^{13}C, see Table VIII, MS parent peak of **40** and **41** 210.0475 (calcd for C$_7$H$_{15}$O$_3$PS, 210.0478).

Phosphate 32. Following a procedure described by Denney et al.[50] for the mercuric oxide oxidation of cyclic phosphites, phosphate **32** was prepared from phosphite **14**[46] in 29% yield, bp 60–62 °C (0.25 mm) [lit.[53] bp 85–86 °C (1 mm)].

Thiophosphate 43. Following the procedure described for the preparation of **35**, thiophosphate **43** was synthesized in 57% yield from phosphite **14** and sulfur. ^{1}H NMR (60 MHz, CDCl$_3$) δ 3.75 (d, J_{HCOP} = 14.0 Hz, 3 H, OCH$_3$), 4.75 (d, J_{HCOP} = 11.0 Hz, 4 H, ring protons).

Dynamic Stereochemistry of Hexakis(dimethylsilyl)benzene

Ingeborg I. Schuster,[1a] Walter Weissensteiner,[1b] and Kurt Mislow*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. Received February 24, 1986

Abstract: Empirical-force-field (EFF) calculations show that hexakis(dimethylsilyl)benzene (**2**) has a C_{6h} ground-state geometry similar in most respects to the statically geared structure reported for hexaisopropylbenzene (**1**). Variable-temperature NMR measurements on the tricarbonylchromium π complex of **2** (**3**) yield a dimethylsilyl group rotation barrier of 14.2 kcal mol^{-1}. A 15.7-kcal mol^{-1} barrier is found for **2** by EFF calculations. According to these calculations, the rotation of the dimethylsilyl groups in **2** and, by extension, in **3** takes place by a stepwise mechanism rather than by correlated disrotation (dynamic gearing) of all six groups.

Hexaisopropylbenzene (**1**)[2,3] owes its exceptional conformational rigidity to a tightly interlocking cyclic tongue-and-groove arrangement of isopropyl groups in a structure of C_{6h} symmetry. The closely related hexakis(dimethylsilyl)benzene (**2**)[4] presumably adopts a similar structure, in which the SiH hydrogen of each dimethylsilyl group is tucked into the cleft formed by the two methyls of the neighboring group. However, because substitution of silicon for carbon significantly increases the interatomic distances in the side chains, the dimethylsilyl groups in **2** should be less tightly geared than the isopropyl groups in **1**, and the energy requirement for dimethylsilyl group rotation in **2** should therefore be considerably less than that for isopropyl group rotation in **1**. The present work was undertaken in order to place this comparison between the two systems on a quantitative basis.

The structural relationship between **1** and **2** was explored by use of the empirical force field (EFF) method,[5] which had previously been found to give results in satisfactory agreement with experimentally determined values for the ground state of **1**.[3] In accord with expectations, the structure of **2** calculated by this

Table I. Calculated Structural Parameters for **1** and **2**[a]

atoms[b]	hexaisopropylbenzene[c] (1)	hexakis(dimethylsilyl)benzene[d] (2)
	Bond Lengths	
C$_{ar}$–C$_{ar}$	1.419	1.415
C$_{ar}$–X	1.542	1.928
X–C$_m$	1.543	1.843
X–H	1.100	1.479
	Bond Angles	
C$_{ar}$–C$_{ar}$–C$_{ar}$	120.0	120.0
C$_{ar}$–C$_{ar}$–X[e]	121.1	120.4
C$_{ar}$–C$_{ar}$–X[f]	118.9	119.6
C$_{ar}$–X–C$_m$	115.8	111.1
C$_m$–X–C$_m$	115.6	116.3
C$_m$–X–H	99.6	99.8
C$_{ar}$–X–H	106.9	118.2
	Torsion Angle	
C$_{ar}$–C$_{ar}$–X–C$_m$	70.1	65.6

[a] Structural parameters calculated by the EFF method (see text). Bond lengths in angstroms, angles in degrees. [b] C$_{ar}$ = aryl carbon, C$_m$ = methyl carbon, X = methine carbon (1) or silicon (2). [c] Reference 3. [d] Present work. [e] Angle anti with respect to X–H. [f] Angle syn with respect to X–H.

method[6-10] has C_{6h} symmetry and is a good deal less congested than that of **1**.[11] Inspection of Table I shows that, with the

(1) (a) On leave from The Pennsylvania State University. (b) Max Kade Postdoctoral Research Fellow, on leave from the Universität Wien.

