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AB INITIO SCFMO CALCULATIONS ON THE STRUCTURE OF THE SILYLMETHYL ANION AND THE C—H ACIDITY OF METHYLSILANE

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Summary

Ab initio SCFMO calculations have been carried out on the structure and stability of silyl-methyl anion and -ethyl anion. Our results show that SiH_3 and CH_3 as substituents effect the geometry of CH_2^- very little but SiH_3 stabilizes CH_2^- by about 50 kcal mol^{-1} compared to CH_3, using the neutral RCH_3 molecules as standard.

Calculations have recently been reported by Streitwieser and coworkers [1] which show that the acidity of the methyl group is enhanced by an additional CH_3 group as a substituent and that the acidity varies with the H—C—H angle of the CH_3 group not involved in the ionization process. These calculations confirm the hypothesis that ring strain in a group adjacent to a C—H bond enhances the acidity [2].

It is well known that electron-attracting substituents also enhance the acidity of methane a prominent example being NO_2; nitromethane has an acidity comparable with that of phenol. In this paper we examine the effect of a silyl substituent on the acidity of methane. SiH_3 has already been shown to have a strong destabilizing effect on the group CH_2^+ although it stabilizes the radical very little, the comparison being based upon the relative energies of RCH_2 and RCH_3 (R = CH_3, SiH_3) [3]. There is some evidence that Me_3Si groups may stabilize carbanion centres to which they are attached [3b].

The equilibrium structure of CH_3^- is a matter of considerable theoretical interest. Recent ab initio SCFMO calculations with configuration interaction by Driessler and coworkers [4] predict a pyramidal structure with bond angles 110° but with a low barrier to inversion (2 kcal mol^{-1}). This is in accord with the Walsh rules [5]. In contrast SCFMO calculations on the nitromethyl anion

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TABLE 1

CALCULATED GEOMETRY AND PROTON AFFINITY OF ETHYL ANION

		Ref. 1
r(C—C) Å	1.585	1.551
$r(C_\beta$—H_{anti} ot lone pair) Å	1.130	1.128
$r(C_\alpha$—H) Å	1.134	1.179
$r(C_\beta$—H_{gauche} to lone pair) Å	1.126	1.126
$\theta(C_\alpha$—C_β—H_{anti} to lone pair)	117.5°	116.0°
$\theta(H_{gauche}$—C—$H_{gauche})$	105.9°	106.3°
$\theta(C_\alpha$—C_β—$H_{gauche})$	112.0°	111.0°
θ(H—C_α—H)	100.7°	99.6°
$\theta(C_\beta$—C_α—H)	102.1°	107.0°
Energy	−78.21536 a.u.	−78.0688 a.u.

H—C—H angle (°)	Total energy (a.u.)		Total energy (a.u.) ref. 1		Proton affinity (kcal mol^{-1}) (same in both calculations)
	Ethane	Ethyl anion[a]	Ethane	Ethyl anion	
103.4	−79.01140	−78.21415	−78.8668	−78.0664	500
108.9	−79.01458	−78.21184	−78.8697	−78.0638	504
113.5	−79.00876	−78.20084	−78.8640	−78.8640	507

[a] The basis of STO's was the same as in ref. 1.

predict a planar geometry [6]. If there is any tendency for SiH_3 to act as an electron attracting group, perhaps through d-orbital participation in π bonding, then this will be likely to favour the planarity of the $(CH_2$—$R)^-$ group. We have therefore examined the geometry of the CH_2 group and the SiH_3 group.

Calculations were carried out using the ab initio SCFMO program ATMOL developed by Hillier, Saunders and Guest and now updated at the Atlas Computer Centre [7]. All calculations used a 3-gaussian expansion of valence orbitals and a 6 G expansion of the 1s orbitals of carbon and silicon.

