The Shape of Chair Six-Membered Rings. 4,4-Diphenylcyclohexanone

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Abstract: The crystal structure of 4,4-diphenylcyclohexanone has been determined so that it may serve as a model for a general discussion of the various distortions available to chair six-membered rings. Complete structural data are now in hand, both from the solid and the liquid state, for the full range of distortions in the chair. Quantitative parameters are introduced for the purpose of conformational classification. A correlation is noted between the quantitative X-ray data from the solid state and the qualitative nmr data from the liquid state.

The boat and the chair families are the recognized conformational modes for six-membered rings.[2] Although the pseudorotational forms of the boat family have been fully discussed and characterized, the many conformational variations of the chair have not been sufficiently analyzed or classified. It is the aim of this paper to present the structural basis for classifying chair forms, exclusive of the half chair, according to their distortions from the ideal shape of cyclohexane. All examples fall into one of four categories: the undistorted chair, the flattened chair, the puckered chair, and hybrids.[3-5] In contrast to a molecule existing in the boat family, with its multitude of interconverting forms, a chair molecule is rigid, or interconverting between two rigid forms. The extent of static distortion is dictated by the composite bond lengths and bond angles. Thus, small angles or short bonds can cause puckering, whereas large angles or long bonds can cause flattening.

For a complete discussion and classification of the conformational ménage that comprises the chair family, detailed structural information is required for each of the various types. Examples of simple puckered and undistorted chairs may be found in the literature.[6] Because no example was available for a simple flattened system that is capable of simultaneous study by the nmr method,[3] we have determined the crystal and molecular structure of 4,4-diphenylcyclohexanone. This molecule is the simplest cyclohexanone analyzed to date by X-ray crystallography. The first portion of this paper is concerned with the structural details of this compound; in the last portions we discuss the conformational generalities of chair six-membered rings. The parameters obtained from the study of 4,4-diphenylcyclohexanone will serve as examples in the general discussion of chair distortions.

Experimental Section

4,4-Diphenylcyclohexanone ($C_{18}H_{18}O$) crystallizes in the monoclinic system with cell parameters $a = 7.092 \pm 0.008$, $b = 16.164 \pm 0.015$, $c = 12.382 \pm 0.012$ Å, and $\beta = 105.7 \pm 0.3°$. The measured density (1.213 ± 0.006 g/cm^3 by flotation in aqueous sodium bromide solution) compares favorably with the value calculated on the basis of four molecules per unit cell (1.216 g/cm^3). The systematic absences are those expected for the space group $P2_1/c$. Cubical crystals, about 0.5 mm on an edge, were used in the data collection. The intensities were recorded at ambient temperatures on film, using Mo Kα radiation, and were estimated visually. The ($h0l$), ($0kl$) through ($3kl$), and ($hk0$) through ($hk4$) layers were collected by the precession method; the ($4kl$), ($6kl$), and ($7kl$) by the equi-inclination Weissenberg technique. The data were corrected for Lorentz and polarization effects, but not for absorption or spot shape.[7]

The individual layers were placed on a common scale and the normalized structure factors (E) were calculated. The sign determination was accomplished by reiterative application of Sayre's equation.[8] With the 300 strongest E's, one extremely likely set of signs was indicated, *i.e.*, one of the signed possibilities fitted the Sayre relation with a much higher consistency index than all the others. The signed E's from this solution gave a Fourier map that clearly showed the positions of all 19 nonhydrogen atoms. The conventional $R = 100\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ for the trial structure thus obtained, based on the 769 strongest structure factors, was 39.2%. Several cycles of refinement by the full-matrix least-squares process for all 1219 independent, nonzero data, with variation of atomic positions, individual isotropic temperature factors, and one over-all scale factor, reduced R to 16.2%. The function minimized during least-squares refinement was $\Sigma\sigma^{-2}(|F_o| - |F_c|)^2$ in which σ, the standard deviation for a reflection, was set equal to 8% of F_o for all but the weakest reflections, which were given less weight ($\sigma = 0.32F_o/I_o$). A difference Fourier map at this stage showed major peaks at all the expected hydrogen positions, so these atoms were included at their calculated positions without refinement. Several least-squares cycles were carried out, with the hydrogen positions reset after each cycle, to give an R of 12.9%.

In the final cycles, isotropic temperature factors were maintained for the phenyl carbon atoms, but anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl +$

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[2] (a) H. Sachse, *Ber.*, **23**, 1363 (1890); (b) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 204 ff; (c) M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965, pp 86 ff, 276 ff; (b) E. L. Eliel, N. L., Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, pp 36 ff, 469 ff.

