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THE MOLECULAR STRUCTURE AND CONFORMATION OF *PER*-ALKYLATED CYCLOHEXANES

Part I. 4,4,8,8,12,12-Hexamethyltrispiro [2,1,2,1,2,1] dodecane

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ABSTRACT

The molecular structure and conformation of 4,4,8,8,12,12-hexamethyltrispiro [2,1,2,1,2,1]dodecane has been studied by gas electron diffraction, and by force field as well as by molecular mechanics (MM2) calculations. The experimental data are in agreement with a molecular model in twist-boat conformation. The MM2 calculations support these results.

The most noticeable geometrical parameters are the following: very long C—C bonds in the methyl substituents (r_a = 1.590(8) Å), small $H_3C—C—CH_3$ valence angles (98.2 (1.8)°) and alternating C—C—C valence angles of ca. 109° and 119° in the cyclohexane ring.

INTRODUCTION

In fully alkylated cyclohexanes strong nonbonded repulsions are unavoidable. Structural and conformational changes, relative to "normal" geometrical and conformational parameters, might reduce the nonbonded repulsions sufficiently to give a lower overall sterical energy in these kinds of molecules, even if such changes increase other sterical energy contributions. The structure and conformation of fully alkylated cyclohexanes are accordingly expected to be governed by strong nonbonded interactions.

4,4,8,8,12,12-Hexamethyltrispiro [2,1,2,1,2,1] dodecane (1) was recently extensively studied by ^{13}C NMR spectroscopy [1]. The NMR signals from the secondary cyclopropane carbon atoms appeared as a singlet at temperatures above —100°C. At lower temperatures the signal split up, and at —155°C three signals (δ = 9.50, 10.51 and 15.77) of approximately equal intensities appeared in this region. The NMR results were interpreted in terms of a twist-boat/twist-boat conformational equilibrium.

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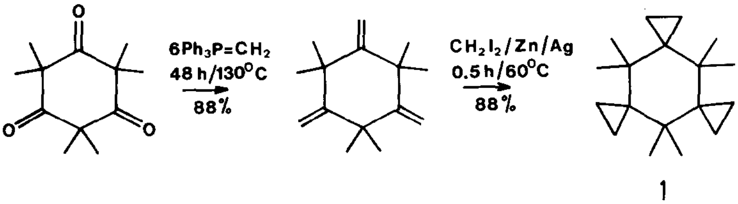
At about the same time as the NMR study, results from molecular mechanics calculations were published [2]. Here the chair conformer was found to be energetically favoured over twist-boat by ca. 0.2 kcal mol^{-1}.

Compound 1 therefore seemed to be a natural choice for an ED study of the structural and conformational problems related to overcrowded cyclohexanes.

EXPERIMENTAL

The sample of 1 was prepared according to the scheme [1]



Electron diffraction diagrams were recorded with the Balzer's Eldigraph KD-G2 unit [3, 4] at a nozzle-tip temperature of 174°C (long camera distance) and 186°C (short camera distance). The electron wavelength was 0.05868 Å, as calibrated against benzene. Electron diffraction photographs were recorded on Kodak Electron Image plates at nozzle-to-photographic plate distances of 497.87 mm (6 plates) and 248.01 mm (6 plates). Ranges of data were 1.50—15.50 and 2.75—30.50 ($Å^{-1}$), with Δs increments of 0.25 ($Å^{-1}$). The experimental data were treated in the usual way [5], and the modification function used was $s \times f_C^{-2}$. The scattering amplitudes and phases were calculated [6] using the partial-wave method, based upon the analytical HF potentials for the C atoms [7] and the best electron density of bonded hydrogen for the H atoms [8]. The inelastic scattering factors used were those of Tavard et al. [9].

