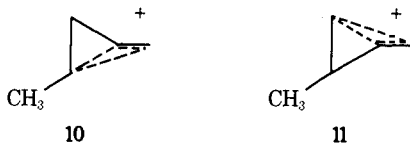


Table I. Relative ^1H and ^2H Intensities in 2-OH, 4-OH, and 5-OH

Compound		H ₁	H ₂	H ₃	H ₄
4 (before hydrolysis)	$^1\text{H}^a$	0.23	0.77		
	$^2\text{H}^b$	0.77	0.23		
	$^2\text{H}^c$	1.00			
4 (after hydrolysis)	$^1\text{H}^a$	0.60	0.67	0.84 ^d	0.89
	$^2\text{H}^b$	0.40	0.33	0.16	0.11
	$^2\text{H}^c$	0.43	0.30	0.18	0.09
6	$^1\text{H}^a$	0.53	0.76		1.71 ^e
	$^2\text{H}^b$	0.48	0.24		0.28
	$^2\text{H}^c$	0.57	0.15		0.28
7	$^1\text{H}^a$	0.68	0.82	0.68	0.82
	$^2\text{H}^b$	0.32	0.18	0.32	0.18
	$^2\text{H}^c$	0.37	0.13	0.37	0.13

^a All ^1H integrated intensities were obtained on a Varian XL-100-15 nmr spectrometer with an external ^{19}F lock. Each value represents the average of 20 integrations and was calculated on the basis $\Sigma^4_{n=1} H_n = 3$. Average deviations ≤ 0.01 . ^b $^2\text{H} = 1 - ^1\text{H}$. ^c Corrected for 23% of the 1S, 1'S, 2'S diastereomer in starting mesylate. ^d Overlaps signal for H₅, total intensity at 1.84. ^e Not sufficiently separated to integrate individually.

conformers of **5** by the C₂' methyl group suggest interaction of the developing p orbital at C₁ with both adjacent cyclopropane bonds. In contrast, an unsymmetrically bridged bicyclobutonium structure²² implies interaction between C₁ and only one of the two adjacent cyclopropane bonds. One might have expected the methyl at C₂' to be more stabilizing than a factor of 3.1 for formation of **10** vs. **11**.²⁴ How-



ever, more compelling evidence for a bisected primary cyclopropylcarbanyl cation comes from comparisons of isotopic distributions in alcohols **4**, **6**, and **7**. Alcohol **4**(1) comprises 71% of **4**(1) + **4**(3) and **4**(2)¹⁵ comprises 77% of **4**(2) + **4**(4). In addition **4**(1) + **4**(2), **6**(1) + **6**(2), and **7**(1) + **7**(2) constitute 73, 72, and 74%, respectively, of alcohols **4**, **6**, and **7**. These similarities indicate that the distributions of ^2H isomers in each skeletal isomer only differ by a factor representative of the proportion of **5** which ionizes from each conformer. Bisected cations **8**(1) and **8**(2) should have nearly identical stereo- and regiochemistries for reaction with solvent and rearrangement in agreement with our findings, whereas bicyclobutonium ions **10** and **11** should not.

Supplementary Material Available. Reduction of the data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-7591.