[3] J. B. Lambert, *J. Am. Chem. Soc.*, **89**, 1836 (1967).

[4] J. B. Lambert and R. G. Keske, *Tetrahedron Lett.*, 4755 (1967).

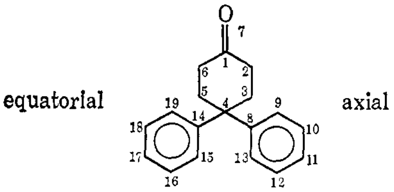
[5] J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Am. Chem. Soc.*, **89**, 5921 (1967).

[6] (a) N. de Wolf, C. Romers, and C. Altona, *Acta Cryst.*, **22**, 715 (1967), and prior references; (b) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

[7] All the equipment and computer programs were made available to us by Professor J. A. Ibers of this department, to whom we are very grateful. We are also indebted to Dr. J. H. Enemark for assistance in some of the computational aspects of this work. This study utilized the NULS, NUGLS, and NUCLS refinement programs and local modifications of Hamilton's INTRSCL data-processing program, Dewar's FAME and Long's REL1 direct-methods programs, Zalkin's FORDAP Fourier program, Johnson's ORTEP thermal ellipsoid plotting program, and the Levy-Busing ORFFE error-function program. Calculations were executed on the CDC 3400 and 6400 computers. The scattering factors used were those tabulated in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202. We thank Dr. J. G. Strong for a sample of 4,4-diphenylcyclohexanone, from which crystals were grown.

[8] D. Sayre, *Acta Cryst.*, **5**, 60 (1952).

Table I. Final Atomic Positional and Thermal Parameters (× 10^4) for 4,4-Diphenylcyclohexanone



Atom[a]	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
1	0.9265 (8)	0.0858 (4)	0.3921 (7)	172 (14)	45 (3)	85 (8)	−21 (5)	−1 (9)	2 (4)
2	0.7378 (8)	0.1167 (4)	0.4163 (6)	218 (13)	46 (3)	58 (6)	−32 (5)	13 (8)	−10 (4)
3	0.5734 (8)	0.0514 (4)	0.3800 (6)	188 (12)	44 (3)	37 (5)	2 (5)	16 (7)	−4 (4)
4	0.5370 (7)	0.0251 (3)	0.2549 (5)	139 (11)	32 (2)	42 (5)	10 (4)	14 (6)	2 (3)
5	0.7307 (7)	0.0125 (4)	0.2451 (6)	131 (10)	39 (2)	100 (7)	16 (4)	34 (8)	−6 (4)
6	0.9063 (8)	0.0457 (4)	0.2835 (7)	144 (11)	60 (3)	96 (8)	−20 (6)	39 (8)	−1 (5)
7	1.0811 (7)	0.0960 (3)	0.4625 (5)	226 (11)	69 (3)	134 (7)	−27 (4)	−37 (7)	−7 (4)
8[b]	0.4726 (7)	0.0998 (3)	0.1788 (6)			32,300 (1200)[c]			
9	0.5341 (8)	0.1108 (4)	0.0824 (7)			42,000 (1400)			
10	0.4672 (10)	0.1764 (4)	0.0092 (7)			52,800 (1600)			
11	0.3401 (9)	0.2316 (4)	0.0328 (7)			49,800 (1500)			
12	0.2741 (9)	0.2241 (4)	0.1237 (7)			42,100 (1400)			
13	0.3414 (8)	0.1578 (3)	0.1992 (6)			37,500 (1200)			
14[d]	0.3810 (7)	−0.0425 (3)	0.2270 (5)			26,200 (1000)			
15	0.2321 (8)	−0.0416 (3)	0.1287 (6)			35,500 (1200)			
16	0.0965 (9)	−0.1058 (4)	0.1018 (6)			43,400 (1300)			
17	0.1059 (9)	−0.1709 (4)	0.1737 (6)			42,100 (1400)			
18	0.2511 (9)	−0.1730 (4)	0.2703 (7)			43,800 (1400)			
19	0.3864 (8)	−0.1087 (3)	0.2971 (6)			39,000 (1200)			

[a] The standard deviation of the last digit of each parameter is listed parenthetically. [b] Atoms 8 through 13 refer to the axial phenyl group. [c] Only the over-all temperature factors are listed for the phenyl carbon atoms. [d] Atoms 14 through 19 refer to the equatorial phenyl group.

