Tetrahedron, 1963, Vol. 19, pp. 1531 to 1537. Pergamon Press Ltd. Printed in Northern Ireland

THE MOLECULAR GEOMETRY OF SOME STRAINED FIVE- AND SIX-MEMBERED RINGS

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Abstract—The atomic coordinates for ideal cyclohexane and cyclohexanone rings are calculated and are compared with those found from the X-ray crystal structure analysis of 2,6-dibromo-3,3,5,5-tetramethylcyclohexanone and 2-bromo-3,3,5,5,-tetramethylcyclohexanone. The angular strain in these molecules is discussed with reference to the ideal molecules and it is shown that the strain has the effect of interchanging the magnitudes of the angles at 1 and 4, and is due primarily to the rocking apart of the axial methyls.

On the assumption that the strain in the cyclopentane-1,2-dione ring is shared approximately equally between the ring angles, it is calculated that this ring would be expected to be planar. This is confirmed by the crystal structure of 3,3,5,5-tetramethylcyclopentane-1,2-dione, where the crystal symmetry requires the molecules to have *mm* symmetry and the observed strain is found to agree well with the calculated strain.

INTRODUCTION

ONE method of obtaining a quantitative measure of the strain introduced into a molecule by steric effects is by a full X-ray investigation of its crystal structure. From the atomic coordinates and their standard deviations, the geometry of the molecule can be calculated and significant differences from ideal molecules can be determined. In this paper the results obtained from such an investigation into the crystal structures of 2,6-dibromo-3,3,5,5-tetramethylcyclohexanone, 2-bromo-3,3,5,5-tetramethylcyclohexanone and 3,3,5,5-tetramethylcyclopentane-1,2-dione[1] are compared with ideal six- and five-membered rings. The calculation of the geometry of these ideal rings follows, in general, the method used by Corey and Sneen,[2] except that a different system of axes is chosen.

2. *Six-membered rings*

An examination of the coordinates of the atoms in a molecule of 2,6-dibromo-3,3,5,5-tetramethylcyclohexanone (hereafter referred to as DTC) (Fig. 1) and of 2-bromo-3,3,5,5-tetramethylcyclohexanone (hereafter referred to as MTC) shows

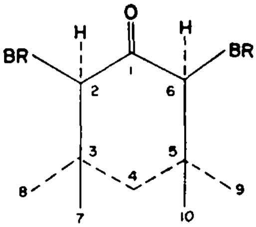

FIG. 1. 2,6-Dibromo-3,3,5,5-tetramethylcyclohexanone.

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[1] A complete account of the crystallographic investigations of these structures will be given elsewhere.

[2] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.* 77, 2505 (1955).

that none of the bond lengths differ significantly from the accepted values and such strain that is introduced appears as a distortion of the bond angles. There are no abnormal intermolecular contact distances, and the symmetry of the molecule in an asymmetrical environment in the crystal suggests that the strain is primarily due to the substituents. Moreover, in both molecules the carbon atoms C$_2$, C$_3$, C$_5$, and C$_6$ lie very close to the best (least-squares) plane through these atoms and so it is appropriate to refer the ideal six-membered rings to the system of axes shown in Fig. 2. The atoms C$_2$, C$_3$, C$_5$ and C$_6$ lie the *xy*-plane, the atoms C$_2$ and C$_6$ lie on the *x*-axis, and the molecule is mirrored in the *yz*-plane.

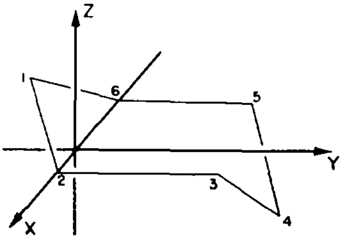

FIG. 2. Axes for six-membered rings.

TABLE 1. THE ATOMIC COORDINATES FOR SOME SIX-MEMBERED RINGS
(The standard deviations of the observed coordinates are about 0·02 Å)