MOLECULAR MECHANICS CALCULATIONS

In a gas-phase electron diffraction (GED) study of a molecule as large as 1, with 48 atoms, it will be necessary to make some assumptions about the molecular geometry, in order to reduce the number of independent geometrical parameters to a manageable size. Some assumptions are sometimes obvious from the symmetry of a molecule, while others are more dubious. Results from molecular mechanics calculations might be of valuable guidance in evaluating which assumptions may be safely introduced and which should be avoided. In the present case it is also of interest to compare sterical energy terms for the two most likely conformers of 1: chair and twist-boat.

A molecular mechanics calculation of 1 was recently reported in the literature [2]. The structural details of importance for a GED study were however, not presented. New calculations, using Allinger's MM2 program [10] were therefore carried out.

Two steric energy parameters were missing in the MM2 program, namely a torsional term of type 1-22-1-22 (atom 1, C_{sp^3}; atom 22, C in cyclopropane ring) and a bending term of type 22-1-22, both relating to the cyclohexane ring. The missing parameters were substituted by the 1-1-1-1 torsion and 1-1-1 bending terms already present in the MM2 program.

The results of the calculations are presented in Table 1, and show the twist-boat conformer to be 10.65 kcal mol^{-1} lower in sterical energy than the chair conformer. 70% of the calculated energy difference stems from the van der Waals energy terms.

The non-bonded distances that are primarily responsible for the increase in van der Waals' energy of the chair compared to the twist-boat conformer, are six $H \cdots H$ repulsions from neighbouring equatorial CH_3 and axial cyclopropyl CH_2 groups (ex. $r(H_{19} \cdots H_{40}) = 2.07$ Å) and three $H \cdots H$ repulsions between axial CH_3 groups (ex. $r(H_{22} \cdots H_{29}) = 1.99$ Å). Each of these nine HH interactions contribute more than 1.0 kcal mol^{-1} to the calculated sterical energy.

According to the present calculations the six-membered ring of the chair conformer of **1** is considerably flattened compared with that of cyclohexane (ring torsional angles ca. 42° vs. 54°). This explains why the torsional energy of the two conformers of **1** are calculated to be approximately equal. In the twist-boat conformer four torsional angles of the six-membered ring are less favourable (ca. 28°) and two are more favourable (59°) than in the chair form.

TABLE 1

Results from MM2 calculations for chair and twist-boat conformers of 1

Parameter[a]	Chair	Twist-boat	Parameter[a]	Chair	Twist-boat
$r(C—C)_{6R}$	1.565—1.567	1.560—1.563	$\theta(C_6—C_1—C_2—C_3)$	−42.6	−29.8
$r(C_2—C_{13})_{3R}$	1.521—1.522	1.518—1.520	$\theta(C_1—C_2—C_3—C_4)$	42.3	58.7
$r(C_{13}—C_{14})_{3R}$	1.512	1.510—1.511	$\theta(C_2—C_3—C_4—C_5)$	−41.8	−26.9
$r(C—CH_3)$	1.552—1.567	1.549—1.557	E_{bend}	17.9	15.45
$r(C—H)_{CH_3}$	1.102—1.113	1.108—1.113	E_{tors}	29.8	30.46
$r(C—H)_{CH_2}$	1.083—1.085	1.084—1.086	E_{vdW}	22.7	15.73
$\angle C_1$[b]	110.9	109.2			
$\angle C_2 = \angle C_6$	119.3	116.6	E_{steric}	78.85	68.22
$\angle C_3 = \angle C_5$	111.3	109.3			
$\angle C_4$	119.3	117.4			
$\angle H_3C—C—CH_3$	100.9	102.8—103.0			
$\angle C—C—H(CH_3)$	112.2—115.0	111.1—114.1			
$\angle H—C—H(CH_2)$	108.0—109.7	109.5—110.4			
$\angle \alpha$	0.0	1.0			

[a] Distances in Å, angles in degrees, energies in kcal mol^{-1}. [b] $\angle C_i = \angle C—C_i—C$ in cyclohexane ring.