Table II. Bond Lengths and Bond Angles in 4,4-Diphenylcyclohexanone[a]

Bond	Length, Å	Angle	Deg
C(1)–O[b]	1.214 (7)	C(6)–C(1)–C(2)	116.8 (5)
C(1)–C(2)	1.532 (9)	C(1)–C(2)–C(3)	110.5 (5)
C(2)–C(3)	1.547 (8)	C(2)–C(3)–C(4)	112.6 (6)
C(3)–C(4)	1.560 (9)	C(3)–C(4)–C(5)	105.9 (5)
C(4)–C(5)	1.537 (7)	C(4)–C(5)–C(6)	113.8 (5)
C(5)–C(6)	1.530 (8)	C(5)–C(6)–C(1)	115.2 (6)
C(6)–C(1)	1.465 (10)	C(6)–C(1)–O	124.4 (7)
C(4)–C(8)	1.524 (8)	C(2)–C(1)–O	118.8 (7)
C(8)–C(9)	1.389 (10)	C(3)–C(4)–C(8)	109.9 (5)
C(9)–C(10)	1.392 (9)	C(5)–C(4)–C(14)	107.9 (4)
C(10)–C(11)	1.356 (10)	C(8)–C(4)–C(14)	110.5 (4)
C(11)–C(12)	1.336 (11)	C(3)–C(4)–C(14)	109.5 (5)
C(12)–C(13)	1.417 (8)	C(5)–C(4)–C(8)	112.9 (5)
C(13)–C(8)	1.391 (8)	C(4)–C(8)–C(9)	121.4 (5)
C(4)–C(14)	1.526 (7)	C(4)–C(8)–C(13)	121.7 (6)
C(14)–C(15)	1.380 (8)	C(8)–C(9)–C(10)	121.8 (6)
C(15)–C(16)	1.392 (8)	C(9)–C(10)–C(11)	119.3 (8)
C(16)–C(17)	1.368 (8)	C(10)–C(11)–C(12)	121.8 (7)
C(17)–C(18)	1.352 (9)	C(11)–C(12)–C(13)	119.5 (6)
C(18)–C(19)	1.392 (8)	C(12)–C(13)–C(8)	120.8 (7)
C(19)–C(14)	1.371 (8)	C(13)–C(8)–C(9)	116.8 (6)
		C(4)–C(14)–C(15)	121.8 (5)
		C(4)–C(14)–C(19)	121.4 (5)
		C(14)–C(15)–C(16)	121.2 (6)
		C(15)–C(16)–C(17)	120.6 (6)
		C(16)–C(17)–C(18)	119.1 (6)
		C(17)–C(18)–C(19)	120.2 (6)
		C(18)–C(19)–C(14)	122.1 (6)
		C(19)–C(14)–C(15)	116.7 (5)

[a] The numbering system is depicted in Table I. [b] The numbers given in parentheses are one standard deviation in the last decimal place.

$2\beta_{23}kl)$] were assigned to the other nonhydrogen atoms. At this point, hydrogen-atom positions were permanently fixed, since changes had become very small. For the first cycles with anisotropic temperature factors, the phenyl rings were treated as rigid hexagons. In the final cycle, all atomic positions were varied independently. The final R for the 1219 data was 9.9%.

Table III. Dihedral Angles between Planes Defined by Three-Atom Sets in 4,4-Diphenylcyclohexanone[a,b]

