Conformation and Rotational Barriers in *sym*-Tetra-*tert*-butylethane and *sym*-Tetra(trimethylsilyl)ethane[1]

S. Brownstein,[2a] J. Dunogues,[2b] D. Lindsay,[2a] and K. U. Ingold*[2a]

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R9, and the Laboratoire de Chimie Organique et Laboratoire des Composés Organiques du Silicium et de l'Etain associé au C.N.R.S., Université de Bordeaux I, 33 Talence, France. *Received June 14, 1976*

Abstract: *sym*-Tetra-*tert*-butylethane, **1**, and *sym*-tetra(trimethylsilyl)ethane, **2**, have been studied by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. Both compounds adopt a gauche conformation at room temperature with the Me_3C (or Me_3Si) groups appearing as two magnetically inequivalent pairs. This conformational preference is attributed to distortion of the tertiary carbons from tetrahedral geometry because of steric repulsion between the geminal alkyl groups. The rotation of one pair of Me_3C in **1** can be hindered at low temperatures, but irreversible decomposition sets in at a temperature (140 °C) below that required to make the two pairs of Me_3C equivalent. However, with compound **2** the two pairs of Me_3Si groups can be made equivalent by raising the temperature. It is suggested that equivalence is achieved by a gauche $\rightleftharpoons$ anti $\rightleftharpoons$ gauche interconversion rather than by a direct gauche $\rightleftharpoons$ gauche process. The rate constant can be represented by $\log (k, \mathrm{s}^{-1}) = (8 \pm 3) - (10.2 \pm 0.4\ \mathrm{kcal/mol})/2.3RT$. The large, negative, activation entropy for Me_3Si exchange ($\Delta S^{\ddagger} = -26 \pm 13$ gibbs/mol) is attributed to the requirement for a cooperative movement among many groups. Values of T_1 for **1** suggest that the tertiary C-H bonds in this molecule are of normal length. Problems associated with measuring the lifetime of the free radical derived by removal of the tertiary hydrogen from **2** are also considered.

Nuclear magnetic resonance is the most commonly employed technique for studying the hindered internal rotation of molecules in solution.[3] Measurements of barriers to rotation about carbon-carbon single bonds by NMR spectroscopy must generally be made at low temperatures.[4,5] In the course of our work on persistent carbon-centered radicals[6] we prepared a compound that we tentatively identified as 1,1,2,2-tetra-*tert*-butylethane, **1**. The identification was only tentative mainly because the ^{1}H and ^{13}C NMR spectrum of **1** at room temperature indicated that the four *tert*-butyl groups were not all magnetically equivalent. Instead, they appeared to be equivalent in pairs. The spectra were not changed by heating until the temperature reached ca. 140 °C, at which point the compound decomposed irreversibly.

$$[(CH_3)_3C]_2CHCH[C(CH_3)_3]_2$$

1

In crowded molecules and radicals the replacement of *tert*-butyl groups by trimethylsilyl groups gives less strained and thermally more stable species.[6-10] We therefore prepared 1,1,2,2-tetra(trimethylsilyl)ethane, **2**, by the same procedure we had used to make **1**. At room temperature, the trimethylsilyl groups in this molecule were found to be equivalent in pairs. However, on raising the temperature the four trimethylsilyl groups all became equivalent.

$$[(CH_3)_3Si]_2CHCH[Si(CH_3)_3]_2$$

2

In this paper we present the results of a detailed dynamic NMR study of **1** and **2** and discuss their preferential conformation.

Experimental Section

Materials. 1,1,2,2-Tetra-*tert*-butylethane, 1, was prepared by coupling di-*tert*-butylmethyl chloride[11] with sodium by the procedure described previously.[7] The purified material (mp 168-172 °C) was isolated in 28% yield (based on chloride).