		(1) Cyclohexane ring (Å)	(2) Cyclohexanone ring (Å)	(3) "Reversed" cyclohexanone ring (Å)	(4) In DTC (Å)	(5) In MTC (Å)
C$_1$	x	0	0	0	−0·043	+0·011
	y	−0·515	−0·582	−0·454	−0·478	−0·502
	z	+0·755	+0·505	−0·764	+0·722	+0·780
C$_2$	x	+1·258	+1·335	+1·259	+1·246	+1·287
	y	0	0	0	$-0{\cdot}000_5$	+0·002
	z	0	0	0	$-0{\cdot}000_1$	−0·024
C$_3$	x	+1·258	+1·259	+1·335	+1·329	+1·275
	y	+1·541	+1·539	+1·539	+1·543	+1·564
	z	0	0	0	$-0{\cdot}000_1$	+0·024
C$_4$	x	0	0	0	−0·018	−0·096
	y	+2·056	+1·993	+2·121	+1·975	+2·091
	z	−0·755	−0·764	−0·505	−0·631	−0·475
C$_5$	x	−1·258	−1·259	−1·335	−1·310	−1·354
	y	+1·541	+1·539	+1·539	+1·570	+1·558
	z	0	0	0	−0·002	+0·071
C$_6$	x	−1·258	−1·335	−1·259	−1·245	−1·287
	y	0	0	0	−0.002	+0.002
	z	0	0	0	+0·006	+0·017

Following the procedure of Corey and Sneen, and assuming all bond lengths to be 1·541 Å and bond angles to be 109·47°,[3] the calculated coordinates of the atoms in an ideal cyclohexane ring are given in Column 1 of Table 1. The introduction of an exocyclic double-bonded oxygen at C_1 changes this ring angle to 120° and the calculated coordinates of the atoms in this (unstrained) ring are given in Column 2 of Table 1.

The coordinates of the atoms in the molecules of DTC and MTC, referred to the crystallographic axes, were transposed to the same system of axes. The procedure was to find the equation of the best (least-squares) plane through the ring atoms C_2, C_3, C_5 and C_6, then to find the equation of the plane perpendicular to this and passing through the atoms C_2 and C_6, and finally to find the equation of the plane perpendicular to both these planes and passing through the mid-point of the line joining C_2 and C_6. The coordinates of the atoms in the rings of DTC and MTC referred to such axes are given in Columns 4 and 5 of Table 1 and a comparison with the ideal cyclohexanone ring coordinates in Column 2 shows some large differences.

TABLE 2. THE RING ANGLES OF DTC AND MTC
(The standard deviations of the observed angles are about 2°)

Ring angle at	Ideal cyclohexanone	DTC	MTC
C_1	120°	111°	108°
C_2	109·5°	110°	107°
C_3	109·5°	104°	110°
C_4	109·5°	120°	121°
C_5	109·5°	104°	108°
C_6	109·5°	111°	110°

From the atomic coordinates, the internal ring angles were calculated for DTC and MTC and are given in Table 2 which shows that the greatest distortion of these angles occurs at C_1 and C_4. Also, the distortion of these angles is very similar in DTC and MTC, indicating that the prime cause of the distortion of the ring is due to the presence of the two di-methyl groups; the presence of one or two bromine atoms having a much smaller effect. The angle at C_1 has been reduced from 120° to about 110° and that at C_4 increased from 109° to 120°, i.e. the steric effects have reversed the magnitudes of these angles. The atomic coordinates of an ideal "reversed" cyclohexanone ring (i.e. a ring in which the angle at C_4 is 120° and that at C_1 is 109·47°) are given in Column 3 of Table 1, and a comparison with Columns 4 and 5 shows a strong resemblance between these coordinates. A calculation of the coordinates of the substituents emphasizes that the rings of DTC and MTC resemble the "reversed" cyclohexanone ring (Table 3). It may be concluded, therefore, that the presence of these bulky substituents has the effect of distorting the cyclohexanone ring, the distortion taking place almost entirely at C_1 and C_4.

[3] Tables of interatomic distances, *Chemical Society* p. S12 (1958).

Table 3. The atomic coordinates of the substituents in some six-membered rings
(The standard deviations of the observed coordinates are about 0·02 Å)

Substituent		Ideal cyclohexanone	"Reversed" cyclohexanone	DTC	MTC
		(Å)	(Å)	(Å)	(Å)
Equatorial methyl (C_8)	x	+2·483	+2·458	+2·431	+2·390
	y	+2·113	+1·997	+1·969	+2·000
	z	−0·641	−0·876	−1·027	−0·894
Axial methyl (C_7)	x	+1·217	+1·621	+1·645	+1·656
	y	+2·051	+2·038	+2·157	+2·133
	z	+1·406	+1·381	+1·277	+1·501
Equatorial methyl (C_9)	x	−2·483	−2·458	−2·428	−2·476
	y	+2·113	+1·997	+1·962	+1·949
	z	−0·641	−0·876	−0·902	−0·930
Axial methyl (C_{10})	x	−1·217	−1·621	−1·619	−1·642
	y	+2·051	+2·038	+2·125	+2·045
	z	+1·406	+1·381	+1·340	+1·480
Oxygen	x	0	0	+0·003	+0·086
	y	−1·510	−1·082	−1·163	−1·200
	z	+1·312	+1·822	+1·704	+1·691
Bromine (equatorial)	x	+2·747	+2·798	+2·839	+2·854
	y	−0·576	−0·721	−0·824	−0·821
	z	−1·101	+0·806	+0·794	+0·618
Bromine (equatorial)	x	−2·747	−2·798	−2·815	
	y	−0·576	−0·721	−0·854	
	z	+1·101	+0·806	+0·818	