8,10,12–14,16,18	88.3 ± 0.3	2,3,4–4,5,1	57.4 ± 0.6
9,11,13–15,17,19	88.3 ± 0.3	5,6,1–4,5,1	43.1 ± 0.7
4,11,17–4,2,6	93.9 ± 0.3	5,6,1–4,5,2	43.2 ± 0.7
3,4,5–2,3,5	53.8 ± 0.6	5,6,1–4,1,2	35.9 ± 0.7
3,4,5–2,3,6	53.8 ± 0.6	5,6,1–5,1,2	35.7 ± 0.7
3,4,5–2,5,6	49.7 ± 0.6	1,2,3–2,3,4	54.8 ± 0.7
3,4,5–3,5,6	49.6 ± 0.6	2,3,4–3,4,5	60.9 ± 0.6
6,1,2–2,3,5	40.5 ± 0.7	3,4,5–4,5,6	56.3 ± 0.7
6,1,2–2,3,6	40.2 ± 0.7	4,5,6–5,6,1	48.3 ± 0.8
6,1,2–2,5,6	36.2 ± 0.8	5,6,1–6,1,2	40.8 ± 0.8
6,1,2–3,5,6	36.3 ± 0.8	6,1,2–1,2,3	43.6 ± 0.8
1,2,3–3,4,1	49.0 ± 0.7	6,1,2–3,4,5	13.6 ± 0.7
1,2,3–3,4,6	49.2 ± 0.7	6,7,2–3,4,5	13.7 ± 0.5
1,2,3–3,6,1	38.0 ± 0.7	1,2,3–4,5,6	7.5 ± 0.5
1,2,3–4,6,1	38.5 ± 0.7	2,3,4–5,6,1	14.6 ± 0.7
4,5,6–3,4,6	53.3 ± 0.7	7,1,2–1,2,3	136.6 ± 0.7
4,5,6–3,4,1	53.9 ± 0.7	7,1,6–1,6,5	139.4 ± 0.7
4,5,6–3,6,1	43.1 ± 0.7	3,4,8–2,3,4	61.4 ± 0.6
4,5,6–4,6,1	42.5 ± 0.8	8,4,5–4,5,6	64.0 ± 0.7
2,3,4–4,5,2	57.2 ± 0.6	3,4,14–2,3,4	177.0 ± 0.4
2,3,4–4,1,2	49.9 ± 0.6	5,4,14–4,5,6	173.5 ± 0.6
2,3,4–5,1,2	50.0 ± 0.6		

[a] The numbering system is depicted in Table I. [b] The errors given are one standard deviation.

Discussion of the Structure

The final atomic parameters, bond lengths, and bond angles are given in Tables I and II. Certain dihedral angles are set out in Table III. A stereoscopic representation of the structure is presented in Figure 1.[9] The cyclohexanone ring is in a chair conformation that

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[9] A table of the observed and calculated structure factors has been deposited as Document No. NAPS-00331 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be obtained by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASI–NAPS.

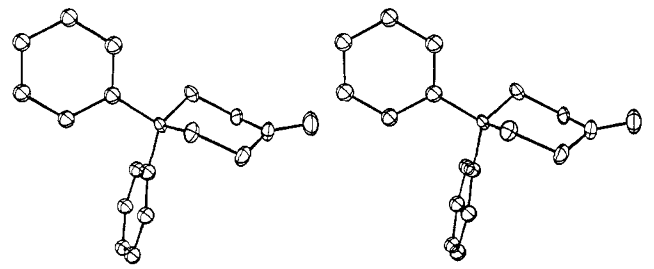

Figure 1. A stereoscopic representation of the structure of 4,4-diphenylcyclohexanone, as determined from X-ray data. The phenyl rings are seen to be closely perpendicular to each other. The cyclohexanone ring is flattened in the vicinity of the carbonyl group. The atomic parameters on which this illustration is based are listed in Table I.

is flattened at the carbonyl end, in agreement with the nmr analysis.[3,10]

The phenyl groups are very closely perpendicular to each other. The aromatic rings themselves are essentially planar: no atom deviates more than 0.02 Å from the least-squares plane. The internal angles at the aromatic carbons attached to the cyclohexanone ring [C(8): 116.8°; C(14): 116.7°] are slightly lower than the normal 120° (see Table I for the numbering system). All the angles around the quaternary carbon [C(4)] are close to tetrahedral except the angle internal to the cyclohexanone ring [C(3)–C(4)–C(5)]. The decrease to 105.9° is probably a direct compensation for the enlarged internal angle (with respect to cyclohexane) at the sp^2 carbonyl carbon [C(1)]. There appears to be no mutual crowding of the geminal phenyl groups; the intergroup angle [C(8)–C(4)–C(14)] is 110.5°. The dihedral angles between the bond to the equatorial phenyl group and the C(2)–C(3) and C(5)–C(6) bonds are close to the expected 180° (177.0, 173.5°); the corresponding dihedral angles for the axial phenyl group are close to the expected 60° (61.4, 64.0°). Thus, the geometry around the quarternary carbon appears to be relatively uncrowded and strain-free.