1,1,2,2-Tetra(trimethylsilyl)ethane, 2, was formed only in very low yield by reaction of bis(trimethylsilyl)methyl chloride[14,15] with sodium under the same conditions. Three high molecular weight products, A, B, and C, were formed in a ratio of 1:5.5:3.5 as determined by VPC on an SE 30 column. Reaction of the chloride with a tenfold excess of lithium for 48 h at 100 °C under argon gave A and B in a 15:1 ratio, from which A was isolated in 3% overall yield, mp 206 °C. Compound A was shown to be identical to **2** prepared (in high yield) by reaction of vinyltrimethylsilane and trimethylchlorosilane with magnesium in hexamethylphosphoramide.[16]

NMR Spectra. Proton resonance spectra were recorded on a Varian HA-100D spectrometer. Carbon-13 and silicon-29 resonance spectra were recorded on a Varian XL-100 spectrometer. The temperature of the sample was controlled[17] and calibrated[18] by the methods described previously. Hexachlorobutadiene containing some perdeuteriodimethyl sulfoxide was used as the solvent at high temperatures, while at room temperature and below C_6D_6, $CDCl_3$, $CHFCl_2$, $CHCl{=}CH_2$, and CS_2 were employed at various times.

Theoretical spectra were calculated by a stochastic approach,[19] and "goodness of fit" was evaluated by superposition upon the experimental spectra. Activation parameters were calculated by a least-squares correlation and the errors quoted are one standard deviation about the mean values.

Spin-lattice relaxation times (T_1 values) were obtained from an inversion recovery sequence on a solution in deuteriobenzene at 30 °C using a Varian CFT-20 spectrometer.

Results

NMR Spectra of 1 and 2. In the ^{1}H NMR spectra of **1** at room temperature the methyl protons appear as two groups of 18 H each and the two tertiary protons are equivalent (see Table I and Figure 1). The spectra do not change on raising the temperature until irreversible decomposition sets in at ca. 140 °C. On lowering the temperature to below ca. −100 °C, the signal due to the low-field methyl protons separates into two peaks in the ratio 1:2 (see Figure 1). The peaks due to the high-field methyl protons and to the methine protons both remain single. The changes in the spectra at low temperature are reversible.

In all solvents the ^{13}C NMR spectra of **1** show two types of quaternary carbon and one type of tertiary carbon and in some solvents the primary carbons are also resolved into two equal groups (see Figure 2).

The ^{1}H and ^{13}C NMR spectra of **2** at room temperature show two equivalent tertiary hydrogens and two equivalent tertiary carbons, respectively. The primary hydrogens appear

Table I. Proton Chemical Shifts[a] for **1** and **2**

Compd	Solvent	Temp, °C	Primary ^1H 18 H	18 H	Tertiary ^1H 2 H
1	$CDCl_3$	25	1.13	1.23	2.30
1	CH_2Cl_2	25	1.15	1.25	2.32
1	C_4Cl_6[b]	25	1.23	1.33	2.36
1	CH_2=CHCl	25	1.19	1.29	2.36
1	CH_2=CHCl	−100	1.16	1.25	2.32
1	CH_2=CHCl	−120	1.16	1.24	2.32
1	CH_2=CHCl	−125	1.15	1.20,[c] 1.32[d]	2.31
1	CH_2=CHCl	−130	1.16	1.21,[c] 1.33[d]	2.30
1	CH_2=CHCl	−135	1.18	1.19,[c] 1.34[d]	2.31
2	$CHCl_3$[e]	25	0.10	0.17	0.40
2	C_4Cl_6[b]	25	0.13	0.21	1.33

[a] Shifts are given in ppm downfield from TMS. [b] Hexachlorobutadiene. [c] 12 H. [d] 6 H. [e] Reference 16.

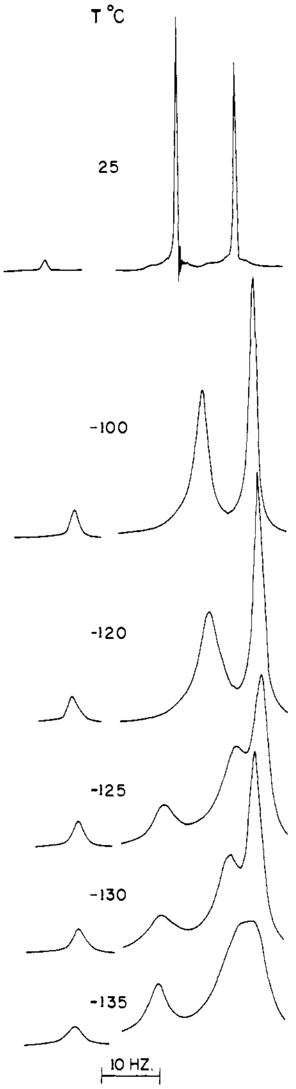


Figure 1. Proton NMR spectra of **1** in vinyl chloride at various temperatures.

