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THE *ab initio* OPTIMIZED GEOMETRY OF THE 6-SILYLCYCLOHEXADIENYL RADICAL[1)]

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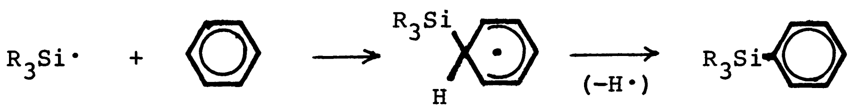
The optimized geometry of the 6-silylcyclohexadienyl radical calculated by the energy gradient method with the STO-3G basis set shows that the radical has a distorted ring structure with the energy minimum at 4.3° of out-of-plane angle.

The key intermediate in homolytic aromatic silylation is 6-silylcyclohexadienyl radicals (1), the existence of which has been evidenced by an ESR experiment.[2)]

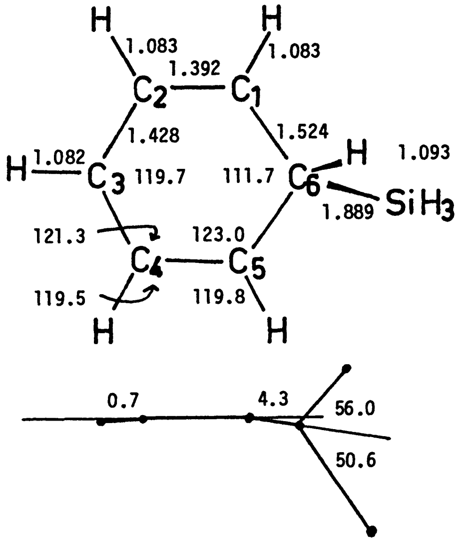


In a previous paper,[3)] we have shown experimentally that 6-trimethylsilylcyclohexadienyl radicals (1a, R=Me) have a bent structure at the energy minimum with the 6-trimethylsilyl group at the axial position. The CNDO/2 calculation for the 6-silylcyclohexadienyl radical (1b, R=H) also indicates that the energy minimum is at the bent structure with out-of-plane angle of 4°.[3)] Very recently, however, a number of substituted cyclohexadienyl radicals have been investigated with the *ab initio* MO method under a *planar* ring constraint in relation to the Birch reduction.[4)] Since our previous CNDO/2 calculation used a minimized energy geometry determined by the INDO calculation,[5)] it seems to us important to examine the theoretical geometry of cyclohexadienyl (2) and 6-silylcyclohexadienyl (1b) radicals under only C_s constraint.

Standard *ab initio* UHF-SCF MO calculations were carried out with a modified version of the GAUSSIAN 70 programs,[6)] where the H_3Si group was placed in a staggered conformation. Geometries were optimized by using the energy gradient method[7)] with the STO-3G basis set. The geometric parameters and total energies for the optimized geometry of 1b are shown in Figure 1. The total energy of 1b was also calculated by using the 6-31G basis set[8)] for the optimized geometry. The distortion angle, θ, was calculated as 4.3°. A geometrical optimization, starting with the distorted cyclohexadienyl structure with an equatorial SiH_3 group, gave no minimum at around θ=4° to lead to nearly planar ring structure (θ=0.4°), whose total energy was a little higher than that of the structure depicted in Figure 1: ΔE=0.12 (STO-3G) or 0.25 kcal/mol (6-31G//STO-3G).

The calculation shows a similar distorted ring structure for the parent cyclohexadienyl radical (2) at the energy minimum with θ=3.4°, but the energy difference from the planar structure[4)] is so small (ΔE=0.036 kcal/mole) that 2 should be taken to be essentially planar structure with a very shallow energy minimum.

These findings are in good agreement with the previous result from ESR experiments and CNDO/2 calculations, indicating the importance of σ-π conjugation between the C-Si bond and the π system.[3)] The distorted structure of the 6-silylcyclohexadienyl (as well as 6-germylcyclohexadienyl) radicals with considerable spin delocalization onto the C-Si (and C-Ge) bond may be related to the reversibility of the addition of silyl (and germyl) radicals to an aromatic ring.[9)] We will discuss this problem in detail in a forthcoming paper.



$l_{(Si-H)}$ = 1.423

E(STO-3G) = -515.253635

E(6-31G//STO-3G) = -521.153918

Figure 1. Optimized UHF/STO-3G structure and total energies (E, hartrees) for 1b. Bond lengths are in Å, and bond and dihedral angles are in degrees.

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References

(1) Chemistry of Organosilicon Compounds 158.
(2) M. Kira and H. Sakurai, *Chem. Lett.*, 927 (1981).
(3) M. Kira and H. Sakurai, *J. Am. Chem. Soc.*, 99, 3892 (1977).
(4) A. J. Birch, A. L. Hinde and L. Radom, *J. Am. Chem. Soc.*, 102, 4075 (1980).
(5) M. B. Yim and D. E. Wood, *J. Am. Chem. Soc.*, 97, 1004 (1975).
(6) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton and J. A. Pople, GAUSSIAN 70, Program 236, QCPE, Indiana University, 1974.
(7) (a) A. Komornicki, K. Ishida, K. Morokuma, R. Ditchfield and M. Conrad, *Chem. Phys. Lett.*, 45, 595 (1977); (b) S. Kato and K. Morokuma, *ibid.*, 65, 19 (1979).
(8) The 6-31G basis set for silicon is taken from M. S. Gordon, *Chem. Phys. Lett.*, 76, 163 (1980).
(9) H. Sakurai, *J. Organometal. Chem. Library*, 12, 267 (1981).

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