The ring geometry in the vicinity of the carbonyl group is controlled by the sp^2 hybridization of C(1). Thus, the C(6)–C(1)–C(2) angle (116.8°) is about the same as the corresponding angles in acetone (116°)[11] and in 1,4-cyclohexanedione (116.2°).[12] It also corroborates the geometric basis for the revised cyclohexanone calculations of Moffitt, *et al.*[13] The inequality of the C(6)–C(1) and C(1)–C(2) bond lengths must arise either from distortions caused by forces in the crystal or from a systematic error in the data. The average of the two numbers (1.50 Å) is very close to the value expected from other work.[11,12] The general conformation of the ring, as will be seen in the next section, is unaffected by this anomaly. Atoms C(6), C(1), C(2), and O are very closely coplanar.

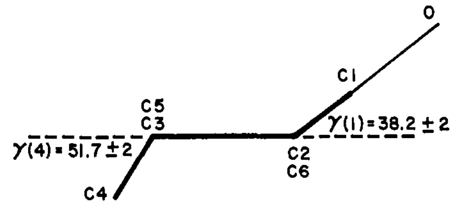

Figure 2. The projection of 4,4-diphenylcyclohexanone onto the plane passing through C(1)–C(4) and perpendicular to the plane of C(2)–C(3)–C(5)–C(6). The quantities γ(1) and γ(4) are discussed in the text.

The ring shape is best viewed in the projection plane that passes through C(1) and C(4) and is perpendicular to the C(2)–C(3)–C(5)–C(6) plane (Figure 2). These four atoms deviate less than 0.05 Å from their least-squares plane. For the sake of comparison, the angle in cyclohexane that corresponds to the γ in Figure 2 is 49.2°.[14] The ring geometry at C(4) is thus very slightly puckered [γ(4) = 51.7 ± 2°][15] with respect to that of the "perfect" cyclohexane geometry. The C(6)–C(1)–C(2) region, however, is considerably flattened [γ(1) = 38.2 ± 2°]. The molecule can therefore serve as a model for a flattened chair in the ensuing exposition.

Chair Distortions

The Silhouette Representation. The question of choosing the most appropriate pictorial representation for the chair must be answered before a scheme for classifying static distortions can be developed. Thus the classification of boat forms according to the pseudorotational parameter θ has immediate reference to spatial depictions.[2] We shall discuss two possible representations, together with their drawbacks: the silhouette (this section) and the dihedral angle (next section).

The shape of any chair six-membered ring can be viewed *in toto* by three two-dimensional representations, in which the molecular bonds are projected onto a plane that passes through two ring atoms that are 1,4 relative to each other and is perpendicular to the least-squares plane of the other four so-called "base" atoms. Figure 2 offers an example of such a representation. If a molecule has elements of symmetry, fewer than three projections will suffice: one in cyclohexane, two in tetrahydropyran or any of the three dioxanes, etc. Such a projection makes sense only if the two opposing bonds that connect the base atoms are parallel in this perspective, *i.e.*, provided these four base atoms are reasonably coplanar. If this is not the case, the bonds appear skewed in the silhouette, and a straightforward analysis of the distortions is not possible. The discussion will therefore be restricted for the while to systems with opposing bonds parallel in perspective.

base atoms coplanar

opposing bonds skewed

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(10) J. B. Lambert, R. E. Carhart, P. W. R. Corfield, and J. H. Enemark, *Chem. Commun.*, 999 (1968).

(11) J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, 31, 1562 (1959).

(12) A. Mossel and C. Romers, *Acta Cryst.*, 17, 1217 (1964); P. Groth and O. Hassel, *Acta Chem. Scand.*, 18, 923 (1964).

(13) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, 83, 4013 (1961).

(14) The acute angle, γ, between the planes determined by atoms C(6)–C(1)–C(2) and by C(2)–C(3)–C(5)–C(6) in a ring of equal C–C bonds and equal internal C–C–C angles (θ) is given by the following equation.

$$\cos\gamma = -2\cos(\theta/2) + 1/[\cos(\theta/2)]$$

For cyclohexane, θ is 111.5°,[6b] so γ is 49.2°. If θ were 109.5°, γ would be 54.7° (half a tetrahedral angle).

(15) A more complete discussion of the angles γ(*i*) is given in the next section.