(2) (a) Arnett, E. M.; Bollinger, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 4729. (b) Bollinger, J. M. Ph.D. Dissertation, University of Pittsburgh, 1965. (c) Hopff, H. *Chimia* **1964**, *18*, 140. (d) Hopff, H.; Gati, A. *Helv. Chim. Acta* **1965**, *48*, 509.

(3) Siegel, J.; Gutiérrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 1569.

(4) Brennan, T.; Gilman, H. *J. Organomet. Chem.* **1968**, *11*, 625. Fink, W. *Helv. Chim. Acta* **1974**, *57*, 1010. See also: Chaffee, R. G. U.S. Patent 3 280 073 (*Chem. Abstr.* **1967**, *66*, 38337r).

(5) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, D.C., 1982.

(6) Input geometries were based on standard bond lengths and bond angles. These structures were then optimized[7] by the program BIGSTRN-3[8] with use of the MM2 force field.[9] Final structures were characterized as minima by the absence of negative eigenvalues in the matrix of analytical second derivatives.
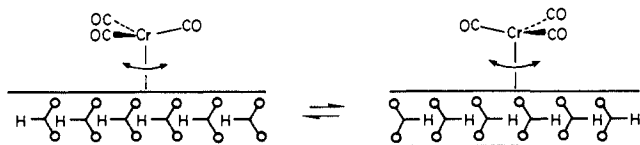
Figure 1. Enantiomerization of hexakis(dimethylsilyl)benzene tricarbonylchromium (3) by rotation of the six dimethylsilyl groups. Methyl groups are schematically represented by open circles. The curved arrows symbolize rapid rotation about the chromium–arene bond.

exception of the C_{ar}–X–C_m and C_{ar}–X–H bond angles, the structural parameters of 1 and 2 are quite similar if account is taken of the difference in covalent radii of carbon and silicon.

As in the case of 1, the structure that results from a process in which each of the six side chains in 2 is rotated by π is operationally indistinguishable from the structure obtained by simply flipping the whole molecule by π. To observe the process of internal motion and to measure the attendant dimethylsilyl group rotation barrier, the symmetry of 2 must therefore be lowered in some appropriate manner. In one approach, which had been successfully employed to determine the ethyl group rotation barrier in hexaethylbenzene,[12] the two faces of the aromatic ring are rendered nonequivalent by complexation with M(CO)$_3$. In the case of 1 and 2, such complexation would destroy plane and center of symmetry and lead to a chiral structure. Depending on its magnitude, the barrier to internal rotation could then be obtained either from VT-NMR (DNMR) measurements, by monitoring the site exchange of proximal and distal methyl groups resulting from rotation of the side chains, or from conventional kinetics, by monitoring the racemization of the potentially optically active complex. While this approach failed in the case of 1, which resists complexation,[3] there was reason to expect that it might succeed with 2, because of its less congested structure. Reaction of 2 with tris(acetonitrile)tricarbonylchromium[13] in tetrahydrofuran did indeed yield a tricarbonylchromium π complex (3), whose 250-MHz ^{1}H NMR spectrum in CD_2Cl_2 at $-30\ ^\circ$C shows two well-separated doublets at δ 0.50 and 0.63, corresponding to the diastereotopic methyl groups, and a SiH septet at δ 4.66. At elevated temperatures the two doublets broaden and collapse, and at 100 $^\circ$C, in hexachlorobutadiene, the methyl signal appears as one sharp doublet. Rates of exchange were obtained by line-shape analysis for measurements (a) in CD_2Cl_2 at -48 to $+34\ ^\circ$C and (b) in hexachlorobutadiene at $+20$ to $100\ ^\circ$C. Least-squares fitting of the rate data to the Eyring equation gave values for $\Delta G^{\ddagger}$ at 27 $^\circ$C of (a) 14.2 and (b) 14.4 kcal mol^{-1}.

The observed site exchange process is a manifestation of internal rotation of the dimethylsilyl groups in 3 (Figure 1).[14] In the

(7) Geometry optimizations were routinely begun with the variable-metric method and concluded with the full-matrix Newton-Raphson method; analytical second derivatives were used at both stages. The final convergence criteria for the Newton-Raphson stage were as follows: rms gradient less than 10^{-6} kcal mol^{-1} Å^{-1} and rms atom movement less than 10^{-6} Å.

(8) BIGSTRN-3 (Nachbar, R. B., Jr.; Mislow, K.) is available as QCPE No. 514 from QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47405.

