A Gas-phase Electron Diffraction Study of Tris(trimethylsilyl)methane. A C–H Bond of High p-Character

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Summary The $Me_3SiCSiMe_3$ angles in $(Me_3Si)_3CH$ are unusually large (117°), implying an unusually high degree of p-character in the orbital used to form the C–H bond.

Special interest attaches to compounds in which bond angles at a formally sp^3-hybridized carbon atom are much larger than 109·5° (see, for example, ref. 1 and references therein). Examination of models suggested that the $Me_3SiCSiMe_3$ angles in $(Me_3Si)_3CH$ could be expected to open up considerably to minimize steric strain. This should result in a high proportion of p-character in the unique C–H bond, and in agreement with this the value of ^1J(CH) for this bond, 100 Hz,[2] is unusually low. However, the hydrogen atom of this bond has a high acidity [the kinetic acidity of $(Me_3Si)_3CH$ is higher than that of triphenylmethane[3]], a feature not normally associated with a bond of high p-character. It thus seemed of interest to determine the structure of $(Me_3Si)_3CH$.

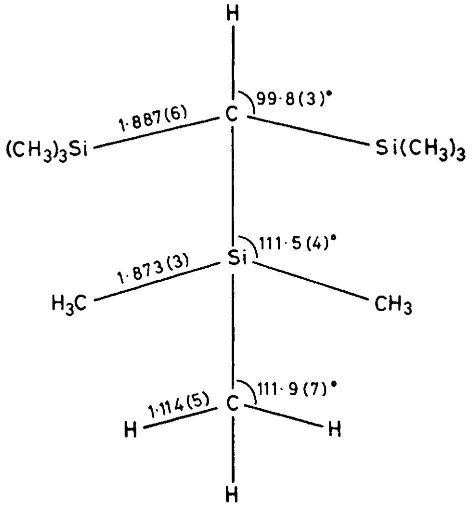

Figure 1. Bond lengths (Å) and angles (°) in $(Me_3Si)_3CH$ (e.s.d.s in parentheses).

Gas-phase electron-diffraction patterns recorded photographically in the Balzers KDG2 instrument[4–6] at UMIST were scanned microdensitometrically[7] and the data obtained were processed by standard methods[8–10] to molecular intensity curves suitable for least-squares refinement of the molecular structural parameters. Refinements employing the recently developed programme LSQ3[11] were based on a molecule with overall three-fold symmetry, local three-fold symmetry for the $-CH_3$ and $-Si(CH_3)_3$ groups, and vibrational amplitudes grouped according to distance type. Although all refinements led to similar bond lengths and angles, three least-squares minima were revealed, differing largely in the values of the two torsional angles τ_1 and τ_2 (see Figure 2). The first two minima, which arose from different initial sets of parameters, were found to correspond with molecules possessing unreasonably short H $\cdots$ H and C $\cdots$ H distances. Molecular mechanics non-bonded interaction functions[12] for H $\cdots$ H and C $\cdots$ H contacts were employed to calculate the van der Waals potential energy for possible combinations of τ_1 and τ_2 values. The global energy minimum occurred at τ_1 82 and τ_2 10°. A least-

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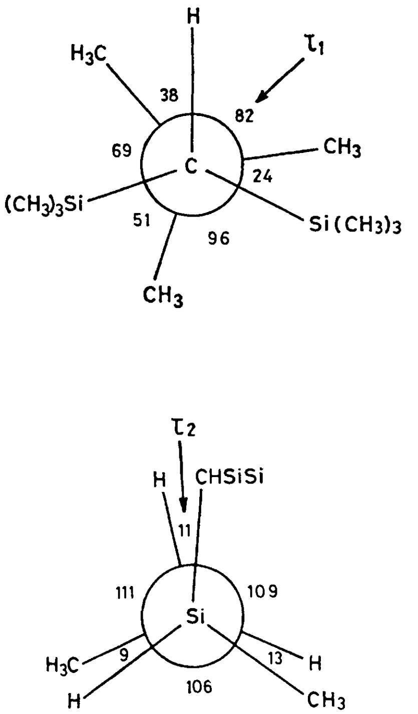