The quantity of central interest in this description of the distortion around a particular atom, C(*i*), is the acute angle, $\gamma(i)$, between the plane determined by the three-atom segment, C(*i* − 1)–C(*i*)–C(*i* + 1), and the plane formed by the four base atoms, C(*i* − 2)–C(*i* − 1)–C(*i* + 1)–C(*i* + 2).[16] Figure 2 illustrates the silhouette that shows $\gamma(1)$ and $\gamma(4)$ in 4,4-diphenylcyclohexanone. ,A particular chair is characterized by a maximum of six $\gamma(i)$, which are to be compared to the γ of cyclohexane, 49°.[14] If $\gamma(i)$ is less than 49°, that portion of the chair, or even the atom C(*i*), is said to be flattened; if $\gamma(i)$ is greater than 49°, it is said to be puckered. Differences of more than 2–3° probably should be required to assure significance. Table IV presents all the $\gamma(i)$, by way of example, for 4,4-diphenylcyclohexanone. The values of $\gamma(3)$, $\gamma(4)$, and $\gamma(5)$ are close to 49°, since there is little distortion in this segment of the molecule, as discussed in the last section.

Table IV. The Values of $\gamma(i)$ (degrees) for 4,4-Diphenylcyclohexanone[a]

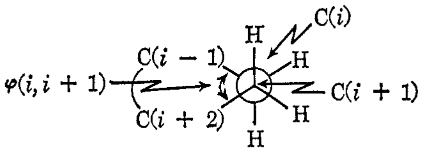
$\gamma(1)$	$\gamma(2)$	$\gamma(3)$	$\gamma(4)$	$\gamma(5)$	$\gamma(6)$
38 ± 2	44 ± 4[b]	53.5 ± 4	52 ± 2	48 ± 4	39.5 ± 4

[a] $\gamma(i)$ is defined in the text and illustrated in Figure 2. [b] The large errors for $\gamma(2)$, $\gamma(3)$, $\gamma(5)$, and $\gamma(6)$ arise because the four base atoms are not coplanar, as discussed in the text.

The $\gamma(6)$, $\gamma(1)$, and $\gamma(2)$, however, are very low, indicative of flattening.[17] Even though only three of the $\gamma(i)$ are significantly less than 49°, the conformation is best termed a "flattened chair." Such a metonymy, in which the whole of the chair is described by an adjective that characterizes only a part, is not always legitimate. From nmr data,[4] 1,1-dibromotellurane has been predicted to have both flattened and puckered segments, and would best be classified as a hybrid. A rigorous description of the chair in such cases requires a section-by-section analysis with regard to specific distortions, since no single adjective can describe the entire conformation.

Molecules in which base-atom sets do not fulfill the requirement of coplanarity occur all too frequently. In half-chair and twist-boat forms, none of the three pairs of opposing bonds are parallel in perspective. In most chairs, at least one pair can be found to be parallel, and the other two do not ordinarily deviate substantially from parallelism. Such is the case for 4,4-diphenylcyclohexanone. Atoms 2, 3, 5, and 6 are closely coplanar, so $\gamma(1)$ and $\gamma(4)$ are readily obtained and interpreted. Atoms 6, 1, 3, and 4, which should form the base plane for the calculation of $\gamma(2)$ and $\gamma(5)$, are not in a single plane. The situation is similar for atoms 1, 2, 4, and 5. In order to obtain $\gamma(2)$, for example, one can compare the C(1)–C(2)–C(3) plane with the least-squares plane of C(6)–C(1)–C(3)–C(4). The resulting uncertainty is quite large (Table IV). Alternatively, one can compare C(1)–C(2)–C(3) to each of the four planes determined by three base atoms, C(6)–C(1)–C(3), C(6)–C(1)–C(4), C(6)–C(3)–C(4), and C(1)–C(3)–C(4), as was done in Table III. The resulting values range from 38 to 49° for $\gamma(2)$ and from 43 to 54° for $\gamma(5)$. As might be expected, C(2) is "flattened" with respect to the 6–1 part of the ring, but normal if compared to the 3–4 portion. Although some information may be obtained from these ranges and averages, it is evident that the silhouette method rapidly loses relevance as the base atoms deviate from coplanarity. For the molecule serving as our example, $\gamma(1)$ and $\gamma(4)$ are fully functional quantities, from which valid conformational conclusions can be drawn with regard to the flattening of the ring. Fortunately, the other γ are not so important in this molecule. The silhouette method can thus serve adequately in many cases.