(9) Allinger, N. L.; Yuh, Y. H. *QCPE* **1981**, *13*, 395. Two modifications were introduced for the purpose of the present calculations. (a) For C_{ar}–C_{ar} bonds, $l^0 = 1.3937$ Å and $k_s = 8.0667$ mdyn Å^{-1}. All torsional parameters for C_{ar} were taken to be the same as for C(sp^2). See also: Ōsawa, E.; Onuki, Y.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 7475. (b) For two torsional parameters not included in the MM2 force field, Si–C_{ar}–C_{ar}–Si and C_{ar}–C_{ar}–C_{ar}–Si, respectively, the following values of V_n (kcal mol^{-1}) were employed: $V_0 = 10.40, 10.23$; $V_1 = -0.10, -0.27$; $V_2 : -10.5, -10.5$; $V_3 = 0.0, 0.0$. See: Weissensteiner, W.; Schuster, I. I.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.*, following paper in this issue.

(10) The X-ray structure of 2 is under current investigation (West, R., private communication).

(11) For example, the interatomic distance between the hydrogen on X (X = methine carbon in 1 and silicon in 2) and the nearest X on the neighboring side chain is 2.34 Å for 1 and 2.85 Å for 2.

(12) Iverson, D. J.; Hunter G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073.

(13) Sneeden, R. P. A. *Organochromium Compounds*; Academic Press: New York, 1975; pp 20–21. King, R. B. *J. Organomet. Chem.* **1967**, *8*, 139.

CONFORMATIONAL DESCRIPTOR | **SYMMETRY** | **RELATIVE STERIC ENERGIES**

		1	2
R_0	C_{6h} (C_{6h})	0.0	0.0
R_1	C_s (C_1)	12.3	6.5
R_{12}	C_s (C_1)	14.3	7.9
R_{123}	C_{2v} (C_2)	14.2	7.1
R_{13}	C_s (C_1)	23.2	11.2
R_{14}	C_{2h} (C_2)	24.6	12.3
R_{124}	C_{2v} (C_2)	25.0	13.0
R_{125}	C_{2v} (C_2)	25.2	11.5
R_{135}	D_{3h} (D_3)	31.9	14.9

Figure 2. The nine conformational isomers of hexaisopropylbenzene (1) and hexakis(dimethylsilyl)benzene (2), and their descriptors. The isomers are schematically represented by figures with lines in the plane of the benzene ring projecting from the methine carbon (1) or silicon (2) atoms and pointing in the direction of the methine (1) or silicon (2) hydrogens. Methyl groups are not shown. For each isomer, the highest symmetry is given and also, in parentheses, the symmetry of the EFF-optimized structure. EFF-calculated relative steric energies are in kcal mol^{-1}.

absence of suitable parameters for 3, the mechanistic details of the corresponding motion in 2 were explored by the EFF method.[6] There are nine conformational isomers of 2 in which all six dimethylsilyl groups adopt a bisected conformation. These conformers, which correspond to nine energy minima on the potential energy hypersurface, are displayed schematically in Figure 2,[15] along with their symmetries, their calculated relative steric energies, and the previously reported[3] values for the nine corresponding conformers of 1.[16] The conformers are partitioned into four sets according to the number of gearing interactions between dimethylsilyl groups in neighboring positions, e.g., 6, 4, 2, and 0 interactions for R_0, R_1, R_{13}, and R_{135}, respectively. As in the

(14) A site-exchanged process involving arene–metal bond dissociation was ruled out by the observation of a doublet at δ 0.48, due to admixed 2, that remained sharp over the whole temperature range (-30 to $+100\ ^\circ$C). No decomposition of the chromium complex was noted during these measurements, as gauged by the constancy of the ratio of complexed to uncomplexed ligand.

(15) The schematic representations and conformational descriptors are those adopted in our previous work:[3] the numbering is clockwise from the top, and the subscripts refer to the positions of the turned alkyl groups relative to a standard structure (R_0).

(16) In the course of optimization,[6] the Si–C bond was found to increase without limit in all but two of the structures (R_0 and R_{135}). To avoid this problem, optimizations were carried out without the cubic term in the potential function for bond stretching.[17] Structural parameters calculated for R_0 and R_{135} with and without this term differ only slightly: the largest differences in bond lengths, bond angles, and torsion angles are 0.03 Å (R_0, Si–C_{ar}), 1.3° (R_0, C_{ar}–Si–H), and 0.7° (R_0, C_{ar}–C_{ar}–Si–C_m), respectively. Accordingly, neglect of this term is unlikely to have a significant effect on the calculated structures and steric energies of the remaining seven isomers.