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- (1) Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, Research Corporation, and the Research Committee of the University of Utah for support of this research.
- (2) For excellent reviews see (a) H. G. Richey, Jr., "Carbonium Ions," Vol. 3, G. A. Olah and P. v. R. Schleyer, Eds., Wiley, New York, N.Y., 1972, p 1201; (b) K. B. Wiberg, B. A. Hess, and A. J. Ashe, III, *ibid.*, p 1295.
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- (7) The observed rotation for **4**, $[\alpha]^{30}_{\text{D}} -26.0^\circ$ (*c* 0.85, CHCl_3), corresponds to 77% 1S, 1'R, 2'R and 23% 1S, 1'S, 2'S if one assumes that the deuterium at C₁ does not contribute to the observed rotation. An nmr spectrum of **4** with $\text{Eu}(\text{fod})_3$ shows clearly resolved diastereotopic protons at C₁ ($\Delta\delta$ up to 0.3 ppm). The two broad doublets of unequal intensity collapse to two singlets of unequal intensity, 0.77 ± 0.01 and 0.23 ± 0.01 protons, upon irradiation at the H₆ resonance frequency. The upfield signal results from hydrogen in the pro-R position of the 1S, 1'R, 2'R diastereomer, and the downfield signal, from hydrogen in the pro-R position of the 1S, 1'S, 2'S diastereomer.
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- (9) Nmr spectra were taken in carbon tetrachloride and chemical shifts are reported as ppm (δ) downfield from internal tetramethylsilane.
- (10) $J_{1,2} = 11$ Hz, $J_{1,6} = J_{2,6} = 7$ Hz, $J_{3,4} = J_{4,5} = 4$ Hz, $J_{4,6} = 11$ Hz, $J_{5,\text{CH}_3} = 6$ Hz.
- (11) $J_{1,6} = 17.6$ Hz, $J_{2,6} = 10.5$ Hz, $J_{3,5} = J_{4,5} = J_{5,\text{CH}_3} = 6.4$ Hz, $J_{3,6} = J_{4,6} = 7.3$ Hz.
- (12) $J_{1,2} = 4.8$ Hz, $J_{1,3} = 9.4$ Hz, $J_{1,4} = 5.3$ Hz, $J_{1,6} = J_{3,6} = 4.8$ Hz, $J_{2,3} = 5.2$ Hz, $J_{2,4} = 8.8$ Hz, $J_{2,6} = J_{4,6} = J_{5,6} = 8.0$ Hz, $J_{3,4} = 4.2$ Hz, $J_{5,\text{CH}_3} = 6.0$ Hz.
- (13) Reduction of the data will appear following these pages in the microfilm edition of this volume of the journal. See paragraph at end of paper regarding supplementary material.
- (14) A detailed treatment of the data will be furnished in the full paper. Isotope effects should be small but may introduce small errors for comparisons between skeletal isomers or positional ^2H isomers.¹⁵
- (15) B. Boricnik, Z. Majerski, S. Borcic, and D. E. Sunko, *J. Org. Chem.*, **38**, 1881 (1973).
- (16) A careful analysis of the data suggests that a small amount of **4**(2) is formed from **5** by a *k_s* process.
- (17) The stereochemistries of the cyclopropylcarbanyl-cyclopropylcarbanyl rearrangements agree with previous work,² and a high degree of stereoselectivity is expected. The large uncertainty for **8**(1) → **8**(2) arises because the concentrations of **4**(3) and **4**(4) cannot be determined with the same accuracy as those of **6**(1), **6**(2), **7**(1), and **7**(2).
- (18) H. G. Richey and J. Richey, *J. Amer. Chem. Soc.*, **88**, 4971 (1966).
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- (22) The structure shown on p 151 (ref 4a), for a "C_{2,4}-cyclopropylcarbonyl ion," is very similar to that used by Roberts²³ and coworkers (p 281, Figure 6) to describe a "bicyclobutonium ion."
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- (24) Ionization of **5a** should give **10**, while ionization of **5b** should give **11**.
- (25) University of Utah Research Fellow, 1971-1973.

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Structure of Hexameric Trimethylsilyllithium, a Folded Chair

Sir:

We wish to report the first crystal structure of a hexameric lithium derivative which provides a detailed picture of the lithium aggregate in $(\text{LiSiMe}_3)_6$ and also shows the participation of silicon in an electron deficient structure.[†] Two views of this structure are shown in Figure 1a and 1b. It is found that the trimethylsilyllithium framework can best be represented as a chair-form six-membered lithium ring of approximate D_{3d} symmetry with each face occupied by a bridging trimethylsilyl group. This is in contrast to the distorted octahedron with two open faces previously postulated for simple hexameric organolithium derivatives,¹ and to the hydrogen-bridged structure proposed by Craubner.² The 12 shortest lithium-lithium distances fall into two classes of six distances each. The shorter of these two classes averages 2.70 Å (av esd 0.03 Å) and occurs between the lithium atoms adjacent to one another on the edge of the ring. This distance is close to twice the covalent radius (1.23 Å) and is similar to the lithium-lithium bond distance (2.42-2.63 Å) observed in the methyl-³ and ethyllithium tetramers⁴ and to that recently reported in the dimeric bicy-

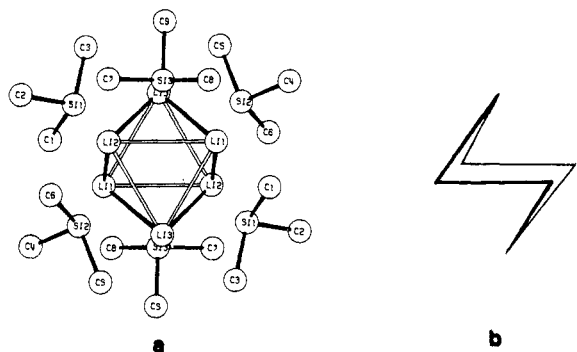


Figure 1. (a) The $(\text{LiSiMe}_3)_6$ hexamer. (b) A schematic view of the "folded-chair" conformation of Li_6 in $(\text{LiSiMe}_3)_6$.

clo[1.1.0.]butan-1-yl lithium-tetramethylenediamine (2.74 Å).⁵ The second distance is between lithium atoms meta to each other on the edge of the ring and averages 3.27 Å (av esd 0.04 Å), which is much greater than the observed bond distance and slightly over twice the van der Waals radius (1.55 Å). Thus, it is clear that there is no significant interaction except between adjacent lithium atoms.

