position of the SiO_3 chains with respect to Zn atoms is mainly determined by the Zn(2)–O(1) and Zn(2)–O(2) distances. An apparent relative displacement of the SiO_3 chains along the c axis is clear in the structure of $ZnSiO_3(M)$ so that the β angle increases in comparison with the structure of johannsenite.

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The Structure of the Cyclopentane Ring. 1-Phenylcyclopentanecarboxylic Acid

By T. N. MARGULIS

Department of Chemistry, University of Massachusetts at Boston, Boston, Massachusetts 02125, U.S.A.

The structure of 1-phenylcyclopentanecarboxylic acid, $C_{12}H_{14}O_2$, has been determined by analysis of 824 diffractometer-measured X-ray reflections and refined by least-squares calculations to an R of 0·066. The crystals are monoclinic, space group $P2_1/c$, $Z=4$, $a=6\cdot009$, $b=6\cdot781$, $c=24\cdot976$ Å, $\beta=92\cdot08°$. The cyclopentane ring is rigid with a conformation intermediate between the C_2 and C_s forms.

Introduction

The saturated five-carbon cyclopentane ring may exist in two symmetric, non-planar conformations. These are the envelope form with C_s symmetry (four carbon atoms in a plane and one out of plane) and the half-chair or twisted form with C_2 symmetry. These two forms are of about the same energy and lie about 5 kcal mole^{-1} below the planar structure with D_{5h} symmetry (Carreira, Jiang, Person & Willis, 1972). The C_2 form has been observed in *trans*-1,2-cyclopentane-

dicarboxylic acid (Benedetti, Corradini & Pedone, 1972) while the C_s form has been observed in several bicyclic systems (Chiang & Bauer, 1968). In addition to these two symmetric conformations, an infinite number of asymmetric conformations exists. These have about the same energy as the symmetric forms, so that the cyclopentane molecule rapidly converts from one to another. This process, called pseudorotation, has been demonstrated in the gas phase by electron diffraction (Adams, Geise & Bartell, 1970) and was used by Kilpatrick, Pitzer & Spitzer (1947) to explain the high-

phase entropy of cyclopentane. Pseudorotation effects have been demonstrated in the solid state (Margulis, Dalton & Kwiram, 1973) by an X-ray diffraction and magnetic resonance study of 1,1-cyclopentanedicarboxylic acid (I) showing the γ carbon atoms to be rapidly moving. Free pseudorotation for cyclopentane is described by Pitzer & Donath (1959) by the equation

$$Z_j = |\, 2/5q \cos [2(2\pi j/5 + \varphi)]$$

where z_j is the displacement of atom j from an unpuckered ring, q is the amplitude and φ the phase of the ring puckering. A phase angle of 0° corresponds to a ring with C_s symmetry and a phase angle of 9° to a ring with C_2 symmetry. An alternative equation has been given by Altona, Geise & Romers (1968) in terms of a maximum torsion angle. The X-ray study of 1-phenyl-cyclopentanecarboxylic acid (II) described below, allows comparison of a 1,1-symmetrically substituted ring which shows pseudorotation effects (I) with a 1,1-unsymmetrically substituted ring (II) which turns out to have a rigid cyclopentane ring.

HOOC　　　COOH

α

β

γ

(I)

HOOC　　C_6H_5

(II)
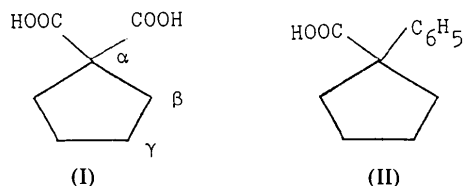
Experimental

Material from Aldrich Chemical Company was recrystallized from aqueous solution. A block with dimensions $0.1 \times 0.15 \times 0.2$ mm, mounted with the short (a^*) axis vertical on a Picker full-circle manual diffractometer with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.54178$), was used for all X-ray work. Cell dimensions were calculated from 2θ measurement at room temperature in the region where $K\alpha_1$ and $K\alpha_2$ are resolved. Intensities were measured with symmetric θ–2θ scan (2θmax $= 130°$), scan rate 2° min⁻¹, range $\pm 1°$, background counted for 20 s on either side of the peak. No correction for absorption was made ($\mu r \approx 0.09$). All computations were carried out in a time-shared mode by teletype machine located in the author's office or home. The computer itself is a CDC 3800 located in Amherst, Massachusetts, about 100 miles away from Boston. Programs used include time-sharing versions of the Gantzel–Sparks–Trueblood least-squares, Zalkin's DISTAN, and local Fourier routines (Margulis, 1970).