Figure 2. Newman projections down the C–$SiMe_3$ and Si–CH_3 bonds showing torsion angles (°).

squares refinement starting from this point led to the third minimum (having $\tau_1 = 81°$, $\tau_2 = -18°$) and produced better agreement between observed and calculated diffraction data than any of the previous refinements (Figure 3). Finally, the two distinct Si–C distances were allowed to refine independently, with the results shown in Figures 1 and 2 [$\tau_1 = 81{\cdot}5(3)°$ and $\tau_2 = -11(5)°$]. The agreement with the observed data improved further, but hardly significantly. However, the torsional angles were then within *ca.* 4 e.s.d. of the calculated values.

As expected, the potential strain is mainly accommodated by distortion of bond angles, especially those at the central carbon atom, where $\angle SiCSi = 117{\cdot}2(4)°$ and $\angle CHSi = 99{\cdot}8(3)°$, but there is also considerable deviation of the torsional angles from the values typifying staggered conformations (Figure 2) and a slight lengthening of the Me_3Si–C (1·887 Å) compared with the CH_3–Si bonds (1·873 Å). There is a markedly greater lengthening of the Me_3C–C bonds in $(Me_3C)_3CH$, in which the Me_3CCCMe_3 angle is 116°.[13]

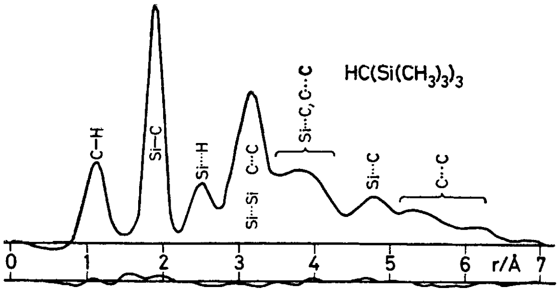

Figure 3. Observed and difference radial distribution curves (longer distances involving H not indicated).

The angles around the central carbon atom correspond to s and p^{13} character in the orbital used for the C–H bond. This contrasts with a value of sp^4 which can be derived from the observed $^1J(CH)$ value of 100 Hz by use of the relationship $^1J(CH) = 5 \times \%$ s-character, or the modified version[14] $^1J(CH) = (5{\cdot}7 \times \%$ s-character$) - 18{\cdot}4$. (A value of 111·5° for $\angle Me_3SiCSiMe_3$ would be required for sp^4 character in the C–H bond.) The electronic effect of the Me_3Si groups must have some influence on the coupling $^1J(CH)$, but would be expected to favour an even lower value than would be implied by the geometry alone [compare the $^1J(CH)$ values of 118 and 125 for Me_4Si and CH_4, respectively]. The apparent discrepancy might be related, at least in part, to the possibility that the inter-orbital angles in the $Me_3SiCSiMe_3$ linkages may be smaller than the internuclear angles,[1,13] but it is also possible that the relationships mentioned above between $^1J(CH)$ and s-character, which were derived by use of $^1J(CH)$ values of 120 Hz or more, do not apply satisfactorily to substantially lower values. Detailed analysis is complicated by the report that the value of $^1J(CH)$ for the corresponding bond in $(Me_3C)_3CH$ is 124 Hz.[13]

The high acidity associated with a C–H bond of high p-character can be most simply attributed to delocalization of the lone pair of the conjugate carbanion into the d-orbitals of the silicon atoms, and the inherent effect may be substantially enhanced by the geometry of $(Me_3Si)_3CH$, since the near-planarity of the three silicon and central carbon atoms means that very little movement of atoms will be needed to give the maximum conjugative stabilization on going to the carbanion.

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