The cause of the strain in the ring is primarily due to the close approach of the axial methyls; in the unstrained cyclohexanone ring these methyls would be 2·43 Å apart, whereas if the angle at C_4 is increased to 120° this distance is increased to 3·24 Å. The calculated and observed distances between these and other substituents are given in Table 4. This rocking apart of the axial methyls through as much as 20° for DTC and MTC (15° for the "reversed" cyclohexanone ring) has been used by Sandris and Ourisson[4] to account for the preferential formation of the di-equatorial form of the dibromo compound (the "reflex" effect). A possible explanation of the accompanying reduction in the ring angle at C_1 to produce the "reversed" cyclohexanone ring, is that the forcing apart of C_3 and C_5 tends to cause the distance between C_2 and C_6 to contract; the effect may also result from a stiffening at C_3 and C_5 due to interactions of the methyls between themselves and their neighbours. The distortions of the angles involving the substituents (Table 5) can be interpreted in terms of the hindrance

[4] C. Sandris and G. Ourisson. *Bull. Soc. Chim. Fr.* 1524 (1958).
B. Wacgell and G. Ourisson, *Bull. Soc. Chim. Fr.* 2443 (1961).
B. Wacgell, P. Pouzet and G. Ourisson, *Bull. Soc. Chim. Fr.* (1963) In press.

TABLE 4. CALCULATED AND OBSERVED DISTANCES BETWEEN SUBSTITUENTS

Distance between	Ideal cyclohexanone ring	Ideal "reversed" cyclohexanone ring	DTC	MTC
	(Å)	(Å)	(Å)	(Å)
Axial methyls	2·43	3·24	3·37	3·30
Equatorial methyls	4·96	4·92	4·86	4·87
Bromine-axial methyl	3·04	3·09	3·24, 3·25	3·19
Bromine-equatorial methyl	3·21	3·21	3·33, 3·36	3·35
Bromine-bromine	5·49	5·60	5·65	—
Bromine-oxygen	2·91	3·00	2·99, 2·97	2·99

TABLE 5. EXOCYCLIC ANGLES WHICH ARE SIGNIFICANTLY DIFFERENT FROM THE ACCEPTED VALUES
(The standard deviations of the angles are as shown)

	DTC		MTC	
Angle	θ	$\sigma(\theta)$	θ	$\sigma(\theta)$
$C_4—C_3—C_7$	118°	2·0°		
$C_6—C_1—O$	127°	1·9°	129°	2·3°
$C_3—C_2—Br$	113°	1·3°	116°	1·7°
$C_5—C_6—Br$	113°	1·3°		

between these large groups, the effect being greater in DTC than in MTC. Despite the change in the angle at C_1 the atoms C_1, C_2, C_6 and O remain planar within the accuracy of the determination, and the asymmetry of the angles involving the oxygen atoms is probably due to the way in which the molecules are arranged about screw axes in the crystal.

3. *Five-membered rings*

All cyclopentane rings must be strained since it is not possible to form such a ring without changing the tetrahedral angle from 109·47°. The strain introduced and the form of ring assumed ("envelope" or "half-chair") by a substituted cyclopentane ring will depend on the nature of the substituents.[5] If, however, two exocyclic double-bonded oxygen atoms are introduced at C_1 and C_2, then the ring would assume the

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[5] K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.* **81**, 3219 (1959).

envelope form, since the atoms C_5, C_1, C_2, and C_3 would now be planar (Figs. 3 and 4); the strain in such a ring would be large. If it is assumed that the total distortion of the ring is as small as possible and distributed as equally as possible between the ring angles,[1] then the geometry of this strained ring can be calculated. Using the system of axes shown in Fig. 4, and assuming all carbon-carbon bond lengths to be 1·541 Å (except C_1—C_2 = 1·50 Å)[6], the coordinates of the ring atoms are

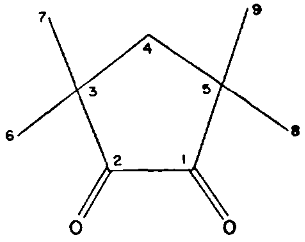

FIG. 3. 3,3,5,5-tetramethylcyclopentane-1,2-dione.

