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Molecular Structure and Internal Rotations of Tetracyclohexylmethane

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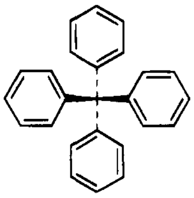
The stereochemistry of tetracyclohexylmethane (**2**), obtained by catalytic hydrogenation of tetraphenylmethane, is analyzed. The Cahn−Ingold−Prelog conformational descriptors of the ideal conformers of tetrasubstituted methanes are reevaluated and an alternative method presented. Methane **2** exists in the crystal in a (g/a/-g) conformation (of approximate S_4 symmetry) in which all the rings are in a chair arrangement and are skewed from their perfectly staggered D_2d conformation. Molecular mechanics (MM) calculations indicate that the crystallographic conformation is the lowest energy form. Analysis of the ^{1}H and ^{13}C NMR data indicates that, even at low temperatures, the molecule undergoes a fast rotational process which exchanges the ortho and meta groups. On the basis of the MM calculations it is concluded that the preferred rotational pathway involves libration of the four rings via a transition state of D_2d symmetry in which all the rings are perfectly staggered.

Introduction

In spite of their apparent simplicity, the stereochemical analysis of methanes tetrasubstituted by identical groups lacking local C_3 axes is far from trivial.[1−6] In contrast to the corresponding trisubstituted methanes, for a CR_4 system (e.g., tetraphenylmethane (**1**)) there is no natural or unique reference orientation. Consequently, the visualization of the different conformations and their possible rotational interconversion pathways is more complex for the tetrasubstituted systems.[7] In addition, these systems are more strained than their corresponding trisubstituted systems. The tetrasubstitution may hinder the release of steric strain by bond angle deformation around the central quaternary carbon (C_q) since the bond opening of a given $C-C_q-C$ angle from its ideal tetrahedral value (109.56°) comes at the expense of closing other $C-C_q-C$ angles.[8]

In continuation to our studies on the stereochemistry of polycyclohexyl systems,[9] we describe in this paper the static and dynamic stereochemistry of the saturated analogue of **1**, tetracyclohexylmethane (**2**). This compound is of stereochemical interest due to its arrangement of four cyclohexyl rings attached to a single quaternary carbon (C_q) and in which each ring sterically interacts with the three remaining rings.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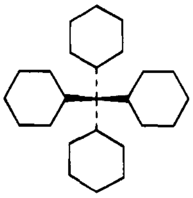
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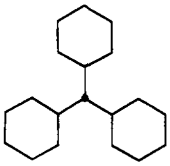
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Early Work on Tetracyclohexylmethane. Early reports in the literature described unsuccessful attempts of the preparation of **2** by catalytic hydrogenation of tetraphenylmethane, and it was reported that the reaction resulted in the formation of tricyclohexylmethane (**3**) and dicyclohexylmethane, i.e., the reduction was accompanied by the reductive cleavage of $C-C_q$ bonds.[10] The cleavage was rationalized as the result of the high strain present in **2**, evidenced in the difficulty in building a space filling model of the system.[11] Reinvestigation of the hydrogenation reaction by Buell and Spialter showed that, if the hydrogenation is carried out with 5% Rh/C at 100 °C and 1250 psi H_2, **2** could be obtained in 80%.[12] The investigators suggested, by examination of space filling models, that the rotation of the cyclohexyl groups may be hindered ("partially frozen"). Although it was stated that crystallographic studies of the system were at that time in progress,[12] they were never reported later on.

Enumeration and Nomenclature of the Ideal Staggered Conformers of 2. (a) Possible Symmetries Attainable by 2. In order to analyze the stereochemistry of **2**, it is necessary as a first step to enumerate the different ideal conformations of the sys-

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1994.

(1) For a review on conformational flexible molecules see: Hoffmann, R. W. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1124.

(2) For a recent review on the stereochemistry of cyclohexanes see: Mann, G. *Z. Chem.* **1990**, *30*, 1.

(3) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 385.

(4) (a) Alder, R. W.; Maunder, C. M.; Orpen, A. G. *Tetrahedron Lett.* **1990**, *31*, 6717. (b) Alder, R. W; Allen, P. R.; Khosravi, E. *J. Chem. Soc., Chem. Commun.* **1994**, 1235.

(5) Hutchings, M. G.; Nourse, J. G.; Mislow, K. *Tetrahedron* **1974**, *30*, 1535. Hutchings, M. G.; Andose, J. D.; Mislow, K. *J. Am. Chem. Soc.* **1975**, *97*, 4562.

(6) For a review on the stereochemistry of tetraphenylmethanes see: Willem, R.; Gielen, M.; Hoogzand, C.; Pepermans, H. *Advances in Dynamic Stereochemistry*; Gielen, M., Ed.; Academic Press: New York, 1985; Vol. 1, p 207.

(7) These difficulties can be demonstrated by **1**. Two conformations of **1** ("closed" and "open") may attain the maximal D_2d symmetry, with the four rings either lying in the mirror planes or perpendicular to them.[3] As pointed out by Mislow, if all the rings are rotated in the same sense and by equal amounts from one of these conformations, the symmetry is lowered to D_2.[5] One would expect naively that the transformation of the "open" to the "closed" conformation would require 90° rotations of all rings. However, if all the rings are rotated in the same sense by just 60°, the D_2d symmetry is recovered with the S_4 axis at right angles to the original direction.[5,6]

(8) Anderson, J. E. in *The Chemistry of Alkanes and Cycloalkanes;* Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1992; Ch. 3.

(9) (a) Columbus, I.; Biali, S. E. *J. Org. Chem.* **1993**, *58*, 7029. (b) Columbus, I.; Biali, S. E. *J. Org. Chem.* **1994**, *59*, 3402. (c) Columbus, I.; Cohen, S.; Biali, S. E. *J. Am. Chem. Soc.* In press.

