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Cyclohexyl Rings in Spatial Proximity: Stereochemistry of Tricyclohexylmethane

Ishay Columbus and Silvio E. Biali*

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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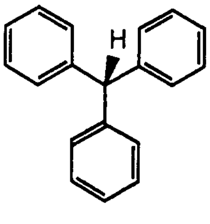
The static and dynamic stereochemistry of tricyclohexylmethane (2) is analyzed. The ^{13}C and ^{1}H NMR of 2 were assigned by means of the 2D NMR techniques INADEQUATE and DQF COSY. Molecular mechanics calculations were performed in order to estimate the influence of the torsional angles of the cyclohexyl rings and their mode of attachment (equatorial or axial) on the relative energy of the conformations. MM3 calculations of 2 indicate that in the lowest energy conformation the cyclohexyl rings are attached to the central carbon via their equatorial positions and are oriented in a chiral gauche,gauche,anti (g,g,a) arrangement. The compound crystallizes in two crystalline forms. X-ray diffraction analysis of 2 indicates that, in both crystals, the conformation is (g,g,a), but in the higher melting form only homochiral molecules are packed in a single crystal while in the lower melting one both enantiomers are present. Upon lowering the temperature, decoalescence was observed in the ^{13}C NMR signals, and a barrier of 7.3 ± 0.2 kcal mol^{-1} was calculated for the rotational process. The conformational interconversion of 2 was calculated by MM3 calculations which indicate that the process followed by NMR corresponds to an enantiomerization process.

Introduction

Molecules consisting of two or three aryl rings attached to a central carbon (e.g., triphenylmethane (1)) adopt a conformation in which all rings are twisted in the same sense with regards to a reference plane (a "propeller" conformation).[1] The conformation and internal rotations of molecular propellers such as 1 have been intensively studied,[1,2] but considerably less attention has been devoted to tricyclohexylmethyl systems. In principle, the formal replacement of phenyls by cyclohexyl rings should result in systems which are more rich conformationally.[3,4] In contrast to a phenyl group, a cyclohexyl ring is nonplanar and conformationally flexible and it may exist in chair or nonchair conformations (e.g., twist boat). In addition, each cyclohexyl group may be attached to the central carbon by an equatorial or axial position. Alkyl monosubstituted cyclohexanes prefer to locate the substituent in an equatorial position as shown by the "A" values for the alkyl substituents,[5] but one exception was found for this rule. If the substituent is U-shaped the axial conformation may be energetically favored due to repulsive steric interactions present in the equatorial form.[6] If several cyclohexane rings are in spatial proximity their mutual steric interaction should affect the axial/equatorial energy gap. As the subject for the present study we choose tricyclohexylmethane (2).[7] This compound is the saturated analog of 1 and its conformational behavior may shed light on the stereochemical consequences of the presence of three cyclohexyl rings in spatial proximity.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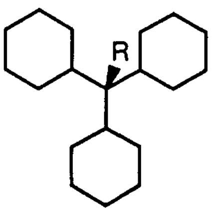
2 R = H
3 R = OH

Preparation of 2. The preparation of tricyclohexylmethane by hydrogenation of triphenylmethane has been described in the literature.[7] Interestingly, different melting points were reported for the compound (48 °C,[7a] 58.5–59.5 °C,[7b] 58.2–59.4 °C[7c]). Since the literature conditions for the hydrogenation resulted in our hands in only partial reduction of the rings, we attempted more drastic conditions. Hydrogenation of 1 in cyclohexane (Pd/C, 700 psi H_2, 170 °C) resulted in the formation of 2 in 95% yield. 2 could also be prepared from the commercially available tricyclohexylmethanol (3) by ionic hydrogenation.[8] Treatment of 3 with Et_3SiH/CF_3COOH resulted in the formation of 2 in 90% yield. An analytically pure sample of 2 recrystallized from MeCN had mp 52 °C, but when this sample was recrystallized from $CHCl_3/MeOH$, a sample of higher mp (58 °C) was obtained. Neither sample did include solvent of crystallization as shown by NMR. In order to obtain accurate melting point values for the samples we examined their melting behavior by the differential scanning calorimetry (DSC) method. The low melting sample had an enthalpy of melting of 15.14 kJ/mol (3.6 kcal mol^{-1})) and a peak maximum at 53.2 °C while the high melting form had an enthalpy of melting of 19.19 kJ/mol (4.6 kcal mol^{-1}) and a peak maximum at 55.4 °C.

• Abstract published in *Advance ACS Abstracts*, October 15, 1993.

[1] For reviews on the static and dynamic stereochemistry of molecular propellers see: Mislow, K.; Gust; D.; Finocchiaro, P.; Boettcher, R. J. *Forthschr. Chem. Forschr.* **1974**, *47*, 1. Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. Meurer, K. P; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 1. Willem, R.; Gielen, M.; Hoogzand, C.; Pepermans, H. *Adv. Dyn. Stereochem.* Gielen, M., Ed.; Academic Press: New York, 1985; Vol. 1, p 207.

[2] Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535.

[3] For a recent review on the stereochemistry of cyclohexanes see: Mann, G. *Z. Chem.* **1990**, *30*, 1.

[4] For a review on conformational flexible molecules see: Hoffmann, R. W. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1124.