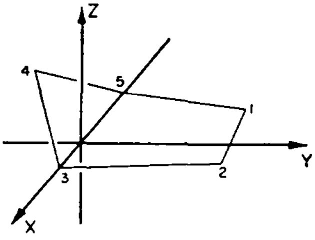

FIG. 4. Axes for five-membered rings.

C_4	0	y_1	z_1
C_3,C_5	$\pm x_2$	0	0
C_1,C_2	$\pm\dfrac{1{\cdot}50}{2}$	y_3	0

If it is assumed that the angle at C_2 is deformed by the same amount ($\Delta\theta$) as the angle at C_4, then

$$x_2 = 1{\cdot}541 \sin(109{\cdot}47 + \Delta\theta)/2$$
$$= 1{\cdot}50/2 + 1{\cdot}541 \sin(30 - \Delta\theta).$$

Expanding and putting the usual approximations for small angles, a cubic equation in $\Delta\theta$ is obtained

$$0{\cdot}1597(\Delta\theta)^3 - 0{\cdot}1479(\Delta\theta)^2 - 1{\cdot}1545(\Delta\theta) + 0{\cdot}1698 = 0.$$

Solving gives $\Delta\theta = 0{\cdot}145$ radians or 8·32°, and hence $x_2 = 1{\cdot}319$ Å. If the same deformation of $\pm 8{\cdot}32°$ is applied to the angle at C_3, then it is not possible to obtain a solution for

$$z_1^2 = 0{\cdot}632 - (1{\cdot}658 \cos\theta_5 - 0{\cdot}524)^2.$$

A solution is obtained if $\theta_5 < 99{\cdot}4°$, i.e. $z_1 = 0$ when $\Delta\theta = 10{\cdot}0°$. Smaller values of θ_5 (i.e. larger strain) will produce a puckering of the ring. For the total strain to be as

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[6] Tables of Interatomic Distances, *Chemical Society* p. S13, (1958).

TABLE 6. CALCULATED AND OBSERVED ATOMIC COORDINATES AND BOND ANGLES FOR A MOLECULE OF DKP
(Standard deviation of the coordinates about 0·02 Å, and of the bond angles about 2°)

		Coordinates			Bond angles	
		Calculated (Å)	Observed (Å)	Ring angle at	Calculated	Observed
C_2	x	+0·750	+0·721			
	y	+1·432	+1·435	C_4	117·8°	121°
	z	0	0	C_3	99·4°	99°
C_3	x	+1·319	+1·274	C_2	111·7°	111°
	y	0	0			
	z	0	0	Angles		
C_4	x	0	0	C_2—C_3—C_6	109·5°	116°
	y	−0·795	−0·718	C_4—C_3—C_6	109·5°	112°
	z	0	0	C_6—C_3—C_7	109·5°	102°
C_6	x	+2·070	+2·122			
	y	−0·254	−0·389	C_1—C_2—O	120°	128°
	z	+1·192	+1·124	C_3—C_2—O	120°	121°
O	x	+1·506	+1·563			
	y	+2·404	+2·452			
	z	0	0			

small as possible, the five-membered ring would therefore be expected to be planar producing almost equal strain at the ring angles.

The crystal structure analysis of 3,3,5,5-tetramethylcyclopentane-1,2-dione (hereafter referred to as DKP) shows that the molecule lies in a special position in the Space Group $P\bar{4}2_1m$, and requires the molecule to have *mm* symmetry. The ring of the molecule of DKP must therefore be strictly planar and the four methyl groups must also conform to the *mm* symmetry. The atomic coordinates for the calculated strained ring are compared with the observed coordinates for DKP, referred to the same system of axes, in Table 6. The calculated and observed ring angles are also compared in Table 6, together with the angles involving the substituents. The significant differences of these latter angles from 109·5° or 120° are consistent with the atoms taking up positions so as to minimize the steric hindrance between oxygen and oxygen and between oxygen and methyl.

Sandris and Ourisson[7] assumed that the α-diketo-cyclopentane ring is planar and have explained the unusual U.V. spectra in terms of the angular strain. This work on DKP confirms this assumption.

The authors wish to thank Professor G. Ourisson, Dr. C. Sandris and Dr. B. Wacgell of Strasbourg for suggesting the problem and for providing the crystals.

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[7] C. Sandris and G. Ourisson, *Bull. Soc. Chim. Fr.* 350 (1958).