Our interpretation of these results is that reduction of 7-methylguanosine disrupts the C$_{13}$-G$_{22}$-m^{7}G$_{46}$ base triple and gives rise to a slightly less ordered tRNA structure. The concomitant, reversible change in the rate of tRNA aminoacylation and photoinduced cross-linking verifies the importance of 7-methylguanosine in maintenance of the tertiary structure of tRNA in solution.

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(15) Phase IV tRNA is obtained at high temperature and is believed to correspond to randomly coiling single-stranded tRNA. Phase II tRNA, corresponding to a "clover leaf or close variant" structure, is obtained at moderate temperature in the presence of a high concentration of Na$^+$, but in the absence of Mg^{2+}.[14a-c]

(16) The reduced nucleoside in phase I tRNA underwent slow reoxidation to reafford 7-methylguanosine; the rate of reoxidation depended on the experimental conditions (pH, temperature, presence of oxygen, etc.) and paralleled observations at the nucleoside level.[9b]

(17) A similar procedure has been utilized successfully with purified tRNA^{Phe}.

(18) Prepared as described previously[9b] from NaBH$_4$ and 7-methylguanosine.

(19) A control was also run using tRNA^{Tyr}, which lacks 7-methylguanosine. Reduction with **2** had no effect on the biochemical activity of the tRNA.

(20) The difference between our results and those of Wintermeyer and Zachau[12] may simply reflect the use of different tRNA species. One may note, however, that the largest difference that we observed between the fully reduced and untreated *E. coli* tRNA^{Phe}s was 23% (±1.5–2.0%) after a 30-min incubation. Since Wintermeyer and Zachau[12] carried out their measurements with ±8% precision using yeast tRNA^{Phe} which was only 60% reduced at position 46, they may not have been able to observe changes comparable to those reported here.

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(22) After reoxidation, the tRNA sample which had been treated with **2** was again photocross-linked at the same rate as untreated tRNA.

(23) Career Development Awardee of the National Cancer Institute, 1975–1980; Alfred P. Sloan Research Fellow, 1975–1977; John Simon Guggenheim Fellow, 1977–1978.

(24) Fulbright-Hays Scholar on leave of absence from la Cattedra di Chimica Biologica, 2nd Medical School, University of Naples, Italy.

(25) American Cancer Society Postdoctoral Fellow, 1975–1976; National Institutes of Health Postdoctoral Fellow, 1976–1977.

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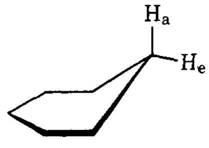
Temperature Dependent Electron Spin Resonance Spectra of Cyclohexadienyl and Silyl-Substituted Cyclohexadienyl Radicals. On the Conformation of the Radicals[1]

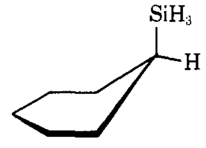
Sir:

Although ESR spectra of a few relatively long-lived cyclohexadienyl radicals in solution have recently been reported from this[2] and other[3] laboratories, most cyclohexadienyl radicals have been too reactive to give good ESR spectra in solution. Therefore, no study on the temperature dependence of the ESR spectra has been made.[4]

The equilibrium structure of the cyclohexadienyl radical is regarded as planar, but at the same time, the energy minimum is rather shallow so that the radical would be expected to vibrate between bent structures such as I.[4g] The INDO calculations of the parent cyclohexadienyl radical predicted that the magnitude of the hfcc of the methylene protons should decrease with increasing temperature due to the increasing out-of-plane deformation from the planar carbon framework.[4g]



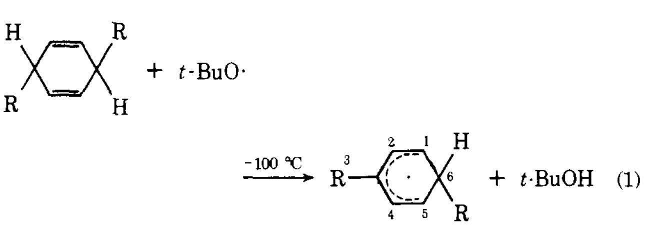
I



II

Our recent studies on the ESR spectra of several 6,6-disilylcyclohexadienyl radicals showed that the silyl group in the radicals had a large ^{29}Si isotopic hfcc due to the enhanced σ-π conjugation that should be reflected in the preferred conformation of the radicals at low temperature.[2a] Consequently, it seemed very interesting and also very important to examine the temperature dependence of the ESR spectra of cyclohexadienyl radicals.