[5] Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199.

[6] Biali, S. E. *J. Org. Chem.* **1992**, *57*, 2979.

[7] (a) Ipatieff, W. N.; Dolgof, B. N. *Compt. Rend.* **1927**, *185*, 210. (b) Adkins, H.; Zartman, W. H.; Cramer, H. *J. Am. Chem. Soc.* **1931**, *53*, 1425. (c) Smith, H. A.; Alderman, D. M., Jr.; Shacklett, C. D.; Welch, C. M. *J. Am. Chem. Soc.* **1949**, *71*, 3772.

[8] Carey, F. A.; Tremper, H. S. *J. Org. Chem.* **1971**, *36*, 758.

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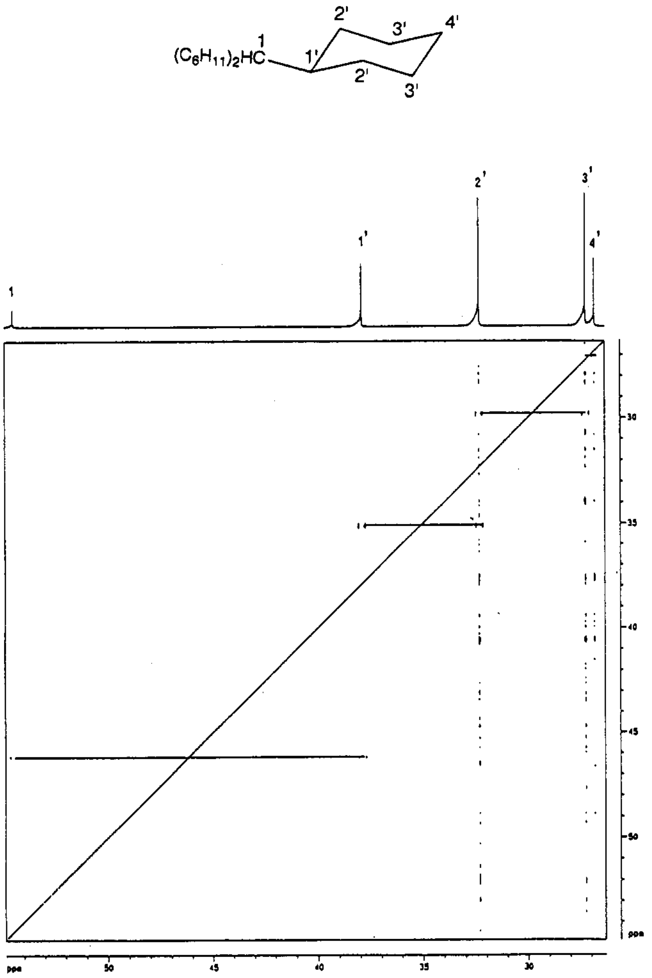

Figure 1. 100-MHz ^{13}C NMR 2D INADEQUATE spectrum of **2**.

NMR Spectra of 2. The ^{13}C NMR spectrum of **2** displays at room temperature ($CDCl_3$, 100 MHz) five signals at δ 54.40, 37.86, 32.28, 27.21 and 26.77 ppm. This spectrum is in agreement with a structure which is conformationally flexible at room temperature on the NMR timescale and in which the three rings as well as the pairs of carbons at the 2/6 and 3/5 positions are equivalent. For the assignment of the signals we resorted to a 2D INADEQUATE spectrum (Figure 1).[9] In this spectrum, cross peaks between a pair of carbons indicate that the two carbons are directly connected. As shown by the spectrum, the signals at both extremes of the spectrum are the only ones which have a single cross peak. These signals must correspond to the central carbon and to the carbons at the 4 position of the cyclohexyl rings, since these are the only two positions which are connected to a single group of equivalent carbons. Empirical parameters for the calculation of chemical shifts indicate that the carbon at the 4 position in a monoalkyl substituted cyclohexane should resonate at about δ 27.1,[10] and therefore the signal at 26.77 ppm is assigned to that position. This assignment and the connectivity indicated by the INADEQUATE experiment allows the assignment of the signals at δ 54.40, 37.86, 32.28, and 27.21 ppm to the central carbon and the cyclohexyl carbons at the 1′, 2′, and 3′ positions, respectively. Interestingly, neighboring carbons (i.e. mutually connected) appear at neighboring positions in the ^{13}C NMR spectrum.