The results from the present MM2 calculations are in serious disagreement with those reported by Ivanov [2]. According to his calculations the chair and twist-boat conformers of **1** have similar sterical energies, with a difference of 0.21 kcal mol^{-1} in favour of the chair. His calculations do not show any flattening of the cyclohexane ring in the chair form (torsional angles in ring: ±55.3°).

The main differences between Ivanov's and our force fields are in the 22-1-22-22 and 22-1-22-1 torsional parameters, where Ivanov has used much higher V_3 terms. This implies that it will be considerably more energy-demanding to deviate from perfect staggering in the cyclohexane ring, and explains why his calculations show no flattening of the cyclohexane ring in the chair form. Other comparisons are difficult to make because of the few details given in Ivanov's paper [2].

Calculated MM2 structures for hydrocarbons are normally found to be in good agreement with experimental results. Because of the very severe sterical strain in **1**, the present MM2 results might be somewhat less reliable than those for unstrained hydrocarbons.

CALCULATION OF VIBRATIONAL QUANTITIES

Normal coordinate calculations [11] have been carried out for twist-boat and chair conformers of **1**, using the force field given in Table 2. R.m.s. amplitudes of vibration (u) and perpendicular correction coefficients (K) were calculated for all structurally different interatomic distances of each

TABLE 2

Valence force constants (in mdyn Å^{-1} or mdyn Å rad-2) used in normal coordinate calculations for **1**

Type	Valence coordinate	Value	Type	Valence coordinate	Value
Stretch	$C—C_{6R}$	4.485	Torsion	$C_1—C_2$[a]	0.03
	$C—CH_3$	4.485		$C—CH_3$[a]	0.017
	$C—C_{3R}$	4.152		$C_2—C_{13}$[b]	0.228
	$C—H(CH_3)$	4.736		$C_{13}—C_{14}$[b]	0.168
	$C—H(CH_2)$	5.125	Str./str.	$C—C; C—C(6R)$	0.198
Bend	$C—C—C(6R)$	0.6477		$C_1—C_2; C_2—C_{13}$	0.364
	$C—C—CH_3$	0.6477	Str./bend	$C_2—C_{13}; C_3—C_2—C_{13}$	0.270
	$C_1—C_2—C_{13}$	0.8		$C_1—C_2; C_1—C_2—C_3$	0.418
	$C—C—H(CH_3)$	0.6172		$C_7—H; C_1—C_7—H$	0.267
	$H—C—H(CH_3)$	0.549			
	$C_2—C_{13}—H$	0.650			
	$H—C_{13}—H$	0.423			

[a] Single *gauche* contribution. [b] Total contribution.

conformer. These quantities were later used in the GED study, and they are available as supplementary material [12].

The torsional force constants ($F^*(CC)$ is the torsional force constant contribution from one *gauche* 1,4 CC distance) at the —C—C— bonds in the cyclohexane ring were difficult to assess, and they proved to be of crucial importance for the calculated K values. Small torsional —C—C— force constants give large K values, corresponding to large shrinkage effects, especially for the $C—CH_3$ bonds. The vibrational amplitudes are also affected, but to a much smaller degree. The torsional force constant for a single *gauche* C_1C_4 fragment relative to a cyclohexane C—C bond, was varied between 0.002 and 0.1 mdyn Å rad^{-2}. A value of about 0.03 mdyn Å rad^{-2} appeared to be reasonable, judging from GED studies based on different sets of u and K values. The lowest (torsional) frequencies calculated for $F^*(CC)$ = 0.002, 0.03 and 0.10 mdyn Å rad^{-2} were 20—47, 60—92 and 105—122 cm^{-1} respectively (twist-boat).

STRUCTURE ANALYSIS

The molecular structure of **1** was studied by interactive least-squares intensity refinements. The non-bonded interatomic distances of the molecular model were calculated on the basis of r_α parameters, which include corrections for shrinkage effects [13].