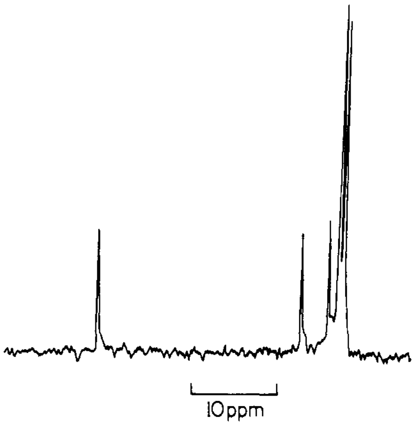


Figure 2. Carbon-13 NMR spectrum of **1** in C_6D_6 at room temperature.

as two groups of 18 H each and the primary carbons as two groups of 6 C each (see Figure 3). The ^1H and ^{13}C spectral patterns are not changed by lowering the temperature. However, on raising the temperature the two groups of primary hydrogens become magnetically equivalent (see Figure 4) and so do the two groups of primary carbons. Moreover, at 32 °C in C_6D_6, **2** shows two ^{29}Si resonances at 1.1 and 4.2 ppm downfield from TMS.[20] At 100 °C in hexachlorobutadiene no ^{29}Si resonance could be detected, a result which can be accounted for if the two types of silicon are exchanging at a rate similar to the methyl exchange, since there would then be only a single line too broad and weak to detect. All changes with temperature in the NMR spectra of **2** were fully reversible. In fact, **2** survived unchanged when heated to 220 °C for 15 h which means that it is thermally very much more stable than **1**.

Measured and calculated ^1H NMR spectra for the primary hydrogens of **2** at various temperatures are shown in Figure 4. The calculated spectra are based on the reasonable assumption that there are only two sites for the methyl groups with random exchange between them. A similar procedure was used to compare measured and calculated ^{13}C NMR spectra for the primary carbons in **2**. The rate constants, k, for exchange calculated for both types of nuclei are shown as an Arrhenius plot in Figure 5. The data in this figure can be represented by,

$$\log (k, \mathrm{s}^{-1}) = (8 \pm 3) - (10.2 \pm 0.4 \text{ kcal/mol})/2.3RT$$

Carbon-13 Spin-Lattice Relaxation Studies on 1. Compound **1** is one of the most hindered molecules to have been prepared in recent years,[21] and the possibility that some bonds are distorted from their "normal" length is obviously of interest.[23] The relation between molecular motion, C-H bond length, r_{C-H}, and ^{13}C spin-lattice relation time, T_1, when only dipole-dipole relaxation is occurring, can be represented approximately by,[24,25]

$$\frac{1}{T_1} = \frac{N\hbar\gamma_C^2\gamma_H^2}{(r_{C-H})^6}\tau_C$$

Table II. Carbon-13 Chemical Shifts[a] for **1** and **2**

Compd	Solvent	Temp, °C	Primary ^{13}C 6 C	Primary ^{13}C 6 C	Quaternary ^{13}C 2 C	Quaternary ^{13}C 2 C	Tertiary ^{13}C 2 C
1[b]	$CDCl_3$	32	35.6	36.1	37.0	39.6	58.4
1	$CDCl_3$	−63	34.4		35.9	38.2	56.0
1	$CHFCl_2$	32	34.7		35.6	38.3	57.1
1	$CHFCl_2$	−96[c]	33.7		35.1	37.4	55.1
1	C_6D_6	32	34.7	35.3	36.0	38.6	57.5
1	$CH_2{=}CHCl$	−99	31.1	35.2	*d*		57.3
2	CS_2	32	2.1	4.3	*e*		12.0
2	CS_2	−96	1.3	3.5			9.6