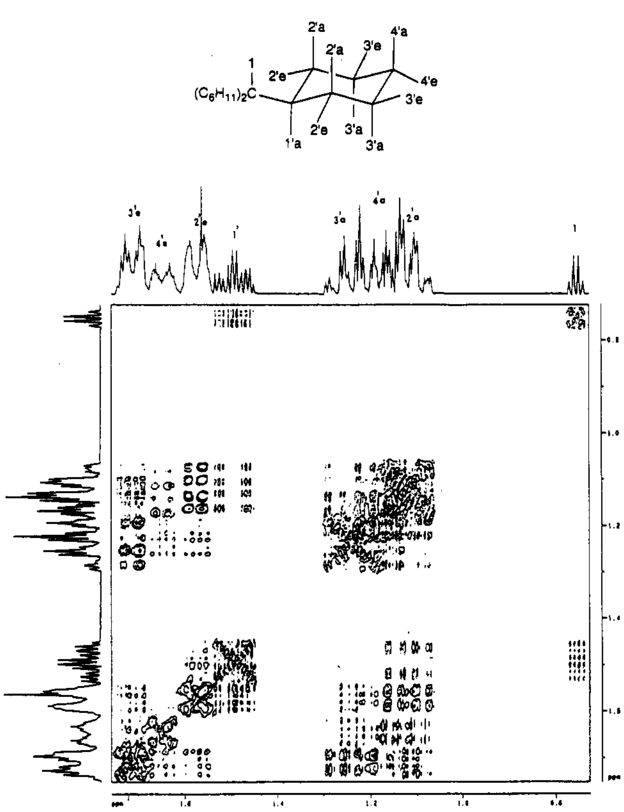

Figure 2. 400-MHz ^1H NMR DQF COSY spectrum of **2**.

The room temperature ^1H NMR spectrum of **2** (400 MHz, $CDCl_3$) displays two groups of several overlapping signals integrating for five protons each at approximately δ 1.6, 1.1 and a quartet (*J* = 4.0 Hz) integrating for one proton at 0.72 ppm. The highest field signal can be assigned to the methine hydrogen of the central carbon. The chemical shift and coupling constant observed are similar to the values reported for triisopropylmethane (δ 0.83 ppm and *J* = 4.53 Hz).[11] In order to assign the different signals and to analyze the conformation of the cyclohexyl groups we measured the ^1H DQF COSY NMR spectrum (Figure 2).[12] Relatively large coupling constants between pairs of protons can be easily spotted since their cross peaks are usually stronger. Strong cross peaks therefore identify pairs of peaks belonging to protons in diaxial positions or pairs of protons in a given methylene group displaying geminal coupling. Weak cross peaks identify pairs of vicinal protons in a gauche relationship, i.e., axial–equatorial or diequatorial pairs within the cyclohexane ring. The signal at 0.72 ppm shows a cross peak with a signal at about 1.45 ppm. This assigns the latter signal to the methine proton of the cyclohexane ring. This signal shows two additional cross peaks, one weak with the signal at 1.55 ppm and one strong with a signal at 1.12 ppm. The presence of both a large and small coupling constant indicates that the cyclohexyl methine hydrogen is located in an axial position, since only in this case both large (diaxial) and small (axial/equatorial) coupling constants can be present for the cyclohexane methine proton. The

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[9] For a review on the INADEQUATE technique see: Buddrus, J.; Bauer, H. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 625.

[10] Wehrli, F. W.; Wirthlin, T. *Interpretation of C-13 Spectra*; Heyden, London, 1976; p 45.

[11] Anderson, J. E.; Koon, K. H.; Parkin, J. E. *Tetrahedron* **1985**, *41*, 561. See also: Anderson, J. E.; Bettels, B. R. *Tetrahedron* **1990**, *46*, 5353.

[12] Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 490.

cyclohexyl rings must therefore be attached to the central carbon through their equatorial positions. On the basis of similar considerations, all signals of the ^{1}H NMR could be assigned as showed in Figure 2. The DQF COSY spectrum is in agreement with a structure in which the cyclohexyl rings rotate rapidly on the NMR time scale and in which there is a strong conformational bias for the equatorial arrangement of the rings. As a result of the dynamic process, the pairs of equatorial and axial protons at the 2′ or 3′ positions, are pairwise equivalent. All the axial signals are grouped together and resonate at a higher field than the equatorial signals, as observed for the parent cyclohexane, for which the axial protons resonate 0.5 ppm higher than the equatorial ones.[13]

Nomenclature. The different conformers of 2 arise from the different torsional angles of the cyclohexyl rings with the central methine group, the different skeletal conformations of the cyclohexyl groups (chair, twist boat, etc.) and by the mode of attachment of the rings to the central carbon (i.e. using an axial or equatorial position). In their stable conformations (see below) the cyclohexyl groups adopt conformations in which the rings are "chair" and exist in staggered conformations. Under these restrictions, the conformations attainable by 2 are analogous to other trisubstituted system such as 2-(chloromethyl)-2-methyl-1,3-dichloropropane[14] and triisopropylmethane.[11] The HCCH torsional angle between the methine protons of the central carbon and of C-1 will be denoted as "anti" or "+" or "−" gauche (±g).[15] For the sake of simplicity the "+" sign will be omitted (e.g., the "+g" form will be designated "g"). In order to describe the arrangement of the three rings the molecule is oriented with the central methine hydrogen pointing to the viewer, and the conformation of the three rings is denoted in a clockwise order. Since one can start from either one of the three rings, if the three descriptors are not identical, three different designations are possible for a given conformation. These designations are obtained by a cyclic permutation of the three descriptors. For example the conformation shown in 4 can be described by any one of three equivalent designations: (−g,g,a), (a,−g,g) and (g,a,−g). In case that a given ring is attached to the central carbon through an axial position, this will be described by the subscript "ax" under the descriptor for the HCCH torsional angle (e.g., $-g_{ax}$).