Each Me_3Si group, is located centrally above a triangular face on the periphery of the Li_6 ring, with three nearly equal lithium-silicon bond distances of average value 2.68 Å (av esd 0.03 Å). Thus the silicons form a nonbonded hexameric ring which is reciprocal to the Li_6 ring. The equivalence of the lithium-silicon bonds implies each silicon participates equally in bonding to each of the three lithium atoms in a delocalized molecular orbital over these centers. One may initially postulate the direct bonding of each lithium to the two adjacent lithiums and to three silicon atoms. The silicons not only serve as bridges along the edges of the ring but also serve to bridge the meta lithium atoms of the rings resulting in the folded configuration observed.

In order to better understand the conformation of the hexameric Li_6 ring, it is instructive to consider the fact that any hexameric conformation involving six symmetry-equivalent atoms and six symmetry-equivalent bonds can be derived from an undistorted octahedron by compressing the octahedron along a $\bar{3}$ axis of the octahedron. The extreme examples are the undistorted octahedron and the planar benzene ring. One may characterize the conformation of such a crown or chair-type ring system by the bond angles along the periphery, by the dihedral angle between the back and the seat of the chair, or by the ratio between the closest nonbonded distances within the ring and the bonded distances. In Table I we have presented such data for the octahedron, for the Li_6 hexamer, for cyclohexane, and for benzene. It will be noted that the Li_6 chair conformation is much closer to the octahedron than to a cyclohexane structure and may be thought of in a "folded chair" conformation.

Certainly this structure may have significant implications concerning the bonding and reactivity of these derivatives. Additional speculation awaits further refinement of the structure and rigorous calculations, both of which are currently in progress, and will be reported at a later date in a full paper.

Trimethylsilyllithium was prepared by cleavage of bis(trimethylsilyl)mercury as previously described.⁶ The crystals for the X-ray structural determination were grown from hot cyclohexane and were loaded into thin-walled capillaries in an argon filled drybox which were then sealed.

Crystals of $(\text{LiSiMe}_3)_6$ are monoclinic, $P2_1/a$ with lattice constants $a = 18.902$ (4) Å, $b = 14.078$ (3) Å, $c = 13.933$ (3) Å, $\beta = 89.60$ (2)°, and $Z = 4$. Intensity data

Table I. Comparison of Conformational Parameters in Hexamers

	Dihedral angle, back to seat (deg)	Bond angle (deg)	Ratio non-bonded: bonded	Symmetry
Octahedron	54.7	60.0	1.0	O_h
$(\text{LiSiMe}_3)_6$	70.5	74.6	1.21	D_{3d}
		(av esd, 1.0°)		
Cyclohexane ^a	130.7	111.6	1.64	D_{3d}
Benzene	180.0	120.0	1.732	D_{6h}

^a E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, p 454.

were collected by a θ - 2θ scan on a Syntex diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation to a value of $\sin \theta/\lambda < 0.423$. The structure was solved by application of the Sayre equation and Fourier techniques. The present discrepancy factors are

$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|} = 0.080$$

and

$$R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2} = 0.103$$

for 1671 data. The contributions of the 56 hydrogen atoms have not yet been included in the calculation. The asymmetric unit contains two independent halves of $(\text{LiSiMe}_3)_6$ hexamers located about crystallographic inversion centers. Thus each molecule possesses $C_i - \bar{1}$ crystallographic symmetry and $D_{3d} - \bar{3}2m$ idealized molecular symmetry.

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† NOTE ADDED IN PROOF. Since submission of this communication, R. Zerger, W. Rhine, and G. Stucky, *J. Amer. Chem. Soc.*, **96**, 6048 (1974), have reported the structure of cyclohexyllithium. This derivative crystallizes as a hexamer of approximately S_6 symmetry with the six lithium atoms in the same configuration as shown in $(\text{LiSiMe}_3)_6$. In addition to the obvious distinction between the bridging ligands, a second significant difference appears to be present, that is, the suggested interaction between the α -hydrogen atoms of the cyclohexyl groups and the lithium framework which leads to stabilization of the hexamer. This type of interaction is highly unlikely in LiSiMe_3 hexamers.

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Determination of the Rate Constant for Homolysis of a Nitrene Carbon-Nitrogen Bond via Crossover Measurements of Isotopically Labeled Substrates. Kinetic Properties of Caged Ambident Radicals¹

Sir:

Methods of estimating true unimolecular homolytic rate constants for systems exhibiting cage return are attracting increasing interest.² An accompanying concern is an understanding of the competitive rates of primary processes involving the perturbation and destruction of the initially formed caged radicals.^{2,3}