The Dihedral-Angle Representation. In the previous section, six parameters, $\gamma(i)$, were used to characterize the shape of a chair six-membered ring. Alternatively, the C(*i* − 1)–C(*i*)–C(*i* + 1)–C(*i* + 2) dihedral angles, $\varphi(i, i+1)$,[16] can serve as a quantitative measure of distortion. As before, the maximum number of six φ is reduced if the molecule possesses symmetry. The slightly flattened ring of cyclohexane possesses only one distinct dihedral angle, 54.5°, from which all distortions will be compared.[18]



Unlike the $\gamma(i)$, which are poorly determined if the four base atoms are not coplanar, the φ can always be measured. A single φ, however, gives less information about the molecule as a whole than does a single γ, because the former is derived from the placement of only four atoms, but the latter from five atoms. The four-atom segment is said to be flattened if φ is less than 54.5°, puckered if φ is greater than 54.5°. Differences of more than 2–3° should be required for significance. A chair molecule could by metonymy be termed "flattened" or "puckered" if any φ are significantly less than or greater than 54.5°, respectively. Hybrids would contain both features.

The six values of φ for 4,4-diphenylcyclohexanone are given in Table V by way of example. The small values of $\varphi(1,2)$ and $\varphi(6,1)$ result from the flattening discussed in the previous section. A slight amount of puckering around C(4) may be indicated by $\varphi(3,4)$ and $\varphi(4,5)$. The $\varphi(2,3)$ and $\varphi(5,6)$ are somewhat low, indicative of some flattening. The molecule is legitimately termed a "flattened chair" by the φ criteria outlined above.[19]

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(16) Of course, to avoid numbers less than one or greater than six, it must be recalled that C(*i*) = C(*i* + 6). Although we use the letter "C" to represent ring atoms, it should be understood that the discussion is general for all atoms, not just carbon.

(17) The inequality of the C(6)–C(1) and C(1)–C(2) bonds, discussed above, carries over to the $\gamma(i)$. Thus $\gamma(2)$ is somewhat too large and $\gamma(6)$ too small. This inequality does not alter the conformational conclusions, since γ (2), an upper bond, clearly indicates flattening. The value of $\gamma(1)$ is not affected by these inequalities.

(18) The dihedral angle, φ, for a sixfold symmetric molecule with internal bond angles, θ, is given by the following expression, *cf.* C. Altona, Thesis, University of Leiden, 1964.

$$\cos \varphi = -\cos \theta/(1 + \cos \theta)$$

For cyclohexane (θ = 111.5°), φ is found to be 54.5°. For an imaginary tetrahedral cyclohexane (θ = 109.5°), φ of course is 60°. The dihedral-angle representation has previously been used in other contexts, *e.g.*, H. J. Geise, C. Altona, and C. Romers, *Tetrahedron*, 23, 439 (1967).

(19) The inequality of $\varphi(6,1)$ and $\varphi(1,2)$ is due to the anomaly noted previously.[17] Again the effects of the anomaly are small, and the conformational conclusions are not altered, since $\varphi(6,1)$ is a lower bond and $\varphi(1,2)$ is an upper bond. Both numbers clearly indicate flattening.

Table V. The Dihedral Angles (degrees), $\varphi(i, i + 1)$, for 4,4-Diphenylcyclohexanone

$\varphi(1,2)$	$\varphi(2,3)$	$\varphi(3,4)$	$\varphi(4,5)$	$\varphi(5,6)$	$\varphi(6,1)$
43.6 ± 0.8	54.8 ± 0.7	60.9 ± 0.6	56.3 ± 0.7	48.3 ± 0.8	40.8 ± 0.8

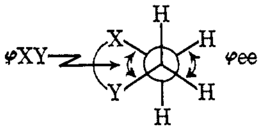
It should be noted that the terms "flattened" and "puckered" have a slightly different meaning in this context from that used in the previous section. The quantity $\gamma(i)$ describes the relation of a single atom, C(i), to the plane of the two pairs of ring atoms on either side of it. The dihedral angle, $\varphi(i, i + 1)$, gives the relative orientation of the two bonds connected to the C(i)–C(i + 1) bond. The $\gamma(i)$ are thus atom oriented and the $\varphi(i, i + 1)$ bond oriented. In hybrid molecules, it is important to consider the $\gamma(i)$ and the $\varphi(i, i + 1)$ independently in order to avoid apparent contradictions between the two systems.

Some correlations between the $\gamma(i)$ and the $\varphi(i, i + 1)$ can be made. A small (large) $\gamma(i)$ should result if both $\varphi(i - 1, i)$ and $\varphi(i, i + 1)$ are small (large). Thus $\gamma(1)$, $\varphi(6,1)$, and $\varphi(1,2)$ are all small, and $\gamma(4)$, $\varphi(3,4)$, and $\varphi(4,5)$ are slightly large in 4,4-diphenylcyclohexanone. If $\varphi(i - 1, i)$ and $\varphi(i, i + 1)$ are very different, $\gamma(i)$ is probably poorly determined because the base atoms are not coplanar.