(10) Ipatiev, V. N.; Dolgov, B. N. *Compt. Rend.* **1927**, *185*, 210.

(11) Kanazashi, M.; Takakusa, M. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 441.

(12) Buell, G. R.; Spialter, L. *J. Org. Chem.* **1965**, *30*, 1662. See also: Buell, G. R.; Spialter, L. *J. Org. Chem.* **1967**, *32*, 3223.

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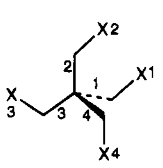
tem which arise from the different orientations of the cyclohexyl rings. These ideal conformations may be generated assuming that the cyclohexyl groups adopt chair conformations and are all attached to the central carbon through their equatorial positions, and that all the C−C bonds are perfectly staggered (i.e., with all HCC_qC angles either 180° or ±60°). Under these restrictions the problem becomes analogous to enumerating all the possible ideal staggered conformations of a $C(CY_2Z)_4$ system. For analyzing the possible symmetries of the resulting conformations it is convenient to view the system as resulting from the formal attachment of four cyclohexyl groups to a central tetrahedral atom of T_d symmetry. The resulting conformations necessarily must belong to one of the subgroups of the T_d point group. Since the cyclohexyls destroy all C_3 axes of the tetrahedral atom, the possible attainable symmetries are restricted to the D_{2d}, S_4, C_{2v}, C_2, C_s, and C_1 point groups. If only the ideal conformations with perfect staggering of the groups are considered, these symmetries are further limited to D_{2d}, S_4,C_2, C_s, and C_1.[13]

(b) Cahn, Ingold, Prelog Conformational Descriptors of Tetrasubstituted Methanes. The ideal staggered conformations of tetrasubstituted methanes of the general form $C(CY_2Z)_4$, as exemplified by a pentaerythritol tetrahalide **4**, were analyzed by Cahn, Ingold, and Prelog (CIP).[3,14] A nomenclature system was proposed based on the description of the torsional angles of the four halogen groups relative to the four C_q−C bonds. In their system the four bonds emanating from C_q are numbered 1−4 and the halogen atoms numbered accordingly (cf., **4**). The torsional angles defined by the C−Cl and C_q−C bonds are described by the descriptors antiperiplanar ("*a*"), and "*M*" or "*P*" synclinal ("*M*" and "*P*", respectively). These descriptors are followed by a superscript and preceded by a subscript denoting the halogen atom (1−4) and the C_q−C bond (1−4) defining the dihedral angle, respectively. For example, ${}_1M^4$ indicates that halogen 4 is in a *M*-synclinal orientation to bond 1. A given conformation is described by a set of four descriptors. For example, one of the two enantiomeric conformations of C_2 symmetry is described by ${}_2a^1$, ${}_1a^2$, ${}_4M^3$, ${}_3M^4$. In this method, a model of any given ideal conformer can be numbered in 24 (4!) different ways, and for a given numbering there are 81 (3^4) different, equivalent ways of describing its conformation.[3]



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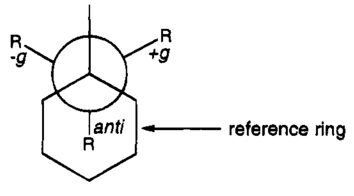

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(c) Nomenclature of the Different Conformations. The disadvantages of the nomenclature of tetrasubstituted systems in the CIP method is that it is relatively cumbersome, and that for a given conformation a very large number of equivalent descriptors are possible. A much simpler method can be devised which requires the specification of only three torsional angles (as opposed to four in the CIP method). The different ideal staggered conformations of a $C(CY_2Z)_4$ system can be described by arbitrarily choosing one of the CY_2Z groups as the reference substituent, and describing the orientations of the three remaining groups which are located +gauche (g), -gauche (-g), and anti (a) to the unique substituent (Z) of the CY_2Z reference group (in the case of **2**, this is the methine proton of the reference ring, cf. **5**). For **2**, these orientations can be characterized by describing the torsional angle defined by the H−C−C_q−C_{ref} atoms (whereas C_{ref} represents the methine carbon of the reference ring) of each of the three cyclohexyl groups. The orientations of the rings (a or ±g) can be given for the three rings in the form (*j*/*k*/*l*) where *j*, *k*, and *l* describe the torsional angle of the rings located at the g, a, and -g positions relative to the C−H in the methine group of the reference ring, respectively. This method is less cumbersome than the CIP since there is no need to arbitrarily number the skeleton; it is more economical, since only three dihedral angles need to be described as opposed to four in the CIP method. Since any of the four CY_2Z groups can be chosen as the reference, four, two, or a single descriptor exists for a given conformation, depending on its symmetry number (σ = 1, 2, or 4, respectively). This is a significant improvement over the 81 equivalent descriptors of the CIP method. The three-dimensional arrangement of the molecule can be readily reconstructed from a given descriptor (Figure 1).

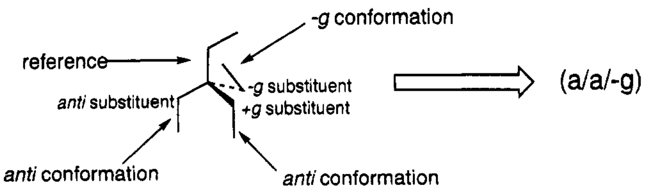

Figure 1. An ideal staggered conformation of **2** and its descriptor. For clarity, only the cyclohexyl methine protons are depicted. One of the rings is arbitrarily chosen as the reference ring. The conformations of the rings located at the +g, anti, and -g positions relative to the methine of the reference ring (in this example these conformations are *anti*, *anti* and *-g*, respectively) are denoted in the form (*j*/*k*/*l*) where *j*, *k*, and *l* describe the torsional angle of the rings located at the g, a, and -g positions, respectively. For the example shown the descriptor is (a/a/-g).