Two models of **1** were studied in parallel, namely the chair conformer, with C_s symmetry and the twist-boat, with C_2 symmetry. Figure 1 shows schematic drawings of these, as well as the numbering of the atoms of the molecule.

Because of the large number of atoms in **1** it was necessary to introduce some assumptions about the geometry. The assumptions were partly based on the results from the MM2 calculations. Each of the following structural fragments were described by one geometrical parameter: C—C bond in six-membered ring, C—C bond in methyl groups, C—C bond in cyclopropyl groups, C—H bond in methyl groups, C—H bond in methylene groups, C—C—H angle in methyl groups, $C—C(CH_3)_2—C$ angle in six-membered ring. In addition local C_{3v} symmetry at the CH_3 groups and local C_{2v} symmetry at the CH_2 groups were assumed. When the assumptions given above were incorporated, a molecular model of **1** could be described by the following twelve geometrical parameters: five bond lengths ($C_1—C_2$, $C_2—C_{13}$, $C—CH_3$, $C—H(CH_3)$, $C—H(CH_2)$), six valence angles ($\angle C_1C_2C_3$, $\angle C_2C_3C_4$, $\angle C_3C_4C_5$, $\angle H_3C—C—CH_3$, $\angle CCH(CH_3)$, $\angle HCH(CH_2)$) and a tilt angle (α) related to the position of the dimethyl groups at C_3 and C_5 (see Fig. 1).

Because of the very large number of different, overlapping nonbonded distances in **1** (ca. 240 for the twist-boat model, not including HH distances; somewhat less for the chair model) it was not easy to interpret the experimental data. The radial distribution (RD) curve has for example no sharp peaks that might clearly be attributed to one of the two conformers. How-

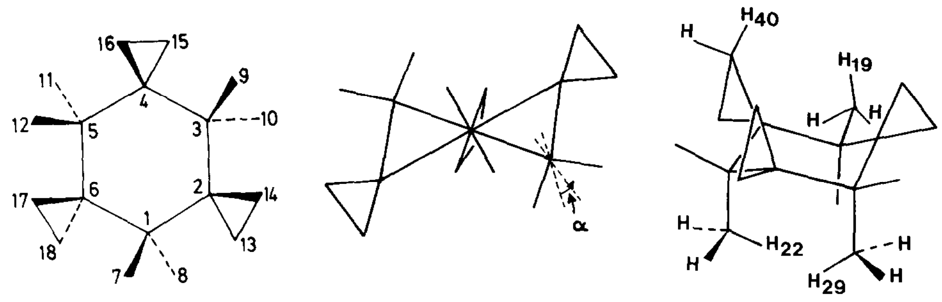


Fig. 1. Molecular models of 1, with the numbering of the carbon atoms and the hydrogen atoms referred to in the text.

ever, in the later stages of the study it became obvious that the twist-boat model was the superior one. This is demonstrated in Figs. 2 and 3, which show the theoretical RD curves calculated for the final twist-boat and chair models of **1**, together with the experimental RD curve and the difference curves.

Even though the experimental GED data of **1** are in accordance with a twist-boat model, it is not surprising that it is possible to refine most of the geometrical parameters also for a chair model, because a large number of the interatomic distances are very similar in the two models. The theoretical RD curve for the chair form shows, however, deviations from the experimental RD curve over the entire *r* range, while the twist-boat RD curve is in very good agreement with the experimental curve.