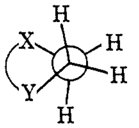
In summary, φ is much more general than γ, since it can always be measured and it may even be used to describe boats, twist boats, and half chairs. A single φ, however, can say nothing about the conformation of the entire ring, although the set of all six φ must of course determine its entire geometry. A glance at the three silhouettes and their $\gamma(i)$ can give the most rapid, qualitative estimation of the conformational distortions.

Correlation of Solid- and Liquid-State Data

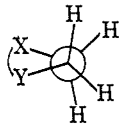
X-Ray crystallography is the prime method for determining the conformations of molecules in the solid. Although no general method exists for molecules in solution, an nmr method has recently been developed specifically for six-membered rings that contain an $X-CH_2-CH_2-Y$ segment.[3–5] The ratio, R, between the averaged J_{trans} and the averaged J_{cis} was found to be independent of the electronegativity of the groups, X and Y, attached to the bismethylene segment; it is hence a conformationally pure number. A molecule with an R value close to 2.0 has a geometry similar to that of cyclohexane (Ia). If R is larger than 2.5, the molecule must be puckered in this region (Ib). An R less than 1.8 indicates flattening (Ic). The geometry around a ring may be mapped by determining R for consecutive segments.[4]



Ia



Ib

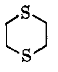
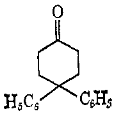
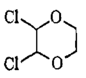
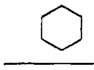


Ic

The spectroscopic R value is related in the following manner to the dihedral angles, $\varphi(i, i + 1)$, discussed above. An increase in the $X-CH_2-CH_2-Y$ dihedral angle [φ_{XY} in Ia, corresponding to a $\varphi(i, i + 1)$] will automatically result in a decrease in the $H_{eq}-C-C-H_{eq}$ dihedral angle (φ_{ee} in Ia), as is seen in Ib. A flattening of the molecule (Ic) involves a decreased φ_{XY} and an increased φ_{ee}. The nmr R value depends directly on φ_{ee},[3–5] an increase in φ_{ee} lowering R and a decrease raising it. A direct comparison can thus be made between the crystallographic dihedral angles, φ_{XY}, and the spectroscopic R value, provided that conformational alterations are small as a result of the change in phase.[20] An R near 2.0 should correspond to a φ_{XY} of about 55°. A large R (>2.5) would correspond to a large φ_{XY}, and a small R (<1.8) to a small φ_{XY}.

There are few systems, other than that used in the present study, for which both R and φ_{XY} are known. Table VI presents the comparison for those data available. The correlation appears to be quite good. Whether it is general remains to be seen. The crystallographic data certainly reinforce the conformational conclusions drawn from the coupling-constant ratio. The R-value method thus appears to be one of the few structural tools applicable to systems in solution, although subject to many limitations. If a molecule were found with values of R and φ that do not correlate in the manner of Table VI, one would suspect that the conformation in the solid and the liquid are quite different.

Table VI. A Comparison of the Crystallographic Dihedral Angle with the Solution R Value

Molecule	R	φ, deg	Type
	3.38[a]	69[b,c]	Strongly puckered
	1.6[d]	51[e]	Slightly flattened
	1.98[f]	54[g,h]	Relatively undistorted
	2.16[i]	54.5[j,k]	Perfect chair

[a] Reference 3. [b] R. E. Marsh, *Acta Cryst.*, **8**, 91 (1955). [c] H. T. Kalff and C. Romers, *Rec. Trav. Chim.*, **85**, 198 (1966). [d] Reference 10. [e] Present work; the average of $\varphi(2,3)$ and $\varphi(5,6)$. [f] Calculated from the data for C(5) and C(6) from D. Jung, *Ber.*, **99**, 566 (1966). [g] C. Altona and C. Romers, *Rec. Trav. Chim.*, **82**, 1080 (1963). [h] Reference 6a. [i] E. W. Garbisch, Jr., and M. G. Griffith, *J. Am. Chem. Soc.*, **90**, 6543 (1968). [j] Reference 6b. [k] Gas-phase data.

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[20] There is no *a priori* method for determining the validity of this assumption. It was our purpose to examine the two types of data in favorable cases to see if a correlation does exist. The identity of the ir spectra in the solid and the liquid for 4,4-diphenylcyclohexanone confirms the assumption for this case.