(d) Generation of the Conformations of 2. The stereochemistry of tetraalkyl-substituted quaternary centers was analyzed by Cahn, Ingold, and Prelog,[3] and more recently by Alder and co-workers.[4] They showed that the basic system $C(CH_2R)_4$ exists in six ideal conformations. According to molecular mechanics calculations, the two low energy forms of 3,3-diethylpentane are the ones devoid of any g^+g^- interaction (i.e., the forms of D_{2d} and S_4 symmetry). The enumeration of all the ideal staggered conformations of **2** (disregarding the possible conformations of the cyclohexyl group) can be rigorously achieved in principle by group theoretical methods.[15] A simpler approach for practical purposes is to start from a known less substituted system and from its ideal staggered conformations to generate all the conformations of

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[13] Although dicyclohexylmethane can exist in a perfectly staggered conformation of C_{2v} symmetry, this symmetry is unattainable by **2**. As seen by construction of a molecular model, if two additional rings are added to the central carbon, their perfect staggered arrangement yields the D_{2d} symmetry structure. In order to obtain a C_{2v} structure, the two additional rings must necessarily be eclipsed.

[14] For electron diffraction and X-ray crystallography studies of $C(CH_2X)_4$ systems see for example: Stovelik, R. *Acta Chem. Scand. A* **1974**, *28*, 327. Cameron, T. S.; Chute, W. J.; Knop, O. *Can. J. Chem.* **1985**, *63*, 586.

[15] Brocas, J.; Gielen, M.; Willem, R. *The Permutational Approach to Dynamic Stereochemistry;* McGraw-Hill: New York, 1983.

Table 1. Generation of the Possible Conformations of Tetracyclohexylmethane 2 from the Staggered Conformations of Tricyclohexylmethane (3)

conformer of **3**[a]	conformer(s) generated of **2**
(-g,-g,a)/(g,g,a)	(a/-g/-g), (-g/-g/a), (-g/a/-g)/(g/g/a), (a/g/g), (g/a/g)
(-g-g-g)/(g,g,g)	(-g/-g/-g)/(g/g/g)
(-g,a,g)	(-g/a/g), (a/g/-g), (g/-g/a)
(-g,-g,g)/(g,g,-g)	(g/-g/-g), (-g/g/-g), (-g/-g/g)/(g/g/-g), (g/-g/g), (-g/g/g)
(g,a,-g)	(g/a/-g), (-g/g/a), (a/-g/g)
(-g,a,a)/ (a,a,g)	(-g/a/a), (a/-g/a), (a/a/-g)/(a/a/g), (a/g/a), (g/a/a)
(a,a,a)	(a/a/a)

[a] Cf. ref 8a.

Table 2. Equivalent Descriptors for the Generated Conformations and Ideal Symmetries[a]

conformation	descriptors	symmetry	g$^+$g- [b]
1	(g/a/-g)	D_2d	4
2	(a/-g/-g), (g/g/a)	S_4	4
3	(-g/g/-g), (a/a/g)	C_2	6
4	(g/-g/g), (-g/a/a)	C_2	6
5	(-g/a/g), (-g/-g/g), (-g/g/g), (a/a/a)	C_s	7
6	(g/a/g), (g/-g/-g), (-g/g/a), (a/a/-g)	C_1	5
7	(-g/a/-g), (g/g/-g), (a/-g/g), (g/a/a)	C_1	5
8	(a/g/g), (-g/-g/-g), (a/g/-g), (a/g/a)	C_1	5
9	(-g/-g/a), (g/g/g), (g/-g/a), (a/-g/a)	C_1	5

[a] (3)/(4), (6)/(7), and (8)/(9) are enantiomeric pairs. [b] Number of g$^+$g$^-$ interactions.

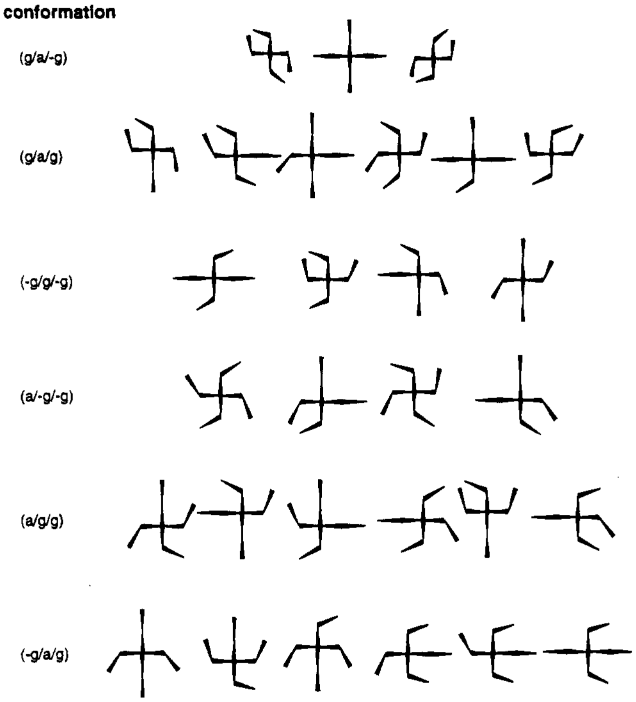

Figure 2. Fisher-like projections of the ideal conformations of **2** viewed from different orientations. The wedges denote the positions of the cyclohexyl methine protons. For the chiral conformations, only one the two enantiomers are shown.

