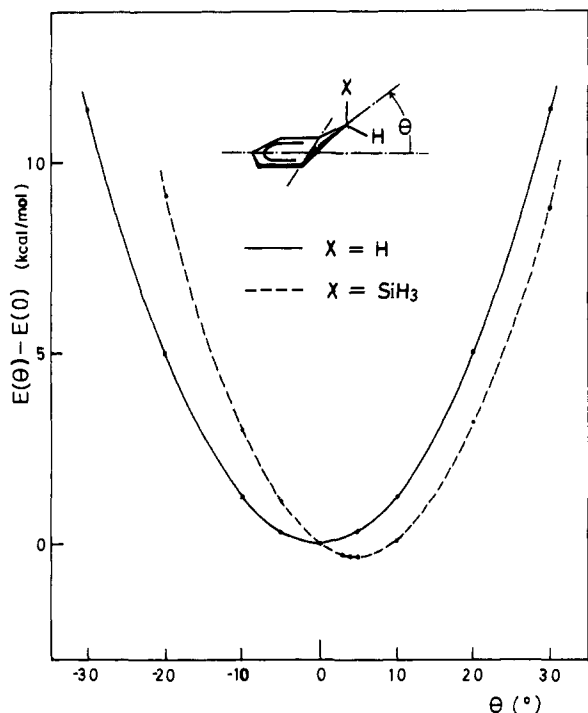


**Figure 1.** Temperature dependence of hfcc values of the methylene protons in the cyclohexadienyl (**1a**) and 3,6-bis(trimethylsilyl)cyclohexadienyl (**1b**) radicals.



**Figure 2.** Relative energy of the out-of-plane distortion for cyclohexadienyl radicals.

These radicals can generate relatively high concentrations to give as good a signal to noise ratio as studying the temperature dependence of the ESR spectra. Figure 1 shows the temperature dependence of the proton hfcc at 6-position of both **1a** and **1b**, and the value of  $\delta a_6/\delta T$  for **1a** is calculated to be  $-6.6 \text{ mG}/^\circ\text{C}$ .

The negative temperature coefficient observed in this study should originate in the out-of-plane deformation of the methylene carbon in the cyclohexadienyl radical (**I**). Thus, the hfcc of the axial hydrogen ( $H_a$ ) should increase with enhanced out-of-plane deformation at higher temperature while that of the equatorial hydrogen ( $H_e$ ) should decrease. However, the average value is expected to exhibit a small net decrease by INDO calculations.<sup>4g</sup> Therefore, the present study shows clearly that the cyclohexadienyl radical is planar but vibrates between bent structures.

Figure 1 contains another interesting feature that the proton hfcc at 6-position of **1b** shows small but definitely positive temperature dependence ( $\delta a_6/\delta T = +2.6 \text{ mG}/^\circ\text{C}$ ). This can be interpreted in terms of the preferred conformation in which the 6-trimethylsilyl group occupies the axial position at the bent structure at low temperature (**II**). Such a preferred conformation should result from  $\sigma$ - $\pi$  conjugation between the C-Si bond and the  $\pi$  system.<sup>6</sup> Unrestricted CNDO/2 calculations<sup>7</sup> for **I** and **II** also support the conclusion on the equilibrium structures of cyclohexadienyl radicals.<sup>8</sup> Thus, as Figure 2 shows, the parent cyclohexadienyl has the energy minimum at  $\theta = 0^\circ$ , where  $\theta$  is the angle of out-of-plane distortion from the planar carbon framework, while the energy minimum of the 6-silylcyclohexadienyl radical is at  $\theta = +4^\circ$ .<sup>9</sup>

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#### References and Notes

- (1) Chemistry of Organosilicon Compounds, 97.
- (2) (a) H. Sakurai, I. Nozue and A. Hosomi, *Chem. Lett.*, 129 (1976); (b) *J. Am. Chem. Soc.*, **98**, 8279 (1976).
- (3) (a) D. Griller, K. Dimroth, T. M. Fyles, and K. U. Ingold, *J. Am. Chem. Soc.*, **97**, 5526 (1975); (b) P. G. Cookson, A. G. Davies, and B. P. Roberts, *J. Chem. Soc. Chem. Commun.*, 289 (1976).
- (4) A number of cyclohexadienyl radicals have been investigated by ESR spectra. See inter alia, (a) H. Fischer, *Kolloid-Z.*, **180**, 64 (1962); (b) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963); (c) *ibid.*, **39**, 2147 (1963); (d) W. T. Dixon and R. O. C. Norman, *Proc. Chem. Soc., London*, 97 (1963); (e) *J. Chem. Soc.*, 4857 (1964); (f) S. DiGregorio, M. B. Yim, and D. E. Wood, *J. Am. Chem. Soc.*, **95**, 8455 (1973); (g) M. B. Yim and D. E. Wood, *ibid.*, **97**, 1004 (1975).
- (5) A Varian Associates E-12 spectrometer was used with a 9.5-GHz microwave bridge.
- (6) (a) T. Kawamura and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 649 (1972); (b) M. C. R. Symons, *ibid.*, **94**, 8589 (1972); (c) *Tetrahedron Lett.*, 793 (1975); (d) D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 6459 (1973); (e) *ibid.*, **96**, 6715 (1974); (f) H. Sakurai, T. Uchida, and M. Kira, *J. Organomet. Chem.*, **107**, 15 (1976).
- (7) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
- (8) The minimized energy geometry determined by the INDO calculation<sup>4g</sup> was used for the present calculations.
- (9) In this connection,  $\delta a(^{29}\text{Si})/\delta T$  would be very interesting to measure. However, the signal to noise ratios of spectra were unfortunately not as good as such a measurement.

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## Additions and Corrections

**Idealized Polytopal Forms. Description of Real Molecules Referenced to Idealized Polygons or Polyhedra in Geometric Reaction Path Form** [*J. Am. Chem. Soc.*, **96**, 1748 (1974)]. E. L. MUETTERTIES and L. J. GUGGENBERGER, Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898.

For the  $C_{3v}$  polyhedron in Figure 10, the calculated edge lengths and dihedral angles should be  $q = 1.212r$ ,  $s = 1.268r$ ,  $t = 1.321r$ ,  $u = 1.670r$ , and  $\delta's = 16.2^\circ$ .

In Table IV, the ideal angles ( $\delta's$ ) for the  $C_{3v}$  model should be 16.2, 16.2, and 16.2°.