Crystal data

Examination of preliminary Weissenberg and oscillation films, diffractometer data, and the final structure indicate that 1-phenylcyclopentanecarboxylic acid, $C_{12}H_{14}O_2$, is monoclinic, space group $P2_1/c$ (C_{2h}^5) with $a = 6.009$ (5), $b = 6.781$ (5), $c = 24.976$ (12) Å,

$\beta = 92.08$ (0.1)°, $Z = 4$. The calculated density is 1.242 g cm⁻³.

Determination of the structure

The program of Hall (1969) modified to run on the time-shared system, was used to solve the phase problem. Designation of three origin-determining and two other E's was sufficient to generate signs for the 125 E's with magnitude greater than 1.4. The tangent formula routine was used four times to calculate signs starting from the four different combinations of the two unknown signs. One set gave a value of $\sum ||E_{obs}| - |E_{cal}||/\sum|E_{obs}|$ of 0.15 whereas the other sets gave values greater than 0.23. An E map based on this set showed all carbon and oxygen atoms clearly.

Refinement

The structure was refined by full-matrix least-squares calculations to a final value of $R = \sum ||F_{obs}| - |F_{cal}||/\sum|F_{obs}| = 0.066$ for 824 observed independent structure factors. An additional 750 reflections were considered unobserved and omitted from all calculations. Neutral atom atomic scattering factors from *International Tables for X-ray Crystallography* (1962) were used.
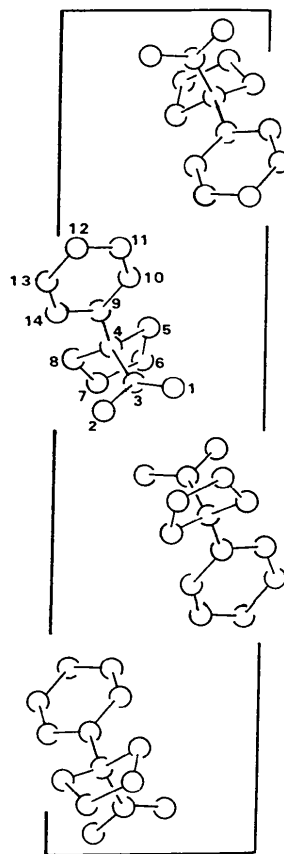
Fig. 1. The crystal structure viewed along (010). Origin in upper left corner with x across, z down. Atoms 1 and 2 are oxygen, others are carbon (hydrogen atoms omitted).

Hydrogen atoms, located in a ΔF map, were refined with isotropic temperature factors; anisotropic temperature factors were used for carbon and oxygen atoms. The function minimized is $\sum w(|F_{obs}| - |F_{cal}|)^2$ with the weights, w, based on standard deviations in the F_{obs}. Tables 1 and 2 give the final atomic parameters.*

Table 1. Positional and isotropic thermal parameters with standard deviations in parentheses

	x	y	z	B (Å²)
O(1)	0·5719 (6)	0·3713 (6)	0·0475 (1)	
O(2)	0·2314 (6)	0·4073 (6)	0·4764 (1)	
C(3)	0·3709 (9)	0·3393 (7)	0·4427 (2)	
C(4)	0·2694 (8)	0·2265 (7)	0·3953 (2)	
C(5)	0·4325 (10)	0·0703 (8)	0·3753 (2)	
C(6)	0·4111 (12)	−0·1040 (10)	0·4142 (3)	
C(7)	0·1905 (11)	−0·0779 (9)	0·4412 (2)	
C(8)	0·0753 (9)	0·0962 (8)	0·4127 (2)	
C(9)	0·2040 (7)	0·3835 (7)	0·3540 (2)	
C(10)	0·3506 (11)	0·4405 (8)	0·3151 (2)	
C(11)	0·2937 (13)	0·5868 (10)	0·2789 (2)	
C(12)	0·0912 (13)	0·6823 (9)	0·2799 (3)	
C(13)	−0·0539 (12)	0·6306 (9)	0·3182 (2)	
C(14)	−0·0013 (9)	0·4815 (8)	0·3545 (2)	
H(15)	0·690 (20)	0·480 (19)	0·480 (5)	23·1 (5)
H(16)	0·380 (8)	0·044 (8)	0·339 (2)	4·8 (13)
H(17)	0·583 (8)	0·119 (7)	0·374 (2)	3·1 (10)
H(18)	0·428 (12)	−0·221 (12)	0·398 (3)	9·4 (22)
H(19)	0·545 (9)	−0·085 (8)	0·441 (2)	4·7 (13)
H(20)	0·230 (8)	−0·039 (8)	0·481 (2)	5·1 (13)
H(21)	0·064 (20)	−0·215 (19)	0·448 (4)	20·4 (42)
H(22)	−0·053 (8)	0·167 (7)	0·433 (2)	3·6 (11)
H(23)	−0·017 (8)	0·061 (7)	0·378 (2)	4·8 (13)
H(24)	0·490 (9)	0·381 (8)	0·311 (2)	6·0 (16)
H(25)	0·405 (9)	0·627 (8)	0·257 (2)	5·5 (15)
H(26)	0·040 (9)	0·792 (9)	0·256 (2)	7·2 (16)
H(27)	−0·207 (9)	0·705 (8)	0·325 (2)	6·6 (15)
H(28)	−0·094 (7)	0·441 (7)	0·382 (2)	3·6 (11)