the more substituted system. We chose for this purpose tricyclohexylmethane (**3**) which may adopt seven perfectly staggered diastereomeric conformations.[9a] The generation of the conformers of **2** was achieved by replacing in each conformation of **3** the methine hydrogen by a cyclohexyl ring and orienting this ring in its three possible staggered orientations. The conformers of **2** generated from a given conformer of **3** are necessarily interconvertible by single ring rotation of a cyclohexyl group. If one chooses the "added" cyclohexyl group as the reference ring, the conformational descriptors of the generated conformers can be obtained in a rather straightforward fashion since they are either identical or the result of a cyclic permutation of the conformational descriptor of the starting conformation of **3**. For example, from the (-g,-g,a) conformer of **3**,[9a] the (-g/-g/a), (-g/a/-g) and (a/-g/-g) conformers of **2** are generated. The results of this treatment on all possible ideal conformers of **3** are collected in Table 1. In some cases distinct (but equivalent) conformational descriptors of the same conformation are generated. The equivalent descriptors generated for the different conformations (a total of 27, i.e., all possible descriptors), their ideal symmetries, and the number of g$^+$g$^-$ interactions in each conformation are collected in Table 2. Six conformations of **2** were obtained (Table 2): three achiral (D_2d , S_4, and C_s symmetries) and three chiral existing as enantiomeric pairs (one pair of ideal C_2 symmetry and two pairs of C_1 symmetry). Each conformation of **3** possessing a three-fold axis collinear with the central C−H bond (i.e., (g,g,g)/(-g,-g,-g), and (a,a,a)) generates a single conformation, since the three staggered arrangements of the formally added fourth ring are equivalent. Conformations of **3** of C_1 symmetry generate three different conformations. Conformations of **3** with mirror plane symmetry (e.g., (-g,a,g)) may generate either achiral or chiral conformations. In the last case both enantiomers must be generated since the fourth ring may be oriented in two mirror symmetric orientations.

(e) Representations of the Ideal Conformations of 2. As stated in the introduction, there is no unique orientation for a system such as **2**, which is the main source of difficulty in visualizing the different conformations and their mutual interconversion by ring rotations, since a given conformation may look very different when viewed from different orientations. For depicting the different ideal conformations of **2** we draw Fisher-like projections of the conformations along the three local C_2 axes of the tetrahedral core. The obtained views can be very different, as shown in the projections in Figure 2.[16]

Preparation and NMR Spectrum of 2. In order to synthesize **2** we hydrogenated **1** using Pd/C as catalyst (720 psi H_2, 160 °C), which gave, as judged by ^1H NMR, **2** as the main product accompanied by small amounts of **3**. From the reaction mixture we isolated by fractional crystallization sufficient quantities of **2** to conduct the present study.

Methane **2** displays in the 400 MHz ^1H NMR spectrum ($CDCl_3$, rt) two groups of signals (Figure 3), one in the 1.1−1.3 ppm region integrating for five protons, and one in the 1.65−1.8 ppm region integrating for six protons. The low field group of signals can be assigned to the equatorial cyclohexyl protons while the high field group can be assigned to the axial protons, by analogy with other cyclohexyl systems.[9,17] The integration ratio ob-

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(16) In Figure 2, the wedges in the projections describe the positions of the cyclohexyl methine protons, whereas Alder et al.[4] who depicted the conformations of $C(CH_2R)_4$ systems (i.e., with primary alkyl groups) denoted in their projections the positions of the carbons in the alkyl chain.

(17) Günther , H. *NMR Spectroscopy;* Wiley: Chichester, 1980; p 72.

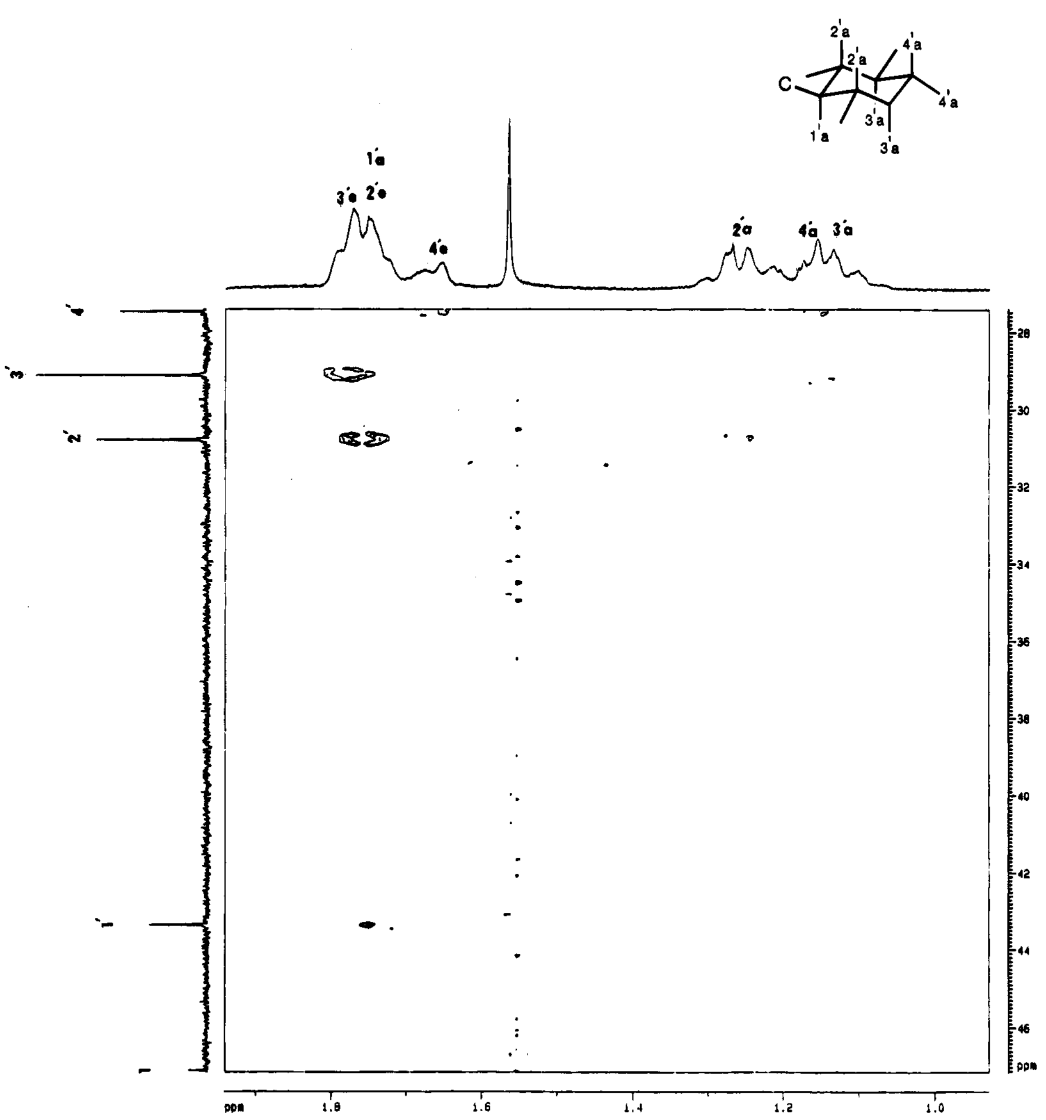
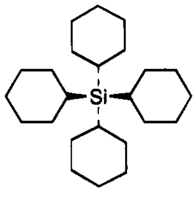