Calculations were first made on $CH_3CH_2^-$ to confirm the optimum geometry found by Streitwieser and coworkers. The geometrical parameters were varied independently by 3-point parabolic interpolation. The results are shown in Table 1. The main geometrical difference between these results and those in ref. 1 is in the smaller C_β—C_α—H bond angle. The orbital energies are all lower as a result of the larger gaussian expansion of the 1s orbitals, but the difference in

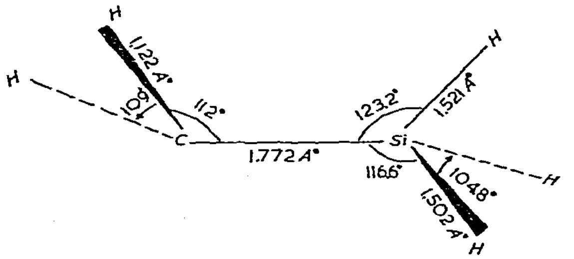

Fig. 1. Calculated Optimum Structure of $(CH_2$—$SiH_3)^-$.

energy between ethane and the ethyl cation is found to be the same to within 1 kcal mol^{-1}.

Figure 1 shows the calculated optimum geometry of $(SiH_3CH_2)^-$. The basis of STO's were the same as in ref. 3 with the inclusion of *d*-orbitals on the silicon. The geometrical parameters were again varied by independent 3-point interpolation. The optimized structure of the silylmethyl anion was found to have a staggered C_s symmetry with an almost tetrahedral angle at the carbon atom. It can be seen from this table that the —CH_2 group is pyramidal but the H—C—Si angle of 112° is considerably larger than the corresponding angle in the ethyl anion (102° in our calculation). The —CH_2 group is however still far from planar. The dominant change in the SiH_3 group is that the H—Si—H angles have closed from tetrahedral values and the Si—H bond *anti* to the carbon lone pair is seen to be slightly longer than the *gauche* bonds. The calculated carbon—silicon bond in silylmethyl anion is shorter than the experimental carbon—silicon bond in neutral methylsilane. After optimizing all other parameters this bond length was reoptimized but no significant further change was found. In contrast the C—C bond of the ethyl anion was found to be longer than the C—C bond length of ethane.

In order to calculate the proton affinity of the silylmethyl anion, calculations were performed on methylsilane using spectroscopically determined bond lengths and bond angles [8]. The geometry used has C—H, Si—H and Si—C bond lengths 1.093, 1.485 and 1.867 Å respectively. The bond angle of the methyl group was taken as the experimental value of 107°40′. Retaining C_3 symmetry in the silyl group, the calculations were repeated for the angles shown in Table 2. For the silylmethyl anion the parameters used were those shown in Fig. 1 except that the silyl group was given a C_3 symmetry structure. The proton affinity of the carbanion was calculated as a function of the angle of distortion. The results are shown in Table 2.

The double basis calculations of Murrell, Vidal and Guest [6] on nitromethane and nitromethane anion lead to a value for the proton affinity of nitromethane as 374 kcal mol^{-1}. Using the results of ref. 4 for CH_3^- and results of ref. 9 for methane, the calculated proton affinity of the methyl carbanion is approximately 488 kcal mol^{-1}. Combining these values with our results given above we conclude that the increasing order of acidity of RCH_3 for these four substituents is R = $NO_2 > SiH_3 > H > CH_3$. Our minimum basis set calculations suggest that SiH_3 and CH_3 do not affect the geometry of CH_2^- very much but

TABLE 2

α(H—Si—H) angle (°)	Total energy (a.u.)		Proton affinity of silylmethyl anion (kcal mol^{-1})
	Methylsilane	Silylmethyl anion	
100	—329.01634	—328.30528	446
104	—329.02176	—328.30340	451
108.2	—329.02389	—328.29661	456
112	—329.02169	—328.28473	462

the SiH_3 group stabilizes the CH_2 group by 50 kcal mol^{-1} more than does CH_3 and 75 kcal mol^{-1} less than does NO_2.

The differences between the proton affinities of CH_3CH_3 and CH_3NO_2 is 130 kcal mol^{-1} and between CH_3CH_3 and CH_3SiH_3 50 kcal mol^{-1}. The differences between the pK values of the first two is 38 [10]. Assuming that the proton affinity differences are roughly proportional to the pK differences, we calculate an approximate pK value for CH_3SiH_3 of 34. If this interpolation is accurate then CH_3SiH_3 is about as strong an acid as diphenylmethane, i.e., the silyl group has a stronger stabilizing effect on CH_2^- than a phenyl group. It is thus relevant that preliminary experiments indicate that $(Me_3Si)_3CH$ has a greater kinetic audity than Ph_3CH [11].

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