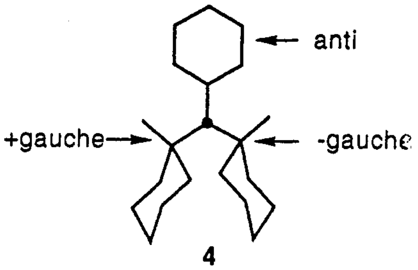

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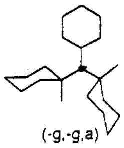
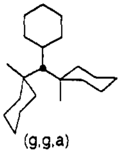
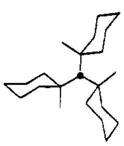
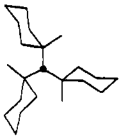
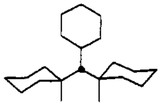
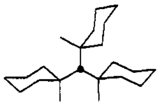
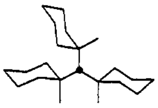
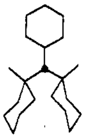
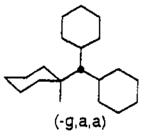
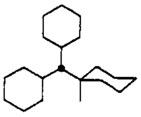
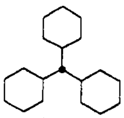
Table I. Calculated (MM3) Relative Steric Energies (in kcal mol^{-1}) of the conformers of 2

conformation	energy
 (-g,-g,a)  (g,g,a)	0
 (-g,-g,-g)  (g,g,g)	0.6
 (-g,a,g)	2.4
 (-g-g,g)  (-g,g,g)	3.4
 (g,a,-g)	3.6
 (-g,a,a)  (a,a,g)	4.3
 (a,a,a)	8.8

Molecular Mechanics Calculations for 2. For the evaluation of the relative energies of the different conformers of 2 we resorted to the MM3(92) program.[16] This program includes as a subroutine the stochastic search program of Saunders.[17] In order to explore the conformational space of 2 we carried out a stochastic search involving 600 "pushes" using a kick-size parameter of 2 Å. The output of the program consisted of about 200 different conformations characterized as minima. Inspection of these conformers showed that in all the low-energy conformations the cyclohexyl rings adopted chair conformations. Examination of the calculated conformations revealed that several conformations which on the grounds on chemical intuition should be low energy forms were not reached by the program. Most likely, the large number of conformations possible for the systems renders the stochastic search impractical. We therefore carried out calculations by the manual input of structures with chair conformations. The relative steric energies of the conformations calculated with equatorial arrangements of the rings are collected in Table I. As shown by Table I, the lowest energy conformation corresponds to a chiral

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[13] Günther, H. *NMR Spectroscopy, an Introduction*; Wiley: Chichester, 1980; p 72.

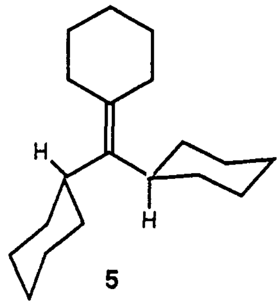
[14] Bushweller, C. H.; Whalon, M. R.; Laurenzi, B. J. *Tetrahedron Lett.* **1981**, *22*, 2945.

[15] In the present paper the terms "anti" and "gauche" will be used in a rather loose fashion. Some conformations which will be denoted "gauche" (such as the ground state conformation (g,g,a), see text) have torsional angles which deviate significantly from 60°. The clinal/periplanar nomenclature (Klyne, W.; Prelog, V. *Experientia*, **1960**, *16*, 521) although quite suitable is somewhat more cumbersome in our case.

[16] Allinger, N. L. *Molecular Mechanics. Operating Instructions for the MM3 Program. 1989 Force Field (updated 5/6/92).* Technical Utilization Corp.

[17] Saunders, M. *J. Am. Chem. Soc.* **1987**, *109*, 3150.

(±(g,g),a) conformation while the ±(g,g,g) form lies 0.6 kcal mol^{-1} above it. The calculated torsional angles of the rings for the (±(g,g),a) conformation (95.4°, 64.0°, and 170.7°), are similar to those calculated by MM2 for the (±(g,g),a) conformation of triisopropylmethane (95.5, 63.1°, and 179.0°).[11] In the lowest energy conformation the two "gauche" rings are oriented in a homodirectional fashion, while heterodirectional arrangements result in higher steric energies. MM2 calculations indicate a similar behavior for the unsaturated analog **5**, for which the homodirectional arrangement of the rings is favored over heterodirectional ones.[18]



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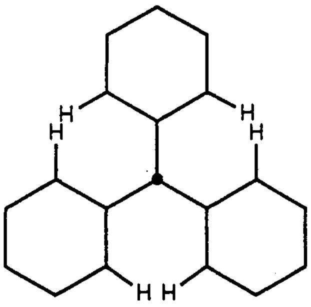
The presence of two or three rings in an anti fashion results in a substantial increase in the steric energy. Inspection of molecular models indicate that if the three rings are in a 180° arrangement, that geometry should result in severe steric interactions between equatorial hydrogen atoms at the 2 and 6 positions (cf. **6**). This interaction can be partially relieved by twisting the cyclohexyl ring. Indeed, for the (a,a,a) conformer the calculations predict an 151° torsion for the three central HCCH angles.