Figure 3. Inverse H−C correlation spectrum of **2**.

served suggests that the methine protons resonate within the low field group. The ^{13}C NMR of methane **2** (100 MHz, $CDCl_3$, rt) is very simple and displays five signals at δ 27.46, 29.10, 30.76, 43.32, and 47.08 ppm. We assign the lowest field signal to the quaternary central carbon since increased substitution on an aliphatic carbon usually results in its lower field absorption in the ^{13}C NMR.[18] By analogy with the signal assignment performed for **3**,[9a] we assign the first four signals to the cyclohexyl carbons at the 4, 3/5, 2/6, and 1 positions, respectively. A corroboration of the assignment in the ^{13}C NMR and an assignment of the ^{1}H NMR signals could be achieved by an inverse C−H correlation 2D spectra (Figure 3).[19] Provided that the cyclohexyl proton signals are well resolved, one should expect two cross peaks for the methylene carbons, one cross peak for the methine carbons, and an absence of cross peaks for the central carbon. Figure 3 indeed shows no cross peak for the ^{13}C signal at δ 47.08 supporting its assignment as the C_q signal, while the signal at 43.32 displays a single cross peak with the signal in the ^{1}H NMR spectrum at 1.75 ppm, corroborating their assignment as methine group signals.

X-ray Structure of 2. The reported X-ray crystallography studies of tetracyclohexylsilane[20] (**6**) and tetraisopropylphosphonium tetraphenylborate[21] (**7**) are noteworthy. Silane **6** exists in a (g/a/-g) conformation of approximate S_4 symmetry, in which the cyclohexyl groups are twisted 7−8° from the perfectly staggered D_{2d} structure.[20] Of particular interest is the structure of **7** since the $C-P^+$ bonds are shorter than the C−Si bonds and near the central tetrahedral atom the mutual steric interactions between cyclohexyl or isopropyl groups should be similar. In contrast to **6**, phosphonium **7** adopts a (a/-g/-g) conformation, also of approximate S_4 symmetry.[21]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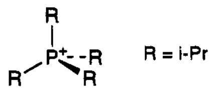

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A single crystal of **2** was grown from petroleum ether

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[18] Breitmaier, E.; Voelter, W. *^{13}C NMR Spectroscopy*, 2nd ed.; Verlag Chemie: Weinheim, 1978; p 71.

[19] For a review on 2D NMR techniques see: Kessler, H.; Gehrke, M.; Griesinger, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490.

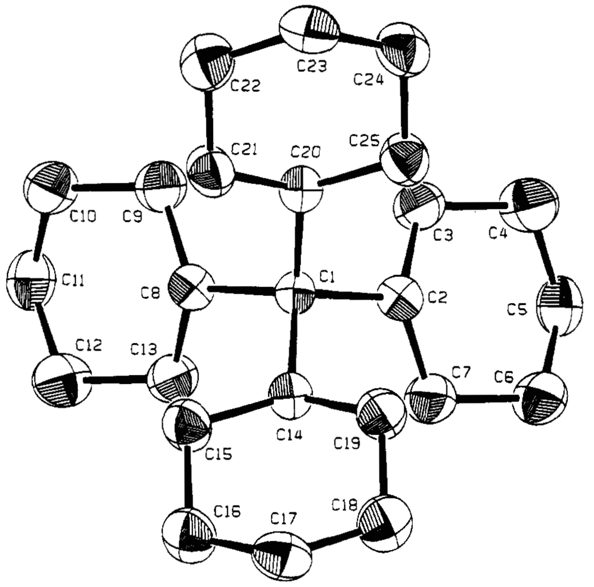

Figure 4. Numbering scheme of the X-ray structure of **2**.