Results

The molecules (Fig. 1) occur as dimers, hydrogen-bonded across centers of symmetry. The structure is

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30801 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

similar to the analogous four-membered ring compound, 1-phenylcyclobutanecarboxylic acid (III) (Soltzberg & Margulis, 1970), which also has a long c axis. The O–H···O distance of 2·665 Å is typical of hydrogen-bonded carboxylic acids. The cyclopentane ring is rigid, showing no evidence of disorder. In contrast, crystalline 1,1-cyclopentanedicarboxylic acid shows disorder in the y carbon atoms due to pseudorotation effects. This is similar to the cyclobutane case in which the 1,1-diacid (IV) (Soltzberg & Margulis, 1971) shows disorder due to rapid changes in structure but the 1-phenyl acid (III) with an asymmetric potential for ring bending is a rigid molecule. In the 1-phenyl acid reported here, the phenyl group occupies an equatorial-like position with respect to the five-membered ring and the carboxyl group occupies an axial position. This is also the case for the cyclobutane analogue.
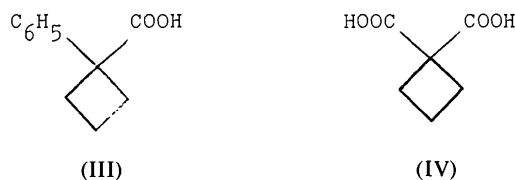
The cyclopentane ring is best described as having a conformation intermediate between the two symmetric forms. The value of q, calculated as the square root of the sum of the squares of the deviations from the least-squares plane through the five-membered ring (Dunitz, 1972) is 0·42 Å. Adams et al. (1970) in an electron-diffraction study of cyclopentane determine q to be 0·435 Å while other estimates, listed by Adams, have yielded values as high as 0·48 Å. Torsion angles are especially sensitive to where on the pseudorotation track a molecule may be. In Table 3 are listed values of the torsion angles found in this molecule. Also listed are values calculated by Adams for the C_s structure with $\varphi = 0$, the C_2 structure with $\varphi = 9°$, and for an intermediate structure with $\varphi = 5°$. Adams uses $q = 0·435$ and assumes equal C–C bond lengths. Although the bond lengths in (II), listed in Table 4 are not found to be equal, the agreement with the $\varphi = 5°$ structure and

Table 2. Anisotropic thermal parameters in the form $\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\right]$

Standard deviations are given in parentheses as deviations in the last significant figure.

O(1)	0·023 (1)	0·028 (1)	0·00162 (7)	−0·008 (2)	−0·0014 (4)	−0·0040 (5)
O(2)	0·028 (1)	0·028 (1)	0·00136 (6)	0·001 (2)	0·0015 (4)	−0·0051 (5)
C(3)	0·025 (2)	0·012 (1)	0·00108 (7)	0·001 (2)	−0·0008 (6)	0·0009 (5)
C(4)	0·022 (1)	0·014 (1)	0·00102 (8)	−0·001 (2)	−0·0005 (5)	−0·0003 (5)
C(5)	0·028 (2)	0·016 (1)	0·0014 (1)	−0·002 (3)	−0·0006 (7)	−0·0015 (6)
C(6)	0·041 (3)	0·020 (2)	0·0023 (1)	0·013 (3)	−0·001 (1)	0·0001 (8)
C(7)	0·045 (3)	0·018 (2)	0·0018 (1)	−0·001 (3)	−0·0019 (8)	0·0013 (7)
C(8)	0·026 (2)	0·017 (1)	0·0015 (1)	−0·006 (3)	−0·0003 (7)	0·0006 (6)
C(9)	0·024 (2)	0·015 (1)	0·00104 (7)	−0·009 (2)	−0·0013 (5)	−0·0008 (5)
C(10)	0·038 (2)	0·019 (1)	0·00126 (9)	−0·005 (3)	−0·0007 (7)	0·0011 (6)
C(11)	0·050 (3)	0·029 (2)	0·0016 (1)	−0·015 (4)	0·0025 (9)	0·0023 (8)
C(12)	0·055 (3)	0·020 (2)	0·0020 (1)	−0·006 (4)	−0·006 (1)	0·0034 (8)
C(13)	0·039 (2)	0·021 (2)	0·0020 (1)	0·010 (3)	−0·0051 (8)	0·0011 (7)
C(14)	0·026 (2)	0·021 (1)	0·0017 (1)	0·001 (3)	−0·0020 (7)	0·0002 (7)