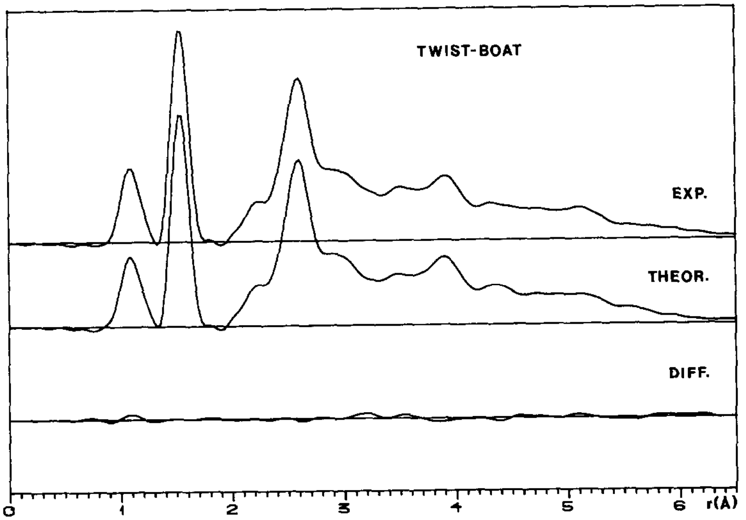


Fig. 2. Experimental and theoretical (final twist-boat model) radial distribution curves and the differences. Artificial damping constant k = 0.001 Å^2.

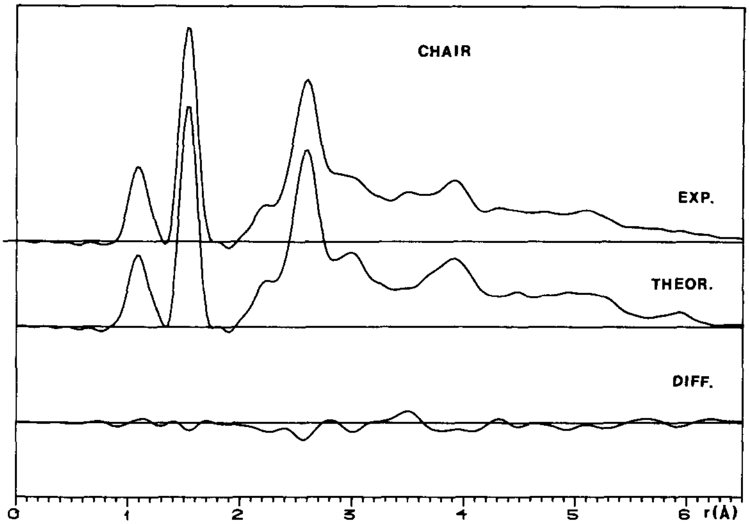


Fig. 3. Experimental radial distribution curve together with that for the best chair model of 1; $k = 0.001$ Å^2.

It was pointed out above that the shrinkage corrections to the interatomic distances in 1 are highly correlated with the torsional C—C force constants of the cyclohexane ring, through the perpendicular vibrational amplitude corrections. The overall structural results will therefore be somewhat dependent on the magnitude of the C—C torsional force constant. Table 3 shows results for the twist-boat model based on $F^*(\mathrm{CC}) = 0.100$ mdyn Å rad^{-2}, in addition to those for the final twist-boat model ($F^*(\mathrm{CC}) = 0.030$ mdyn Å rad^{-2}). The R factors are higher for the former model, but the geometrical parameters are nearly identical to those for the final model.

According to the MM2 calculations the following assumptions made in the GED molecular model, might be dubious: equal C—CH_3 bond lengths (MM2: $r_{eq} - r_{ax} = 0.008$ Å); equal C—C bond lengths in cyclopropyl groups (MM2: $\Delta r = 0.010$ Å); equal C—C—H valence angles in CH_3 groups (MM2: max. difference 2.0°). In the final stages of the study of the twist-boat model, the MM2 differences were therefore introduced as constants. The ∠C—C—H differences and the cyclopropyl C—C bond differences led to slight improvements in the R values, indicating that they might reflect real structural effects, while the r(C—CH_3) differences showed practically no influence. These results are not included in Table 3, as the average of the parameters discussed above as well as the other geometrical parameters remained unchanged.

The final results from the least-squares refinements of 1 are given in Table 3, and theoretical intensity and RD curves calculated from these results are shown in Figs. 2 and 4, respectively. The correlation matrix is given in Table 4.