and submitted to X-ray crystallography.[27] The numbering scheme of the crystal conformation is shown in Figure 4 and its stereoscopic view in Figure 5. The steric crowding of the system is emphasized in a space filling representation of the crystal conformation which indicates that pairs of axial protons on the 2-positions of neighboring rings are in steric proximity (Figure 6). The molecule adopts a (g/a/-g) conformation, of approximately S_4 symmetry, similar to that adopted by **6**. The maximal symmetry possible for that conformation is $D_{2}d$, when all the HCC_qC dihedral angles are perfectly staggered. The crystal conformation shows that the cyclohexyl rings are rotated from their perfectly staggered arrangement (skewing) and for each ring the "anti" HCC_qC dihedral angle is ±170.5–171.5° instead of 180° in the ideal staggered arrangement. No appreciably distortion is observed for the cyclohexyl rings which exist in a chair conformation with all rings attached to C_q through their equatorial positions. The central $C-C_q$ bonds are elongated (1.580–1.584 Å), most likely in order to alleviate the mutual steric interactions between the rings. A similar elongation of the central Si–C bonds was observed for **6**.[20]

Molecular Mechanics Calculations. In order to estimate the relative stabilities of the conformations of **2**, we calculated their steric energies using the MM3(92) program.[22,23] Initial inputs were based on standard bond lengths and angles of the cyclohexyl rings and perfect staggering of all C–C bonds. The relative steric energies, symmetries, and H–C–C–C dihedral angles of the calculated conformations are collected in Table 3. The calculated conformation of lowest steric energy is the (g/a/-g) form of S_4 symmetry, which is the conformation observed in the crystal. Although most of the crystallographic structural parameters of the system are satisfactorily reproduced (Table 4), the MM3 program overestimates the central $C-C_q$ bond length (calculated 1.601 Å, experimental 1.580–1.584 Å). Interestingly, the older MM2 seems to fare better in this respect (calculated $C-C_q$ 1.592 Å).

Table 3. Calculated Geometries, Symmetries, and Relative Steric Energies (RSE) for the Conformations of 2

conformation	HCC_qC angles	symmetry	RSE
(g/a/-g)	51.1/169.8/−71.5	S_4	0
(g/a/-g)	53.5/172.3/−68.8	D_2	0.3
(g/a/-g)	61.4/180.0/−61.4	$D_{2}d$	0.8
(g/g/a)	73.3/47.0/166.3	S_4	4.2
(-g/g/-g)	−40.7/70.3/−40.8	C_2	7.3
(a/a/a)	−154.2/−159.7/−162.8	C_1	12.1
(g/a/g)	82.8/−176.3/61.4	C_1	2.0
(a/g/g)	163.6/70.2/25.3	C_1	4.4

[a] Torsional angles in degrees, RSE's in kcal mol^{-1}. In the chiral structures the dihedral angles of only one enantiomer are given.

Table 4. Experimental (X-ray) and Calculated Selected Structural Parameters for 2[a]

parameter	exp	calc (MM3)	calc (MM2)
C1–C2	1.583(3)	1.601	1.592
C1–C8	1.579(3)	1.601	1.592
C1–C14	1.584(3)	1.601	1.592
C1–C20	1.582(3)	1.601	1.592
H37–C8–C1–C2	171.1	169.8	169.4
H26–C2–C1–C8	171.5	169.8	169.4
H48–C14–C1–C20	−170.5	−169.8	−169.4
H59–C20–C1–C14	−170.7	−169.8	−169.4
H37H50	1.969	1.91	2.00
H35H48	1.981	1.91	2.00
H26H69	1.981	1.91	2.00
H38H59	1.985	1.91	2.00
C2C1C8	112.1(2)	113.7	112.2
C14C1C20	112.1(2)	113.7	112.2

[a] Bond lengths and nonbonded distances (Å); bond and torsional angles (deg).

According to the calculations, the (g/a/-g) conformation may adopt also an arrangement of D_2 symmetry (situated

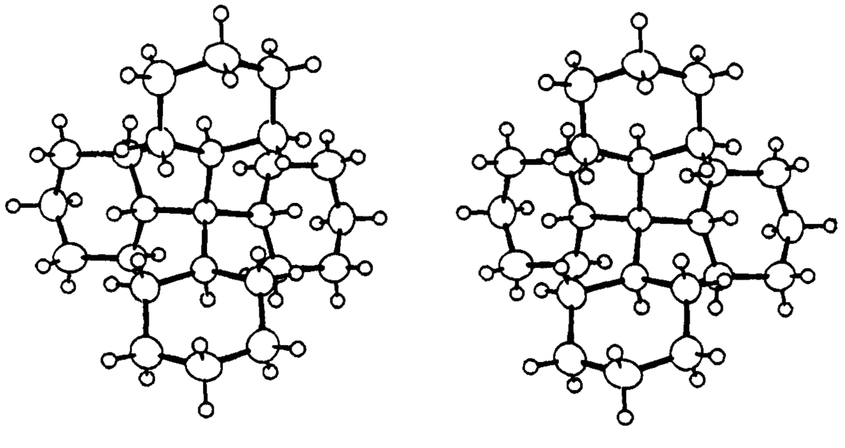

Figure 5. Stereoscopic view of the X-ray structure of **2**.

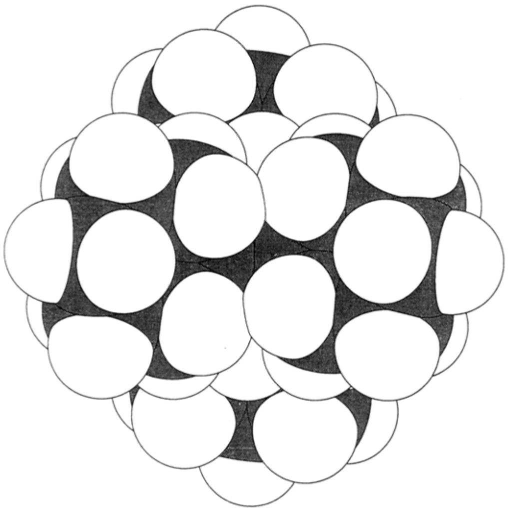

Figure 6. Space filling representation of the crystal conformation of **2**.

