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# The molecular structure of silylcyclopentadiene in the gas phase

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Recent NMR studies of compounds in which a Group IV atom is bonded to a cyclopentadiene ring[1,2] have shown that the group containing the Group IV atom migrates round the ring at a rate which is temperature dependent. This fluxional behaviour leads eventually to the ring protons showing magnetic equivalence. The question of whether 1,2 or 1,3 shifts occur is still not finally settled, although most evidence favours the 1,2 mechanism[3,4].

An electron diffraction study of trimethylsilylcyclopentadiene[5] suggested that the structure of the ring differed considerably from that in unsubstituted cyclopentadiene[6], most notably in its deviation from planarity. The angle between the planes $C_2C_1C_2'$ and $C_2C_3C_3'C_2'$ (see Fig.1a) was reported to be $22 \pm 4°$. We therefore initiated a study of silylcyclopentadiene, hoping to determine whether the silicon atom is situated under the ring (as in Fig.1a), or pointing away from the ring, or a mixture of both, and hence to decide whether a 1,2 or 1,3 shift mechanism is more probable. We find, however, that the cyclopentadiene ring is flat, and that the carbon–carbon bond lengths and ring angles are close to those found in cyclopentadiene itself.

Thus the structure found for silylcyclopentadiene agrees with that predicted on theoretical grounds[7], but differs significantly from that reported for trimethylsilylcyclopentadiene. However, the complexity of the latter molecule is such that assumptions had to be made both about the relative lengths of some of the carbon–carbon bonds, and about one of the ring angles. With our simpler molecule, it was possible to refine more ring parameters.

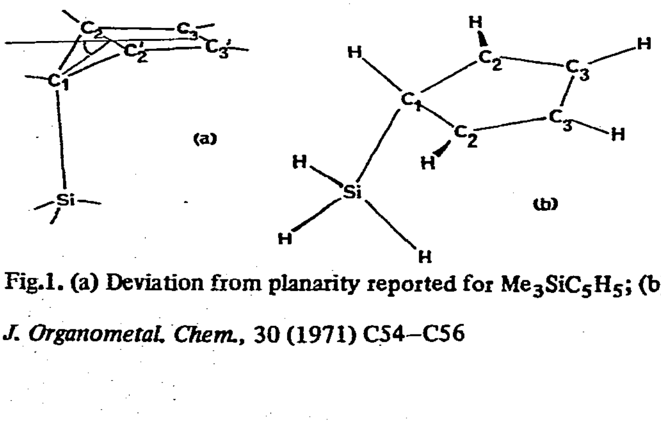

Fig.1. (a) Deviation from planarity reported for $Me_3SiC_5H_5$; (b) Structure of $H_3SiC_5H_5$.

Electron diffraction data were collected using a Balzers' KD.G2 instrument, and data reduction and least squares refinements were performed using our usual programmes[8,9]. $C_s$ symmetry was assumed throughout. Refinements of parameters involving the ring hydrogen atoms have not yet been completed, but the heavy atom positions are all well refined. The ring parameters are dependent mainly on the peaks at about 1.45 and 2.3 Å in the radial distribution curve (Fig.2), and also to some extent on the Si ··· $C_2$ and Si ··· $C_3$ peaks at about

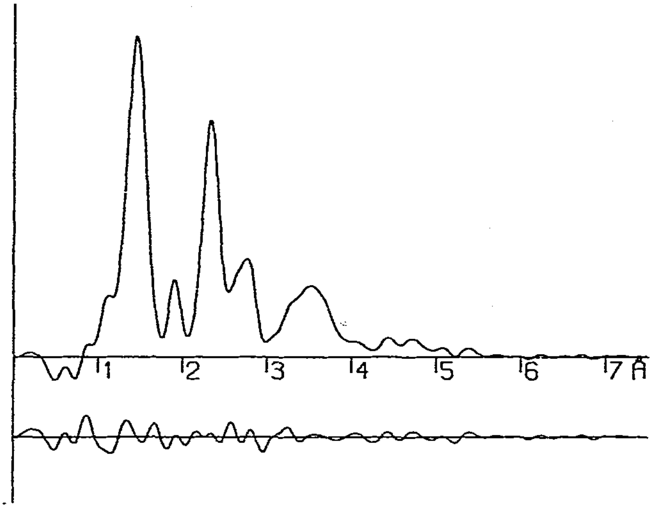

Fig.2. Radial distribution curve for silylcyclopentadiene. Before Fourier inversion, the data were multiplied by $s.\exp(-0.0015\ s^2)/(f_{Si} - z_{Si})(f_C - z_D)$.

TABLE 1

MOLECULAR PARAMETERS FOR SILYLCYCLOPENTADIENE

| | | |
|---|---|---|
| *(A)* | *Bonded distances* (Å) | |
| | $C_1$–$C_2$ | 1.500 ± 0.013 |
| | $C_2$–$C_3$ | 1.389 ± 0.013 |
| | $C_3$–$C_3'$ | 1.436 ± (fixed) [a] |
| | Si–$C_1$ | 1.881 ± 0.010 |
| mean | C–H | 1.109 ± 0.018 |
| *(B)* | *Non-bonded distances* (Å) | |
| | $C_1$–$C_3$ | 2.394 ± 0.017 |
| | $C_2$–$C_2'$ | 2.293 ± 0.036 |
| | $C_2$–$C_3'$ | 2.289 ± 0.014 |
| | Si–$C_2$ | 2.716 ± 0.008 |
| | Si–$C_3$ | 3.621 ± 0.016 |
| *(C)* | *Angles* (°) | |
| | $C_2C_1C_2'$ | 100.3 ± 1.5 |
| | $C_1C_2C_3$ | 112.0 ± 1.0 |
| | $C_2C_3C_3'$ | 107.9 ± 0.6 |
| plane | $C_2C_1C_2'$/plane $C_2C_3C_3'C_2'$ | 0(fixed) [a] |
| plane | $C_2C_1C_2'/C_1$Si | 116.5 ± 0.7 |
| | $SiC_1C_2$ | 106.6 ± 0.6 |

[a] Values found to give lowest *R* factors

2.7 and 3.6 Å. The principle interatomic distances and angles are given in Table 1. These parameters vary a little with the various C–C amplitudes of vibration, but allowances for these variations have been included in the quoted errors.

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