Table 3. *Torsion angles observed in phenylcyclopentanecarboxylic acid compared with values calculated with different values of φ*

Torsion angles (°) are absolute values. Calculated values, taken from Adams, Geise & Bartell (1970), are based on $q = 0.435$ Å and equal C–C bond lengths.

	Observed	$\varphi = 5°$	$\varphi = 0°$	$\varphi = 9°$
C_5–(C_6–C_7)–C_8	6·7	7·4	0·0	13·2
C_6–(C_7–C_8)–C_9	30·4	30·6	25·0	34·3
C_7–(C_8–C_4)–C_5	41·8	41·9	40·3	42·3
C_8–(C_4–C_5)–C_6	37·8	37·4	40·3	34·3
C_4–(C_5–C_6)–C_7	19·6	18·7	25·0	13·2

Table 4. *Interatomic distances (Å) and angles (°)*

Standard deviations of C–O and C–C distances are approximately 0·01 Å. O–H and C–H distances are all $1·0 \pm 0·2$ Å. Standard deviations for bond angles are approximtaely 0·5°. Bond angles involving hydrogen atoms on sp^3 carbon atoms average $110 \pm 6°$. Angles involving hydrogen on sp^2 carbon average $120 \pm 5°$.

C(3)–O(1)	1·229	C(7)—C(8)	1·530
C(3)–O(2)	1·295	C(9)—C(10)	1·388
C(3)–C(4)	1·518	C(9)—C(14)	1·402
C(4)–C(9)	1·525	C(10)–C(11)	1·381
C(4)–C(5)	1·538	C(11)–C(12)	1·379
C(4)–C(8)	1·538	C(12)–C(13)	1·363
C(5)–C(6)	1·538	C(13)–C(14)	1·388
C(6)–C(7)	1·519		

O(1)–C(3)–O(2)	122·0	C(6)—C(7)—C(8)	105·7
O(1)–C(3)–C(4)	122·1	C(4)—C(8)—C(7)	103·9
O(2)–C(3)–C(4)	115·8	C(4)—C(9)—C(10)	120·9
C(3)–C(4)–C(5)	110·9	C(4)—C(9)—C(14)	122·9
C(3)–C(4)–C(8)	110·9	C(10)–C(9)—C(14)	117·1
C(3)–C(4)–C(9)	105·2	C(9)—C(10)–C(11)	120·8
C(5)–C(4)–C(8)	101·2	C(10)–C(11)–C(12)	121·3
C(5)–C(4)–C(9)	114·4	C(11)–C(12)–C(13)	118·8
C(8)–C(4)–C(9)	114·4	C(12)–C(13)–C(14)	120·6
C(4)–C(5)–C(6)	104·8	C(9)—C(14)–C(13)	121·3
C(5)–C(6)–C(7)	106·5	C(3)—O(1)—O(2)	125·4
		C(3)—O(2)—O(1)	112·6

the lack of agreement with either the 0° or 9° structure is striking.

The phenyl group is situated so that it makes a dihedral angle of 18·6° with the least-squares plane through the (non-planar) cyclopentane ring. The plane of the phenyl group also makes dihedral angles of 29·0° and 35·0° with C(4)–C(5)–C(9) and C(4)–C(8)–C(9) respectively. The plane of the carboxyl group makes a 100·7° dihedral angle with the least-squares plane through the cyclopentane ring and makes angles

of 30·3° and 38·2° with the two C–Cα–Cβ planes respectively. It thus shows a significant deviation from the synplanar conformation (0° dihedral angle) often found in carboxylic acids (Dunitz & Strickler, 1968). Other strained ring structures show an angle of about 30° between carboxyl and C–Cα–Cβ. These include 1-phenylcyclobutanecarboxylic acid with an angle of 26°, and *trans*-1,2-cyclopentanedicarboxylic acid (Benedetti, Corradini & Pedone, 1972) with angles of 31° and 33° for the optically active form and 31° for the racemic form. The synplanar rule is thus somewhat limited in predicting COOH orientation in these strained compounds. This could be due to any number of factors including intermolecular interaction, crowding caused by the phenyl group and interaction with hydrogen atoms.

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