The cyclohexadienyl and silyl-substituted cyclohexadienyl radicals were generated by hydrogen abstraction from the corresponding 1,4-cyclohexadienes (eq 1).



1a, R = H; **1b**, R = Me$_3$Si

Photolysis of a mixture of 1,4-cyclohexadiene, di-*tert*-butyl peroxide, and cyclopropane (ca. 1:1:1) in the cavity of an ESR spectrometer[5] gave a well-resolved spectrum of the cyclohexadienyl radical (**1a**) whose hfcc values agreed well with those of the literature:[4b] hfcc(gauss) (−100 °C) 2.65 (H$_{2,4}$), 9.13 (H$_{1,5}$), 13.56 (H$_3$), 48.1 (H$_6$). The peak-to-peak line width was less than 50 mG. Similarly, 2,6-bis(trimethylsilyl)cyclohexadienyl radical (**1b**) was generated: hfcc(gauss) (−100 °C) 2.15 (H$_{2,4}$), 8.00 (H$_{1,5}$), 35.9 (H$_6$).

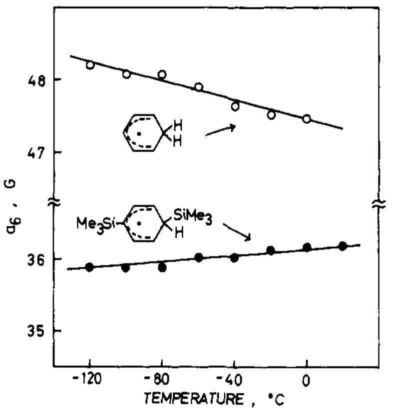


Figure 1. Temperature dependence of hfcc values of the methylene protons in the cyclohexadienyl (**1a**) and 3,6-bis(trimethylsilyl)cyclohexadienyl (**1b**) radicals.

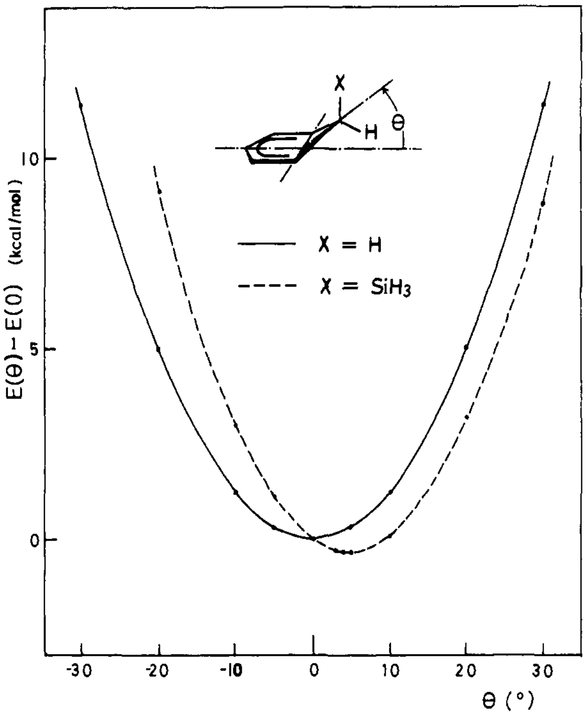


Figure 2. Relative energy of the out-of-plane distortion for cyclohexadienyl radicals.

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 mG/°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.[4g] 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 ($\delta a_6/\delta T = +2.6$ mG/°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 σ–π conjugation between the C–Si bond and the π system.[6] Unrestricted CNDO/2 calculations[7] for I and II also support the conclusion on the equilibrium structures of cyclohexadienyl radicals.[8] Thus, as Figure 2 shows, the parent cyclohexadienyl has the energy minimum at $\theta = 0°$, where θ is the angle of out-of-plane distortion from the planar carbon framework, while the energy minimum of the 6-silylcyclohexadienyl radical is at $\theta = +4°$.[9]

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

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(8) The minimized energy geometry determined by the INDO calculation[4g] was used for the present calculations.
(9) In this connection, $\delta a(^{29}Si)/\delta T$ 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 δ's = 16.2°.

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