[a] Shifts are given in ppm downfield from TMS. [b] Data from ref 7. [c] There was also a small broad peak at 27.6. [d] Not distinguishable from noise. [e] In C_6D_6 there were two ^{29}Si resonances at 1.1 and 4.2 ppm downfield from TMS.[20]

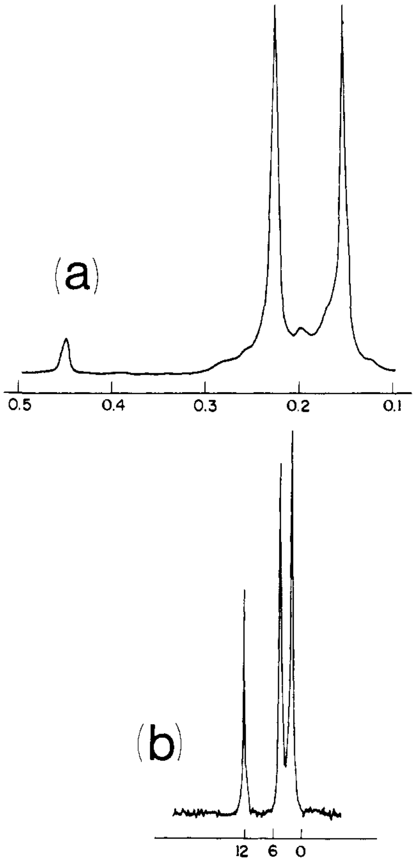


Figure 3. Proton (a) and carbon-13 (b) NMR spectra of **2** in hexachlorobutadiene at 32 °C.

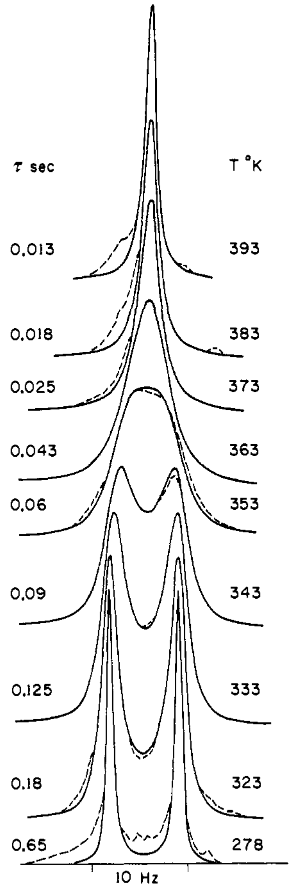


Figure 4. Experimental ^1H NMR spectra for the primary hydrogens of **2** in hexachlorobutadiene at various temperatures (dashed curves). Theoretical spectra calculated for the indicated lifetime, τ, are shown as solid curves. The "extra" peaks of low intensity in the experimental spectra are due to impurities. The intensities of these peaks could be (and were) reduced by recrystallization, but sample loss was too great for them to be entirely eliminated.

where N represents the number of protons attached to the observed carbon, γ_C and γ_H are the gyromagnetic ratios for C and H, respectively, and τ_C is the rotational correlation time. In the present instance, the ^1H and ^{13}C resonance results indicate that intramolecular motion is relatively slow and so it is reasonable to assume that τ_C corresponds to the tumbling motion of the molecule as a whole.[24,25] The same τ_C may therefore be employed for each carbon atom and so the ratio of methyl to methine C-H bond lengths will be given by,[26]

$$\frac{(r_{C\text{-}H})^6{}_{tert}}{(r_{C\text{-}H})^6{}_{prim}} = \frac{T_1(C\text{-}H)_{tert}}{3T_1(C\text{-}H)_{prim}}$$

The T_1 data for **1** are given in Table III. Using the average value of T_1 for the two types of primary carbon the ratio of bond lengths, $(r_{C\text{-}H})_{tert}/(r_{C\text{-}H})_{prim}$ is estimated to be ca. 0.91. This may be compared with a ratio of 1.07/1.10 = 0.97 for normal paraffinic bonds.[27] It would therefore appear that the tertiary C-H bond in **1** is not likely to be longer than a normal tertiary C-H bond. This result is somewhat surprising since steric factors are expected to induce some flattening of the pyramid formed by the three C-C_{tert} bonds (see below). Any such flattening could increase the p character in the tertiary C-H bond and hence increase its length. That is, flattening of the C-C_{tert} bonds suggests that hybridization of C_{tert} could become more sp^2-like with respect to C-C bond formation and hence more p-like with respect to C-H bond formation.