TABLE 3

Structural parameters determined for 1[a]

	I[b]	II[c]	III[d]
$r(\mathrm{C—C})_{6\mathrm{R}}$	1.530(10)	1.531(12)	1.527(13)
$r(\mathrm{C—C})_{3\mathrm{R}}$	1.512(8)	1.511(9)	1.517(11)
$r(\mathrm{C—CH_3})$	1.590(8)	1.589(9)	1.582(13)
$r(\mathrm{C—H})(\mathrm{CH_3})$	1.103(7)	1.102(8)	1.099(12)
$r(\mathrm{C—H})(\mathrm{CH_2})$	1.083(12)	1.082(ass.)	1.081(ass.)
$\angle\mathrm{C_1}$[e]	119.4(1.3)	118.6(1.3)	119.2(1.3)
$\angle\mathrm{C_2} = \angle\mathrm{C_6}$	109.5(7)	109.3(7)	111.9(1.1)
$\angle\mathrm{C_3} = \angle\mathrm{C_5}$	117.0(1.6)	116.8(1.1)	119.2(1.3)
$\angle\mathrm{C_4}$	111.2(1.7)	110.3(1.7)	111.9(1.1)
$\angle\mathrm{H_3C—C—CH_3}$	98.2(1.8)	98.4(1.9)	98.7(3.3)
$\angle\mathrm{C—C—H(CH_3)}$	115.7(2.8)	116.5(3.2)	111.5(4.6)
$\angle\mathrm{H—C—H(CH_2)}$	126.8(4.5)	126.3(5.1)	120.0(ass.)
$\angle\alpha$ (TILT)	1.6(2.1)	1.0(ass.)	0.0(ass.)
$\theta(\mathrm{C_6—C_1—C_2—C_3})$	−25.2(1.5)	−25.8(1.3)	−40.8(2.4)
$\theta(\mathrm{C_1—C_2—C_3—C_4})$	54.4(2.9)	56.1(2.7)	40.8(2.4)
$\theta(\mathrm{C_2—C_3—C_4—C_5})$	−28.1(1.3)	−28.8(1.2)	−40.8(2.4)
R_1[f]	0.052	0.059	0.100
R_2[f]	0.066	0.075	0.118
R[f]	0.061	0.069	0.111

[a] Distances in Å, angles in degrees, standard errors (ca. 3σ) in brackets. [b] I: final molecular model, twist-boat, $F^*(\mathrm{CC}) = 0.030$ mdyn Å rad^{-2}. [c] II: twist-boat, $F^*(\mathrm{CC}) = 0.100$ mdyn Å rad^{-2}. [d] III: chair. [e] $\angle\mathrm{C}_i = \angle\mathrm{C—C}_i\mathrm{—C}$ in the cyclohexane ring. [f] $R = [\Sigma\omega_i(I_i^{\mathrm{obs}} - I_i^{\mathrm{calc}})^2/\Sigma\omega_i(I^{\mathrm{obs}})^2]^{1/2}$; R_1, long camera data; R_2, short camera data.

DISCUSSION

The experimental GED data are in accordance with a twist-boat conformation of 1. The MM2 calculations support this result, as the twist-boat conformation is found to be energetically favoured over the chair form by 10.6 kcal mol^{-1}. Because of the many similar interatomic distances in the twist-boat and chair conformers, the GED results do not exclude the possibilities of minor contributions from a chair conformer.

The experimental GED results for 1 show many interesting structural details. Most noticeable is perhaps the unusually long C—C bond in the methyl groups. Similar elongated $\mathrm{C—CH_3}$ bonds have, however, been observed in other sterically crowded molecules, as for example in di(t-butyl)-amine (1.561 Å) [14] and in bi-2,2,5,5,-tetramethylcyclopentylidene (1.588 Å) [15].

