane of the phenyl ring, i.e., the barrier to aryl rotation. The calculated barriers for the benzyl anion, the 4-methylbenzyl anion, and the 4-silylbenzyl anion are 19.2, 18.2, and 21.3 kcal/mol, respectively. The trend in these calculated barriers is in good qualitative agreement with our results for anions **1** and **2** above. Indeed, a perusal of the Hückel electron-density distribution for the 4-silylbenzyl anion reveals a significant increase in negative charge in the silicon atom of the *planar* anion as compared with the transition state for aryl rotation. Since the extended Hückel method may not reflect accurately the relative importance of different types of orbitals in bonding for these anionic systems, such calculations do not provide an incisive picture of the specific orbital involvement in anion stabilization by silicon. Thus, while our experimental NMR data and the Hückel calculations reveal a clear-cut stabilization of the diphenylmethyl anion by a para trimethylsilyl group, an unequivocal theoretical description of such stabilization remains undefined.

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Isotopic Oxygen Studies on Aqueous Molybdenum(IV)

Sir:

The composition and structure of Mo(IV)$_{aq}$ in acidic aqueous solution has been the subject of several studies,[1-5] but none define the ionic species present unambiguously. Several recent crystal structures of solid complexes[6] have shown a common trimeric core ion, but the extension from the solid state to solution is, as always, open to serious question. The studies reported here, a combination of ^{18}O transfer experiments and an X-ray structure, strongly suggest the basic structure of this ion in acidic solution and allow definitive studies on the kinetic behavior of the bridged oxygens.

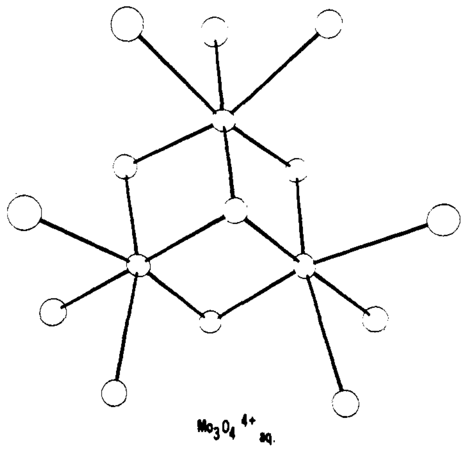

Figure 1.

When Mo(IV)$_{aq}$[7] in 1-3 M HCl or CH_3SO_3H (obtained by reaction of $MoO_4{}^{2-}$ with $MoCl_6{}^{3-}$ followed by ionic exchange separation)[1] is treated for extended periods of time with ^{18}O-enriched water, some of the oxygens in the first coordination sphere of molybdenum are not exchanged with the solvent. This has been established unambiguously by converting Mo(IV)$_{aq}$ into a crystalline solid by the addition of NaSCN and $(CH_3)_4N^+SCN^-$ at 0 °C and measuring its ^{18}O content. The solid product which begins to precipitate within 1 min and is almost completely precipitated in ~20 min has a constant composition with all coordinated waters replaced by SCN^- and no water of hydration in the vacuum-dried material (IR). A representative of about thirty experiments to determine what fraction of the oxygen in the solid SCN^- complex comes from the inner coordination sphere of the Mo(IV)$_{aq}$ is given below. The experiment involved making Mo(IV)$_{aq}$ in normal or ^{18}O-enriched water, separating it on an ion-exchange column, eluting it with 3 M HCl or CH_3SO_3H in water differing in isotopic oxygen content from the original preparation, precipitating the $(CH_3)_4N^+SCN^-$ salt, recrystallization, and determining the ^{18}O content of all the oxygen in the solid complex by conversion into CO_2 by the usual methods. The time of contact at 25 °C between the ion and the solvent at differing ^{18}O enrichments varied between 15 and 45 min in these experiments. The results clearly show that *all* of the oxygens (±3%) in the solid complex come from the inner coordination sphere of Mo(IV)$_{aq}$. If the [SCN^-] is low or the $(CH_3)_4N^+$ added too early, the products contain more unreplaced H_2O and the "apparent exchange" rises to 10-15%. Other experiments allowing extended time periods for exchange between the Mo(IV)$_{aq}$ (^{18}O enriched) and H_2O (normal) showed no more than 10% exchange of these oxygens in 100 h at 25 °C.

	10^3R_n (solvent)[10]	10^3R_n [Mo(IV)]	10^3R_n(SCN$^-$ complex)
A. enriched solvent	9.800	3.920	3.914
B. enriched Mo(IV)$_{aq}$	3.980	8.302	8.179

Analysis of the SCN^- complex was not adequate to establish the O/Mo ratio or the structure of the complex ion. Attempts to produce single crystals met with only marginal success, but from CH_3CN-H_2O mixtures thin plates could easily be obtained in bulk and a few small ($V = 8 \times 10^{-4}$ mm^3) semispherical crystals were prepared. A single-crystal X-ray study[8] showed the complex to be $[(CH_3)_4N]_4[Mo_3O_4(NCS)_8OH_2]\cdot 3H_2O$, a trimeric structure very similar in nature to the oxalate or EDTA[6] complexes. This compound was the same as the bulk plates (film X-ray data) and reversibly forms by aquation of the $(SCN)_9$ complex when a large excess of SCN^- is not present in solution.

Since the complex ion is reversibly formed under mild con-

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