Discussion

Conformation of 1 and 2. The ^1H and ^{13}C NMR spectra for **1** and **2**, as well as the ^{29}Si NMR spectra for **2**, prove that neither compound adopts the anticipated anti conformation,

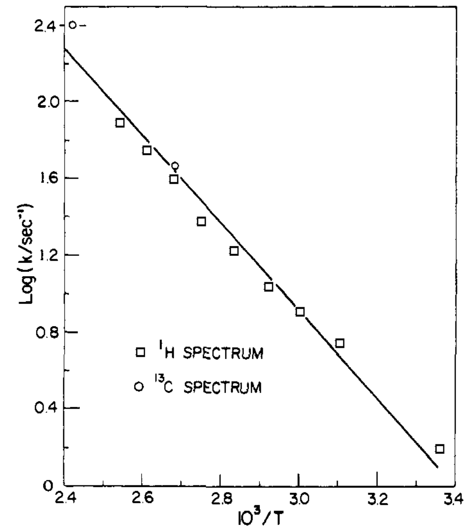
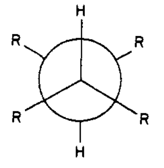


Figure 5. Arrhenius plot for the process that makes the two pairs of trimethylsilyl groups in **2** magnetically equivalent. The squares are data obtained from ^{1}H spectra and the circles are data from ^{13}C spectra.

3. Instead, these compounds must adopt either the eclipsed conformation, **4**, or the gauche conformation, **5**. Both of these conformations have one pair of *tert*-butyls that is more hindered than the other pair. This is consistent with the results of low-temperature ^{1}H NMR studies on **1** which indicated that the rotation of one pair of *tert*-butyls could be retarded much more readily than the rotation of the other pair.[28,29] Molecular models suggest that steric hindrance increases along the series $3 < 5 \ll 4$[30] and for this reason we presume that **5**, or a related structure (see below), is indeed preferred.



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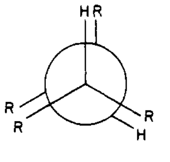

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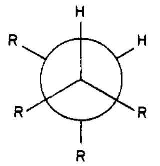


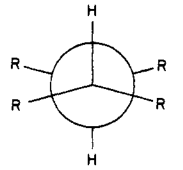
5

The reason that **1** and **2** do not adopt conformation **3** is not immediately obvious, particularly since certain other 1,1,2,2-tetra substituted ethanes (e.g., 2,3-dimethylbutane[31] and 1,1,2,2-tetramesitylethane[32]) have been reported to have a preference for this conformation in the solid state. Unexpected molecular conformations have, in the past, generally been rationalized either in terms of *attractive* steric effects[33,34] or in terms of a conjugative destabilization which is transmitted through bonds and is greater for an anti than for a gauche conformation.[36] However, the magnitude of attractive steric effects and of conjugative destabilization[37] would seem insufficient to overcome repulsive steric effects in fully saturated molecules that are as hindered as **1** or **2**. In fact, the favoring of the gauche conformation over the anti can be most readily explained in terms of the *repulsive* steric effects *between the groups directly attached to each of the tertiary carbons* as was first suggested by Allinger et al.[38] for 2,3-dimethylbutane. That is, the C-C-C bond angles at the tertiary centers are expected to be considerably greater than the tetrahedral angle because of repulsion between the geminal alkyl groups.[38,39] This means that in the anti conformation **3A**, the dihedral angles between the vicinal alkyl groups will be less than 60° and so these groups will be forced uncomfortably close together. That is, **3A** will be destabilized relative to **3**. However, in the gauche conformation **5A**, the same distortion at the tertiary carbons will move the vicinal alkyls further apart so that this conformation will be stabilized relative to **5**. Thus, the three alkyl-alkyl gauche interactions in **5A** are less severe than the two in **3A** and, as a consequence, the former conformation is favored.