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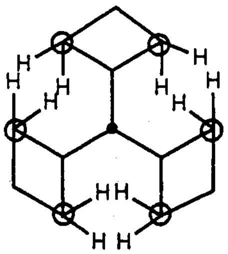

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In order to estimate the effect of the mutual proximity of the rings in the axial/equatorial energy gap, we calculated the steric energies of the two low-energy forms (±(g,g),a) and ±(g,g,g) with all possible combinations of axial and equatorial rings. As shown in Table II, for the (±(g,g),a) conformation the energy gap between the all-equatorial conformation and a conformation in which two rings are connected through equatorial positions and one through an axial position strongly depends on the relative location of the axial ring. The lowest steric energy is obtained when the axial ring is the one oriented anti to the central methine. The axial/equatorial energy gap between the (±(g,g),a) and the (±(g,g),a_{ax}) forms (1.7 kcal mol^{-1}) is similar to the gap calculated for isopropylcyclohexane (1.7 kcal mol^{-1}).[19] In contrast, if one g_{ax} ring is present, this results in a substantial increase in the axial/equatorial energy gap (6.7–9.5 kcal mol^{-1}). For the ±(g,g,g) conformation, the formal replacement of an equatorial by an axial ring results in an increase in the steric energy of ca. 6 kcal mol^{-1}. Since a single cyclohexane ring attached through its axial position favors an anti over a gauche orientation, we calculated also the (a,a,a) form with all the rings connected to the central carbon through their axial positions. Examination of molecular models suggests that for a 180° arrangement of the rings the repulsive steric interaction should be even larger than in **5** since not only the equatorial protons are in contact, but also the axial protons at the 3 and 5 carbons (cf. **7**). The calculated (a_{ax},a_{ax},a_{ax}) form lies 17.4 kcal mol^{-1} above the triequatorial form. Clearly the spatial proximity of the rings widens the axial/equatorial energy gap by increasing the repulsive steric interactions in the axial conformations. Only in the (±(g,g),a_{ax}) conformation the axial ring is relatively unencumbered, and the axial/equatorial energy gap is similar to that of isopropylcyclohexane.

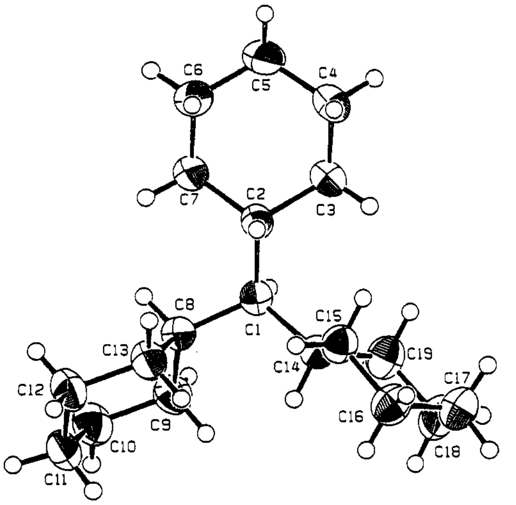

Figure 3. Numbering scheme of the molecular structure of **2**.

Table II. Calculated Relative Steric Energies (RSE, in kcal mol^{-1}) of the (±(g,g),a), ±(g,g,g), and (a,a,a) Conformations with Different Combinations of Equatorial and Axial Cyclohexyl Rings

conformation	RSE	conformation	RSE
(±(g,g),a)	0	(±(g_{ax},g_{ax}),a_{ax})	18.5
(±(g,g)a_{ax})	1.7	±(g,g,g)	0.6
(±(g_{ax},g),a)	6.7	±(g_{ax},g,g)	6.3
(±(g,g_{ax}),a)	9.5	±(g_{ax},g_{ax},g)	12.4
(±(g_{ax},g),a_{ax})	8.5	±(g_{ax},g_{ax},g_{ax})	18.9
(±(g,g_{ax}),a_{ax})	11.6	(a,a,a)	8.8
(±(g_{ax},g_{ax}),a)	16.3	(a_{ax},a_{ax},a_{ax})	26.2

Crystal Structure of 2. Single crystals of **2** were grown from acetonitrile (low melting form) and MeOH/$CHCl_3$ (high melting form) and their structure determined by X-ray diffraction. According to the X-ray data, in both crystals the molecule exists in the same chiral conformation (±(g,g),a). In the low melting form the compound crystallized in an achiral space group (*C*2/*c*) in which both enantiomers are present in the crystal, while in the high melting form the space group is chiral ($P2_12_12_1$) and in a given crystal only molecules of a single chirality are present. The numbering scheme of the crystal conformation (low

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[18] Takeuchi, K.; Toyama, T.; Kubota, Y.; Okamoto, K. *Chem. Lett.* **1983**, 1631.

[19] Golan, O.; Goren, Z.; Biali, S. E. *J. Am. Chem. Soc.* **1990**, *112*, 9300.