(17) A similar problem had been encountered in EFF calculations of the structure of C[C(CH$_3$)$_3$]$_4$. See: Iroff, L. D.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 2121, footnote 44.

case of 1, the fewer the gearing interactions, the higher the steric energy.

Homomerization (topomerization) of 1 proceeds by the stepwise mechanism $R_0 \rightarrow R_1 \rightarrow R_{12} \rightarrow R_{126}$ $(=R_{123}) \rightarrow R_{1256}$ $(=R_{12}) \rightarrow R_{12356}$ $(=R_1) \rightarrow R_{123456}$ $(=R_0)$.[3] Assuming a stepwise mechanism, the first step in the homomerization sequence for 2 must also be $R_0 \rightarrow R_1$. The transition state for this process lies 14.8 kcal mol^{-1} above the ground state (R_0).[18] Two nonequivalent processes, $R_1 \rightarrow R_{12}$ and $R_1 \rightarrow R_{16}$, both lead from R_1 to R_{12} since $R_{12} = R_{16}$. The calculated transition-state energies relative to R_0, 15.4 and 21.2 kcal mol^{-1} for $R_1 \rightarrow R_{12}$ and $R_1 \rightarrow R_{16}$, respectively,[19] indicate that the former is the preferred pathway. Two nonequivalent processes, $R_{12} \rightarrow R_{123}$ and $R_{12} \rightarrow R_{126}$, both lead from R_1 to R_{123} since $R_{123} = R_{126}$. The calculated transition-state energies relative to R_0, 18.5[18] and 15.7 kcal mol^{-1} for $R_{12} \rightarrow R_{123}$ and $R_{12} \rightarrow R_{126}$, respectively, indicate a slight preference for the latter pathway. The remaining three steps, $R_{1256} \rightarrow R_{12356} \rightarrow R_{123456}$, follow from the principle of microscopic reversibility. The homomerization sequence for 2 is thus found to be the same as that for 1, with an overall barrier of 15.7 kcal mol^{-1}.

An alternative mechanism, in which all six dimethylsilyl groups undergo correlated disrotation (dynamic gearing[20]), converts R_0 into R_{123456} in a single step, by way of a statiomer of D_{3d} symmetry in which the six Si–H bonds point alternately up and down around the benzene ring periphery. However, EFF calculations show that the D_{3d} conformation is a local minimum that lies 33.2 kcal mol^{-1} above the ground state.[21] Correlated disrotation of all six dimethylsilyl groups can therefore be ruled out as the mechanism for homomerization. The possibility that two neighboring dimethylsilyl groups undergo correlated rotation, thus leading from R_0 to R_{12} in a single step, was also ruled out by calculations which yield a barrier of ca. 19.5 kcal mol^{-1} for this process, higher—though not by much—than the barrier calculated for uncorrelated rotation. The stepwise mechanism calculated for 2 follows the pattern of uncorrelated rotation observed or calculated for 1,[3] for tetraisopropylethylene,[22] and for other statically geared systems.[23]

The barrier calculated for dimethylsilyl group rotation in 2 is in good agreement with the experimentally determined barrier in 3. The small discrepancy of 1.5 kcal mol^{-1} may be due to the effect of π complexation on the energy of activation for dimethylsilyl group rotation. In more crowded arenes, such complexation has been found to result in a decrease in activation energy of the order of 4–5 kcal mol^{-1}.[24] The agreement between calculated and found barriers in 2 (3) enhances the credibility of the

barrier (35 kcal mol^{-1}) calculated for the homomerization of 1.[3]

Experimental Section

Solution 250.13-MHz ^{1}H and 62.83-MHz ^{13}C NMR spectra were recorded at ambient temperature, in CD$_2$Cl$_2$ on a Bruker WM-250 spectrometer, unless otherwise specified. Infrared spectra were recorded on a Digilab FTS-20C FT-IR instrument. Melting points are corrected.

Hexakis(dimethylsilyl)benzene Tricarbonylchromium(0). Hexakis-(dimethylsilyl)benzene (2) was prepared in 28–30% yields according to the literature procedure.[4] Pure product was obtained by addition of a small amount of methanol to the oily product mixture, filtration, and recrystallization from methanol–ethyl acetate. ^{1}H NMR δ 0.48 (d, J = 3.7 Hz, CH$_3$), 4.83 (septet, J = 3.7 Hz, SiH); ^{13}C NMR δ 1.28 (CH$_3$), 154.64 (C$_{ar}$).