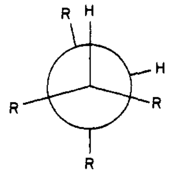
Table III. Spin-Lattice Relaxation Times for **1** in C_6D_6 at 30 °C

Carbon[a]	T_1, s	Carbon[a]	T_1, s
Primary (34.7)	2.6 ± 0.2	Quaternary (38.6)	19.3 ± 1.4
Primary (35.3)	3.2 ± 0.3	Quaternary (36.0)	20 ± 3
Tertiary (57.5)	4.8 ± 0.5		

[a] Chemical shifts (ppm) are given in parentheses.



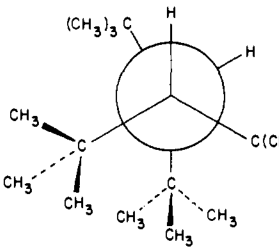
3A



5A

We believe that repulsion between geminal alkyl groups could determine the conformational preference of many other organic molecules. Specifically, we suggest that this effect produces the gauche conformation of tetra-*tert*-butyldiphosphine[42a] and of other tetraalkyldiphosphines.[42b,c]

The ^{1}H NMR spectra[28] of **1** show that the rotation of one pair of *tert*-butyl groups can be hindered at low temperatures.[29] This pair is, presumably, the two *tert*-butyls that are anti to the methine hydrogens. In the limit of slow rotation, the methyl groups on each of these *tert*-butyls divide into two that are magnetically equivalent and one that is unique. Molecular models suggest that steric hindrance would be minimized if the unique methyls pointed toward the center of the molecule. That is, conformation **6** is preferred at low temperatures.



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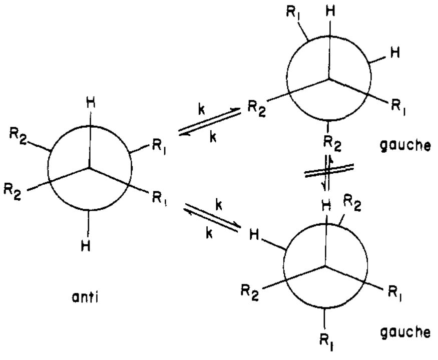
The coalescence temperature for the methyl protons of the hindered pair of *tert*-butyls in **1** is ca. −123 °C. From this an approximate rate constant (53 s^{-1}) and $\Delta G^{\ddagger}$ (7 kcal/mol) may be calculated for the rotation of these *tert*-butyls at this temperature. The value found for $\Delta G^{\ddagger}$ is within the "normal" range for hindered *tert*-butyl rotations.[29]

Barrier to Rotation about the Central C-C Bond in 2. At elevated temperatures the two pairs of trimethylsilyl groups in **2** which are present at room temperature become magnetically equivalent. This implies that the different trimethylsilyls are exchanging positions rapidly on the NMR time scale, but it does *not* imply that there is free and complete rotation about the central C-C bond. In fact, a direct gauche $\rightleftharpoons$ gauche interconversion seems unlikely since the transition state would have all four trimethylsilyl groups eclipsed by trimethylsilyls. An indirect gauche $\rightleftharpoons$ anti $\rightleftharpoons$ gauche interconversion should have a much lower barrier since the transition states would have only two trimethylsilyls eclipsed by trimethylsilyls (see Scheme I). We therefore attribute the process which makes the two pairs of 18 primary hydrogens equivalent and the two pairs of 6 primary carbons equivalent to the gauche ⇌ anti ⇌ gauche partial rotation.

Scheme I



The rate constant for the above mentioned process can be represented by,

$$\log (k, \mathrm{s}^{-1}) = (8 \pm 3) - (10.2 \pm 0.4\ \mathrm{kcal/mol})/2.3RT$$

The rate at the coalescence temperature of 353 K corresponds to a $\Delta G^{\ddagger}$ of 18.8 kcal/mol. A least-squares analysis of the rate data yields an entropy of activation $\Delta S^{\ddagger} = -26 \pm 2$ gibbs/mol. Because of the well-known[43] systematic errors which can occur in such measurements we prefer to be very conservative and claim $\Delta S^{\ddagger} = -26 \pm 13$ gibbs/mol. Such a large negative entropy of activation must raise some questions regarding the accuracy of our results. We believe our data are quite reliable for the following reasons.