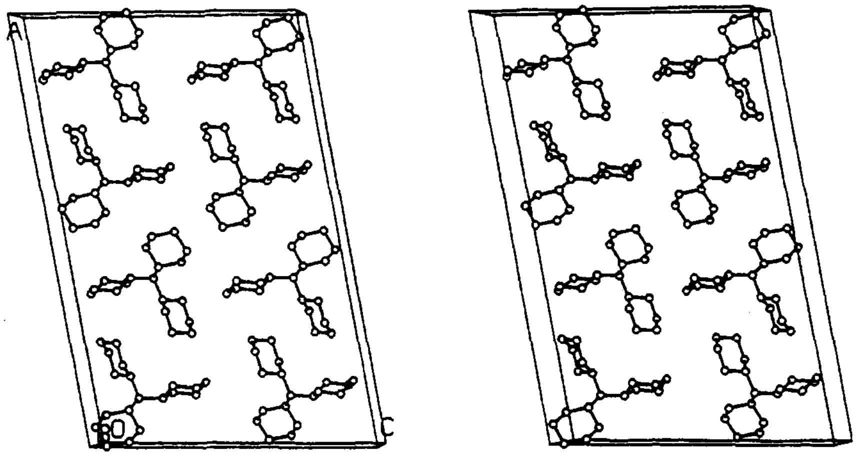

Figure 4. Stereoscopic view of the packing arrangement of the racemic crystal of 2 viewed down the *b* axis. Hydrogen atoms were omitted for clarity.

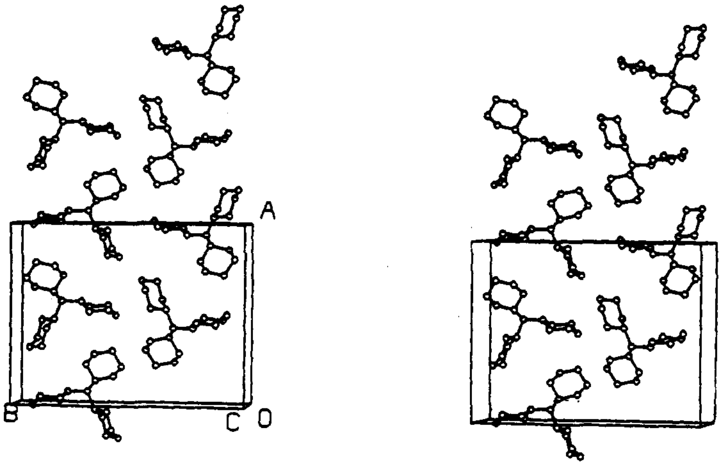

Figure 5. Stereoscopic view of the packing arrangement of the chiral crystal of 2 viewed down the *c* axis. Hydrogen atoms were omitted for clarity. For comparison purposes, four additional molecules are displayed in addition to the four present in the unit cell.

melting form) is shown in Figure 3.[20] Selected structural parameters for the conformations in the two crystal forms, together with the calculated structural parameters for the (gga) form, are collected in Table III, which shows that the molecular geometry in both crystals is similar, and that the calculations reproduce satisfactorily the molecular geometry. The three nonequivalent cyclohexyl–methine bonds are predicted by the calculations to be somewhat elongated (1.563–1.576 Å) and this seems to be corroborated by the X-ray data of the two crystal forms. For the related triisopropylmethane MM2 calculations predict for the (±(g,g),a) form a similar elongation for the isopropyl-CH bonds (1.554–1.558 Å).[11] The torsional angles of the cyclohexyl rings is well reproduced by the calculations.

The presence of both racemic and chiral crystals is of interest since the validity of Wallach's rule ("racemic crystals tend to be denser than their chiral counterparts") was recently reexamined by Brock, Schweizer, and Dunitz.[21] It was concluded that the apparent greater stability and density of the racemic crystal is, at least in part, due to a statistical bias in samples containing noninterconverting enantiomers. We calculated the difference in densities between both crystals ($\Delta\%$) using the equation suggested by Brock et al. (i.e. $(\Delta\%) = 100[(V/Z)_A - (V/Z)_R]/\{[(V/Z)_A + (V/Z)_R]/2\}$), where V and Z represent the volume and the number of molecules in the unit cell, respectively, in the chiral (A) and achiral (R) crystals. Based on the crystal data for 2, a value $\Delta\% = 0.87$ can be calculated for the system, indicating that the achiral crystals are somewhat more dense, in agreement with Wallach's rule. Stereoscopic views of the packing arrangements of the racemic and chiral crystals of 2 are displayed in Figures 4 and 5, respectively. Short nonbonded interatomic distances exist in the racemic crystal between enantiomeric molecules located near the center of the unit cell. The shortest distance is between the two anti rings and in particular between the two C(7) carbons

Table III. Selected Experimental (X-ray) and Calculated (MM3) Structural Data for 2[a]

parameter	Exptl (low mp)	Exptl (high mp)	calculated
C(1)C(2)	1.545(3)	1.550(3)	1.569
C(1)C(8)	1.550(2)	1.565(3)	1.576
C(1)C(14)	1.563(2)	1.549(3)	1.563
C(2)C(1)C(8)	114.0(1)	115.0(2)	114.4
C(2)C(1)C(14)	114.5(1)	113.7(2)	113.0
C(8)C(1)C(14)	111.8(1)	110.9(2)	111.1
HC(1)C(2)H(2)	−165.3	−165.0	−170.7
HC(1)C(14)H(24)	−69.2	−65.9	−64.0
HC(1)C(8)H(13)	−99.0	−103.2	−95.4

[a] Bond lengths in angstroms, bond and torsional angles in degrees.