It was to be expected that the CCC valence angles of the cyclohexane ring would alternate in response to the difference in substitution pattern. However, it came as a surprise that the GED results showed the *gem*-dimethyl-substituted carbons to have the largest CCC ring valence angles. The

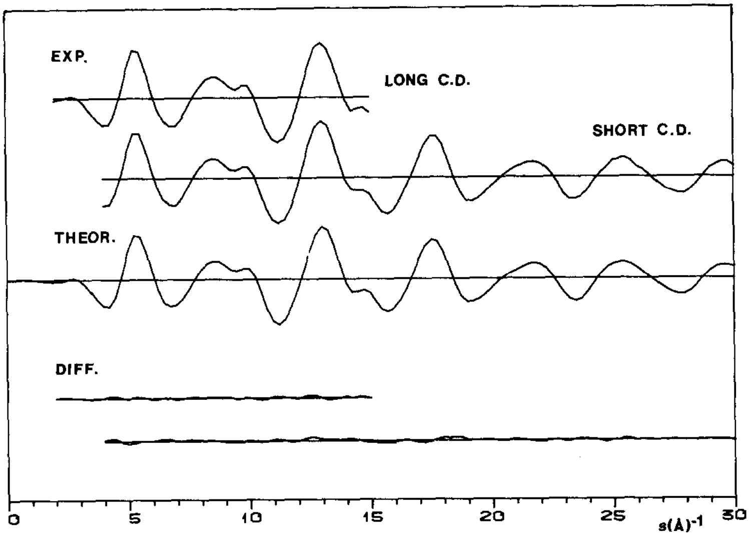


Fig. 4. Experimental and theoretical (final twist-boat model) molecular intensities and the differences.

TABLE 4

Correlation matrix (ρ) and standard deviations (σ_0) from the least squares refinements given as 100ρ and $100\sigma_0$ for compound 1

	$100\sigma_0$[a]	2	3	4	5	6	7	8	9	10	11
1 $r(C_1—C_2)$	0.25	−88	−69	4	−6	−42	79	50	−48	−45	11
2 $r(C—CH_2)$	0.18		51	−7	22	27	−65	−41	45	40	−10
3 $r(C—CH_3)$	0.19			−4	−17	38	−52	−26	26	26	−9
4 $r(C—H)$	0.16				−11	−1	0	−5	14	−2	4
5 $\angle C_1C_2C_3$[b]	23.2					−14	−3	−16	−7	43	−47
6 $\angle C_2C_3C_4$[c]	42.4						−46	−35	32	43	41
7 $\angle H_3C—C—CH_3$	60.4							30	−62	−39	15
8 $\angle C—C—H(CH_3)$	92.4								−2	−56	6
9 $\angle HCH(CH_2)$	151.2									17	−5
10 $\angle\alpha$[d]	69.8										−11
11 $\Delta\angle C_4$[e]	55.7										

[a] Distances in Å, angles in degrees. [b] $\angle C_1C_2C_3 = \angle C_5C_6C_1$. [c] $\angle C_2C_3C_4 = \angle C_6C_1C_2 = \angle C_4C_5C_6$. [d] See text for explanation. [e] $\angle C_3C_4C_5 = \angle C_1C_2C_3 + \Delta\angle C_4$.

difference between the two types of CCC valence angles is ca. 10°, which is approximately five times greater than the combined error limits. The MM2 results reverse the valence angle differences. Accurate experimental data on other overcrowded cyclohexanes are needed in order to establish whether the observed angle differences are artifacts or represent real physical phenomena.

The CCC angle between two *gem*-dimethyl carbons is found to be ca. 11° smaller than the tetrahedral angle. Reduced H_3C—C—CH_3 angles seem reasonable because they imply reduced nonbonded repulsions. The same effect is achieved by the relatively large C—C—H angles in the methyl groups. There is, however, a negative correlation between the observed C—C—H(CH_3) and H—C—H(CH_2) angles, and as the latter is found to be unreasonably large, the observed C—C—H angle is probably an upper limit for this parameter.

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