(i) Compound **2** is uniquely suitable for variable temperature NMR studies because its very structure will minimize the principle causes of systematic errors in calculated activation parameters.[43] Thus, all contributions to the line width in the absence of exchange will be identical for **2** and for tetramethylsilane (the ^{1}H and ^{13}C line widths of which are essentially independent of temperature). Furthermore, differences in chemical shift with temperature are likely to be small since **2** will not be associated in hexachlorobutadiene.

(ii) Rate constants were only calculated from proton resonance spectra when the observed line width was at least *twice* the nonexchanging line width at the low-temperature limit and *three* times its value at the high-temperature limit.

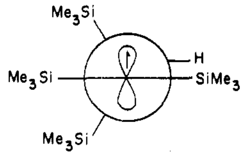
(iii) The rate constants obtained from the ^{13}C spectra agree well with those obtained from the ^{1}H spectra, though different spectrometers were used in the two sets of measurements.

The reason for the large negative $\Delta S^{\ddagger}$ must lie in the extent and nature of the steric crowding in **2.** We presume that in the gauche ⇌ anti transition state there is a cooperative movement of many groups, i.e., a "gear" [44] or "cogwheel" [45] effect is in operation. If the rotational motion about the R–C bond of the mutually eclipsed pair of R groups is completely stopped in the transition state, the negative entropy of activation can be estimated to be ca. $2 \times 9 = 18$ gibbs/mol at 400 K.[46] Even if some rocking of these two R groups is possible in the transition state, it would appear to be more than compensated for by decreases in the rotational freedom of some or all of their six constituent methyl groups as well, perhaps, as by hindrance to the rotation of the other two R groups that are eclipsed by the tertiary H atoms.

It is interesting to find that excessive steric crowding has manifested itself in $\Delta S^{\ddagger}$ rather than in the enthalpy term, $\Delta H^{\ddagger}$, which is in fact in about the middle of the 6–14 kcal/mol range usually found for rotation about hindered C–C single bonds.[4] Since this may be a general phenomenon, we suggest that when high $\Delta G^{\ddagger}$ values are found for a rotation about a single bond in a sterically hindered molecule, the NMR spectra should be subjected to complete line shape analysis to determine $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ (due care being taken to cover an adequate temperature range).

Partial rotation about the central C–C bond in **1** is obviously considerably slower than in **2,** as we would expect. In fact, we estimate that $k < 5\ \mathrm{s}^{-1}$ and $\Delta G^{\ddagger} > 23$ kcal/mol at 140 °C, the temperature where irreversible decomposition sets in. It is perhaps worth noting that if the gauche ⇌ anti barrier is sufficiently large it should, *in principle*, be possible to isolate optical isomers since **1** (or **2**) in conformation **5A** is not superposable upon its mirror image.

Radical Derived from 2. Abstraction of the methine hydrogen from **2** gives an exceptionally persistent radical, the EPR spectrum of which has been reported previously.[8] This radical adopts conformation **7.**



7

We wish to take this opportunity to point out the difficulty of determining a true lifetime for persistent radicals because of their tendency to decay by reacting with impurities in the medium or on (or diffusing from) the surface of the containing vessel.

The radical **7** was generated in concentrations of 10^{-5}–10^{-7} M by photolysis of di-*tert*-butyl peroxide solutions of **2** in carefully degassed quartz EPR tubes. All samples of **7** decayed with "clean" first-order kinetics. After decay the radical could be regenerated by a brief irradiation of the sample. The half-lives for decay were found to increase dramatically with each succeeding measurement. For example, a sample prepared in a quartz tube that had been heated with a flame for 30 min under vacuum had an initial half-life at 23 °C of ca. 3 days. The rate of decay decreased continuously reaching a value which corresponded to a half-life of 300 days after 1 year. It would appear that **7** (and probably many other persistent radicals) is not subject to decay at ambient temperatures by unimolecular or bimolecular self-reactions. Decay probably occurs only when **7** encounter other reactive species.

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References and Notes

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