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[20] The authors have deposited atomic coordinates for 2 with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

[21] Brock, C. P.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* 1991, *113*, 9811.

(3.529(4) Å). Interestingly, the DSC values clearly indicate that the less dense crystal is the more stable, as indicated by its higher melting point and enthalpy of fusion.

Solution Conformation. Since the *(±(g,g),a) conformation* is predicted by the MM3 calculations as the lowest energy conformation, and this conformation was found in the two crystal structures of **2**, it seems reasonable to assume that the molecule exists in solution also preferentially in the (±(g,g),a) conformation. Since at room temperature there is a rapid dynamic process which exchanges the three rings; a single average ^3J HCCH coupling constant ($^3J = 4.0$ Hz) is observed. Using the HCCH torsional angles found by X-ray crystallography one can calculate the coupling constant by means of the Karplus equation using Altona's parameters.[22] According to the equation the predicted average coupling constant for the (±(g,g),a) form is 4.49 Hz, which is in agreement with the presence of the (±(g,g)a) form, and to a lower extent, the ±(g,g,g) form. Interestingly, the ^3J HCCH coupling observed for **2** (4.0 Hz) is smaller than the corresponding coupling constant observed for triisopropylmethane (4.53 Hz). Even though in both molecules the torsional angles of the (±(g,g),a) and ±(g,g,g) forms are fairly similar but not exactly identical, the smaller coupling constant seems to indicate that for **2** there is in solution a larger presence of the ±(g,g,g) form.

Dynamic Behavior of 2. In order to "freeze" the internal rotations we lowered the temperature of a NMR sample of **2** in $CDCl_2F$[23] and followed the spectral changes by ^{13}C NMR spectroscopy. The signals at 32.28 and 27.21 ppm (corresponding to C2′ and C3′) broadened and decoalesced into two signals each (Figure 6). Notably the chemical shift difference between the carbons at the 2-positions (5.68 ppm) is larger than the splitting between the 3-positions (0.48 ppm). From the chemical shift difference between the two pairs of signals and the coalescence temperatures (149 and 174 K), a barrier of 7.3 ± 0.2 kcal mol^{-1} was calculated for the process. For the related triisopropylmethane[11] a lower barrier (6.6 kcal mol^{-1}) was measured.

Conformational Interconversion of 2. The inversion barrier of cyclohexane is about 10 kcal mol^{-1}, i.e., higher than the barrier measured by the DNMR experiment. It is reasonable to assume than the dynamic process followed by NMR does not involve ring inversion but only rotation of the cyclohexyl rings. MM2 calculations of **5** have shown that the energetically favored rotational pathway involves stepwise rotation of the two cyclohexyl rings.[18,24] Assuming that during the rotation of **2** only conformations in which the rings are attached through their equatorial positions are populated and, by analogy with **5**, that the interconversion involves the stepwise rotation of the rings, the interconversion graph can be constructed (Figure 7) in which the vertices represent the different conformations and the edges the interconversion of the conformers by rotation of a ring. This graph is a somewhat different representation of the interconversion graph of triisopropylmethane.[11] The conformational interconversion of **2** was calculated starting from the (g,g,a) conformation

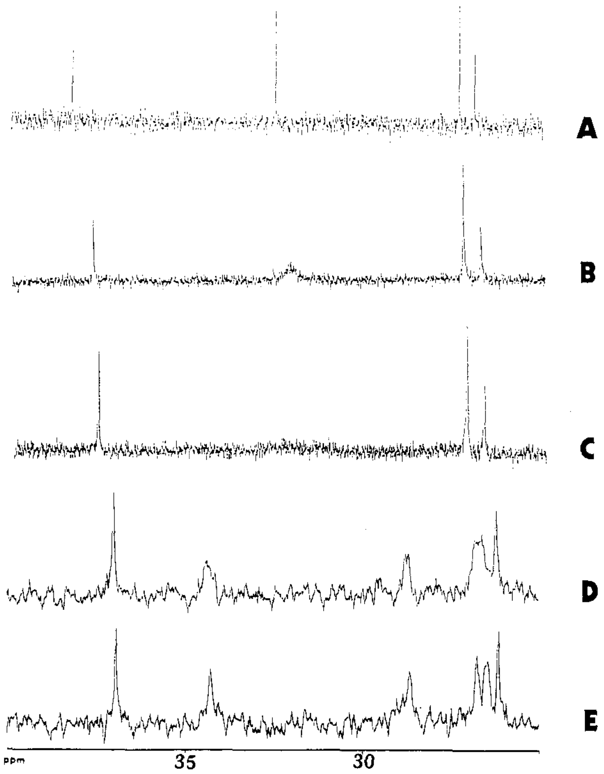

Figure 6. 100-MHz ^{13}C NMR of the cyclohexyl region of **2** in $CDCl_2F$ at different temperatures. A: 295 K; B: 200 K; C: 174 K; D: 149 K; E: 142 K.