0.3 kcal mol^{-1} above the S_4 conformation) while the D_2d arrangement with perfect staggering of the rings is a transition state at 0.8 kcal mol^{-1} above the ground state form (Figure 7).

The form of the highest calculated relative steric energy (12.1 kcal mol^{-1}) is the (a/a/a) in which seven g$^+$g$^-$ interactions are present. According to the calculations, in order to alleviate the mutual steric interactions, the three rings are skewed from their perfectly *anti* arrangement (torsional angles: ±(154.2, 159.7, 162.8)) resulting in a chiral structure of C_1 symmetry. Interestingly, the (g/g/a) form (of S_4 symmetry, Figure 7) has a high relative steric energy (4.2 kcal mol^{-1}) although it has the same number of g$^+$g$^-$ interactions as the ground state (g/a/-g) form.

Dynamic Stereochemistry. The room temperature ^{13}C NMR of **2** is in agreement either with a "frozen" structure of D_2d symmetry or with a conformation (or several conformations) rapidly interconverting in the NMR timescale, resulting in an average structure of effective D_2d symmetry. In principle the rotation of the cyclohexyl rings may involve correlated or noncorrelated (stepwise) rotations of the groups. Although several polyarylmethyl systems display correlated rotation of the rings,[6,24] the corresponding polycyclohexyl systems favor stepwise rotation, as evidenced by the pair triphenylmethane/**3**.[9a,25] In order to analyze the dynamic behavior of **2** we built the interconversion graph of the system assuming that the mutual interconversion involves stepwise rotations of the rings. The construction of the graph is facilitated by the method used for the generation of the conformers of **2**, since any set of conformers generated from a given conformer of **3** necessarily must mutually interconvert by a single ring rotation. This complete graph of single ring interconversions is displayed in Figure 8. The achiral conformations are located in the vertical mirror plane which bisects the graph while enantiomeric pairs (i.e., (g/a/g) and (-g/a/-g)) are pairwise related by that plane. The connectivity of each ideal conformation (i.e., the number of edges emanating from a given node) is inversely proportional to the symmetry number of the conformation, as expected. As shown in Figure 8, some conformations (e.g., (a/g/g)) display loops in the graph, i.e., they homomerize by a 120° rotation of a cyclohexyl ring. This can be easily rationalized since in these conformations there is a ring attached to a

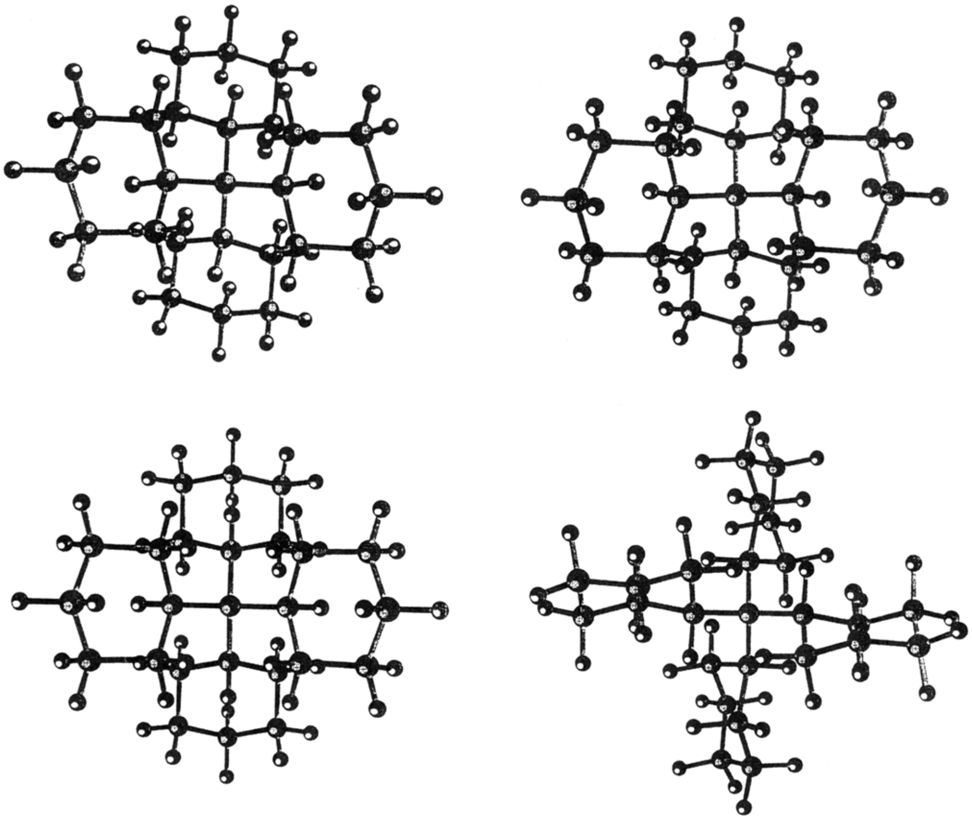

Figure 7. Selected calculated conformations of **2**. Top: (g/a/-g) conformations of D_2 (left) and S_4 (right) symmetries. Bottom: D_2d structure (left) and (g/g/a) conformation of S_4 symmetry (right).