A solution of chromium hexacarbonyl (0.60 g) in 15 mL of acetonitrile (distilled from P$_2$O$_5$) was degassed and heated below 100 °C for 2 days in an inert (Ar) atmosphere. At the end of this period the solvent was removed under vacuum at ambient temperature, and 0.88 g of 2 in 15 mL of dry tetrahydrofuran (distilled from sodium benzophenone ketyl) was quickly added to the air-sensitive, bright yellow residue. The solution was heated under reflux for 15 h, after which the solvent was removed by distillation under vacuum. Pentane was added to the dark brown residual solid, and the resulting suspension was filtered in an argon atmosphere to remove insoluble decomposition products. The clear yellow filtrate was concentrated under reduced pressure and chromatographed on neutral alumina, using pentane as eluent. The first fraction of eluate consisted mostly of 2, and the second consisted of the desired π complex (3). Removal of solvent, further purification by preparative TLC (hexane), and recrystallization from hexane afforded 3; mp 265–266 °C dec. IR (CCl$_4$) 1901.8, 1963.5 cm^{-1}. ^{1}H NMR δ 0.57 (brs, CH$_3$), 4.70 (septet, J = 3.6 Hz, SiH); ^{13}C NMR δ 1.13 (CH$_3$), 115.60 (C$_{ar}$), 233.53 (CO); mass spectrum (high resolution), m/e 562.1117 (562.1154 calcd for C$_{21}$H$_{42}$Si$_6$ ^{52}CrO$_3$).

Variable-Temperature NMR Measurements. Low-temperature ^{1}H NMR spectra of the π complex (3) in CD$_2$Cl$_2$ containing tetramethylsilane were obtained in the temperature range –48 to +34 °C. Although the SiH septet maintained its multiplicity throughout this range, the single resonance of the two exchanging methyls (distal and proximal to chromium), which is somewhat broadened at ambient temperatures, decoalesced below 4 °C into two peaks which, at temperatures near the slow-exchange limit, exhibited the expected coupling with SiH. The positions of all three resonances were temperature dependent according to the following relationships derived near and below the slow-exchange limit (T in degrees Kelvin, δ in Hz):

$$\delta(\text{SiH}) = 0.15625(T) + 1127.938$$

$$\delta(\text{CH}_3)_A = 0.042247(T) + 147.282$$

$$\delta(\text{CH}_3)_B = 0.032562(T) + 118.028$$

Rates of exchange were obtained by line-shape analysis of the methyl coalescence through use of the program DNMR3.[25] Least-squares fitting of the rate data (correlation coefficient 0.9993) to the Eyring equation gave a value for a $\Delta G^{\ddagger}$ of 14.2 kcal mol^{-1} at 27 °C, in good agreement with the value of 13.8 kcal mol^{-1} at 4 °C (the coalescence temperature) calculated by use of the Gutowsky–Holm expression.[26]

^{1}H NMR spectra of 3 in hexachlorobutadiene were recorded in the unlocked mode between 20 and 100 °C. The rate data, processed as before (correlation coefficient 0.9993), yielded a value for $\Delta G^{\ddagger}$ of 14.4 kcal mol^{-1}.

(18) Stationary points on the hypersurface were characterized as partial maxima by the number of negative eigenvalues in the force constant matrix; a single partial maximum (one negative eigenvalue) corresponds to a saddle point (transition state). Convergence criteria for saddle points were the same as for minima.[6] Transition structures were distorted along the negative and positive direction of the eigenvector associated with the negative eigenvalue and optimized by the variable-metric method; this assured that the saddle point connected the expected pair of minima.

(19) The saddle points for these processes did not converge, and the barrier energies were therefore calculated by the incremental group driving technique. The driven dimethylsilyl groups were rotated by 2° increments in the neighborhood of the saddle point (rms gradient 5 × 10^{-6} kcal mol^{-1} Å^{-1}). The constraints were released and the structure was optimized to assure that it converged to an adjacent minimum.

(20) Hounshell, W. D.; Iroff, L. D.; Iverson, D. J.; Wroczynski, R. J.; Mislow, K. *Isr. J. Chem.* **1980**, *20*, 65.

(21) By contrast, the D_{3d} conformation of 1 is not a minimum but a stationary point with three negative eigenvalues and a steric energy of 90.0 kcal mol^{-1} relative to the ground state.

(22) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 998.

(23) Berg, U.; Liljefors, T.; Roussel, C.; Sandström, J. *Acc. Chem. Res.* **1985**, *18*, 80 and references therein.

(24) Iverson, D. J.; Mislow, K. *Organometallics* **1982**, *1*, 3.

(25) Klein, D. A.; Binsch, G. *QCPE* **1970**, *11*, 165.

(26) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 96.