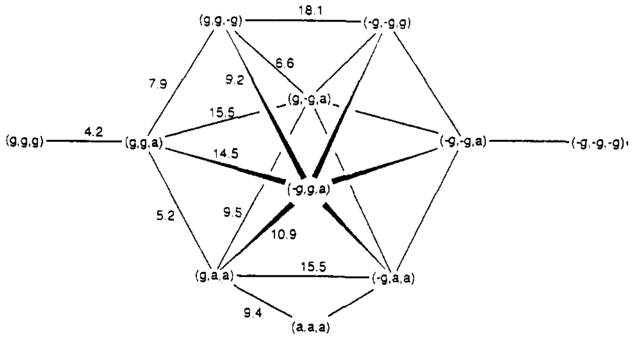

Figure 7. Calculated (MM3) interconversion graph for the internal rotations of **2**. The graph has mirror symmetry which bisects the graph and passes through the achiral conformers (a,a,a), (−g,g,a), and (g,−g,a). In all conformations the cyclohexyl rings are attached to the central carbon through their equatorial positions. Calculated steric energies of the transition states *(relative to the (g,g,a) form) for single cyclohexyl rotations are* marked at the edges of the graph.

using the driver option of the MM3 program. As shown by the graph, the (g,g,g) ⇄ (g,g,a) process (and its enantiomeric pathway (−g,−g,−g) ⇄ (−g,−g,a)) both have a calculated barrier of 4.2 kcal mol^{-1}. These processes, which render the three rings equivalent but do not result in enantiomerization of the molecule are fast on the NMR time scale even at 142 K. Enantiomerization of the (g,g,a) form can be achieved by the pathway (g,g,a) → (g,g,−g) → (g,−g,a) → (−g,−g,a) with a calculated barrier of 7.9 kcal mol^{-1}. The enantiomerization pathway should lead to a mutual exchange between the carbons at the positions 2 and 6 (and 3 and 5). The agreement between the calculated (7.9 kcal mol) and the experimental barrier (7.3 kcal mol^{-1}) is excellent.

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[22] $J = 7.76\cos^2\phi - 0.01\cos\phi + 1.40$ (Haasnoot, C. A. G.; de Leeuw, F. A. A. M., Altona, C. *Tetrahedron.* **1980**, *36*, 2783).

[23] Siegel, J. S.; Anet, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629.

[24] In ref 18 the term "correlated rotation" is used for describing the stepwise rotation of the rings. It should be noted, however, that this term is usually used for describing the synchronous rotation of two or more groups.

The calculated enantiomerization pathway is identical to the one calculated for triisopropylmethane. The higher barrier observed for 2 both experimentally and by calculations may indicate that in this system the intermeshing of two cyclohexyl groups is somewhat more efficient than the intermeshing (static gearing)[25] of two isopropyl groups. Work is now in progress to further study the intermeshing of cyclohexyl groups as compared to that of isopropyl groups.

Experimental Section

DSC measurements were carried out with a Mettler DSC 30 apparatus. Tricyclohexylmethanol was purchased from Aldrich. NMR measurements were carried out on a Bruker AMX-400 pulsed FT spectrometer. The X-ray diffraction data were measured with a PW1100/20 Philips Four Circle Computer-Controlled Diffractometer. Mo K_α (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. All crystallographic computing was done on a VAX 9000 computer using the TEXAN structure analysis software.

Crystal data for 2: low melting form: $C_{19}H_{34}$, space group *C*2/*c*, *a*: 29.032(4) Å, *b*: 6.294(1) Å, *c*: 18.736(2); β = 100.41(1)°, *V*: 3367.2(8) Å^3, *z*: 8, ρ_{calcd}: 1.04 g cm^{-3}, μ(Cu Kα): 3.85 cm^{-1}, no. of unique reflections: 2111, no. of reflections with $I \geq 3\ \sigma_I$: 1683, *R*: 0.042, R_w: 0.056. High melting form: $C_{19}H_{34}$, space group $P2_12_12_1$, *a*: 14.483(1) Å, *b*: 18.380(2) Å, *c*: 6.380(1), *V*: 1698.3(5) Å^3, *z*: 4, ρ_{calcd}: 1.03 g cm^{-3}, μ(Cu Kα): 0.53 cm^{-1}, no. of unique reflections: 2251, no. of reflections with $I \geq 3\ \sigma_I$: 1665, *R*: 0.041, R_w: 0.051.

Preparation of 2. (A) By Reduction of Triphenylmethane. An amount of 1.0 g of triphenylmethane (1) was dissolved in 75 mL of cyclohexane, and to the solution there were added a few drops of acetic acid and 0.5 g of Pd/C. The mixture was hydrogenated in an autoclave (700 psi H_2, 170 °C) for 22 h. Filtration of the catalyst and evaporation of the solvent afforded 2, which was purified by recrystallization from ethanol, mp 52 °C.

(b) By Ionic Hydrogenation of Tricyclohexylmethanol. To 0.4 g of tricyclohexylmethanol (3) dissolved in 20 mL of CH_2Cl_2 there were added 4 mL of CF_3COOH and 3 mL of Et_3SiH. The mixture was stirred at room temperature for 24 h and quenched with aqueous $NaHCO_3$. The phases were separated, and the organic phase was evaporated. Recrystallization of the residue form ethanol gave pure 2 (0.35 g, 90%), mp 52 °C.

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(25) For a review see: Mislow, K. *Chimia* 1986, *40*, 395.