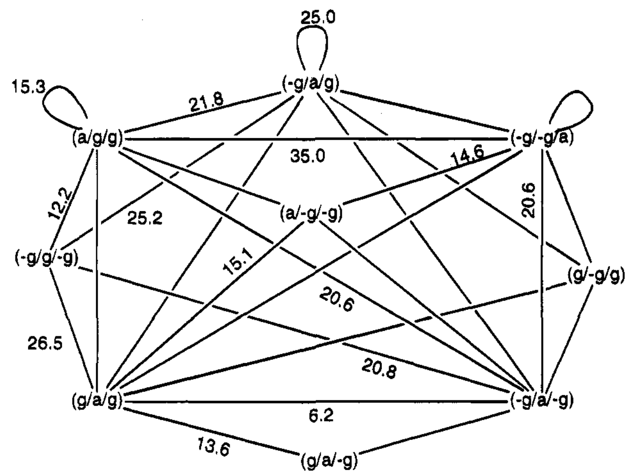

Figure 8. Interconversion graph for the ideal conformers of **2** assuming stepwise rotation of the rings. There is a vertical mirror plane which bisects the graph; pairs of conformations or pathways related by that plane display an enantiomeric relationship. Calculated energies for the different processes (relative to the (g/a/-g) conformation, in kcal mol^{-1}) are shown at the edges of the graph. For clarity, only the energy of one of two enantiomeric pathways is displayed.

tricyclohexylmethyl subunit in an arrangement with a local C_3 axis (i.e., (g,g,g/-g,-g,-g) or (a,a,a) arrangements).

In order to estimate the transition state for the different interconversion processes, we computationally rotated the cyclohexyl groups of **2** by using the dihedral angle driver option of the MM3 program. The calculated energies for the different processes (relative to the lowest energy conformation) are displayed in Figure 8. As shown in Figure 8 the topomerization of the system by single ring rotation can be carried out by the (g/a/-g) → (g/a/g) → (-g/a/-g) → (g/a/-g) pathway with a barrier of 13.6 kcal mol^{-1}. In contrast to early conclusions based on examination of space filling models,[12] the stepwise rotation of the rings by that pathway is not markedly hindered. We also examined the possibility of correlated libration of the rings in the ground state conformation, i.e., their simultaneous rotation by ca. 20° via a D_2d transition state with all rings perfectly staggered. According to the calculations, this process has a barrier of only 0.8 kcal mol^{-1}. The low libration barrier via a correlated rotation is in agreement with previous calculations for other hydrocarbons.[26] The libration of the rings results in the topomerization of the system since a pair of ortho and meta carbons mutually exchange (Figure 9). Libration of only two rings related by the C_2 axis results in mutual interconversion between the structures of S_4 and D_2 symmetries, with a barrier of 0.5 kcal mol^{-1}, but this process does not result in topomerization.

Conclusions. Tetracyclohexylmethane exists in in the crystal in a (g/a/-g) conformation (of approximate S_4 symmetry) in which the rings are skewed from their perfectly staggered conformation. The molecule undergoes a fast rotational process in solution which results in topomerization and involves libration of the four rings via a transition state of D_2d symmetry.

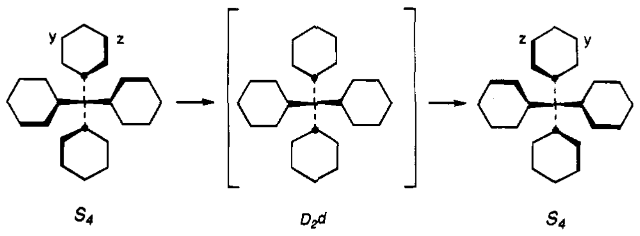

Figure 9. Topomerization process for **2**. The four rings librate from their lowest energy conformation (S_4) through a transition state of D_2d symmetry in which all rings are perfectly staggered. As a result of this process, which involves rotation of the rings by ca. 20°, there is a mutual exchange between pairs of symmetry nonequivalent *ortho* and *meta* carbons. This is exemplified by the meta carbons "y" and "z" which exchange sites as a result of the process.

Experimental Section

Tetraphenylmethane was purchased from Aldrich. The X-ray diffraction data were measured with a PW1100/20 Philips Four-Circle computer controlled diffractometer. Mo $K_\alpha(\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the SHELXS-86 direct method analysis. After several cycles of refinements the positions of the hydrogen atoms were calculated and added to the refinement process. All crystallographic computing was done on a VAX 9000 computer using the TEXSAN structure analysis software.

Crystal data for **2**: $C_{25}H_{44}$ space group $P\bar{1}$, $a = 9.509(2)$ Å, $b = 15.431(3)$ Å, $c = 8.035(2)$ Å, $\alpha = 105.12(2)$, $\beta = 114.97(2)$, $\gamma = 83.81(1)$, $V = 1031.8(8)$ Å^3, $Z = 2$, $\varrho_{calc} = 1.11$ g cm^{-3}, μ(Mo K_α) = 0.57 cm^{-1}, no. of unique reflections = 2867, no. of reflections with $I \geq 3\sigma_I = 2119$, $R = 0.047$, $R_w = 0.065$.

Tetracyclohexylmethane (2). To a solution of 0.4 g tetraphenylmethane dissolved in 70 mL methylcyclohexane there were added 0.2 g Pd/C and the mixture was hydrogenated (160 °C, 750 psi H_2) for 70 h. After filtration of the catalyst, the solvent was evaporated. Examination of the crude compound by NMR showed that is was composed of **2**, some unreacted starting material, and **3**. The solid was recrystallized twice from $CHCl_3$/EtOH yielding 20 mg pure **2**, mp 270–272 °C. ^{13}C NMR (100 MHz, $CDCl_3$, RT) δ 27.46, 29.10, 30.76, 43.32, 47.08. Microanalysis calcd for $C_{25}H_{44}$ C:87.13, H:12.87; found C: 87.48, H:12.58.

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