Crystal and Molecular Structure of *trans*-2,*trans*-3-Dimethylcyclopropanecarboxylic Acid

By **P. A. Luhan** and **A. T. McPhail,*** Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706, U.S.A.

Single-crystal *X*-ray analysis of the title compound has established its constitution and molecular dimensions. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$, in a cell of dimensions: $a = 6{\cdot}39$, $b = 10{\cdot}98$, $c = 9{\cdot}76$ Å, $\beta = 105{\cdot}6°$. The structure was solved by direct phase-determining methods and refined by full-matrix least-squares calculations to R 0·085 over 638 reflections. The crystals contain centrosymmetric hydrogen-bonded dimers with a conformation in which the C=O bond points over the cyclopropane ring.

DURING their investigations on the mechanism of cyclopropane formation from epoxides *via* the Wittig reaction, Ghirardelli and Izydore[1] obtained mixtures of isomeric 2,3-dimethoxycyclopropanecarboxylic acids, (I)—(III), from reactions involving (+)-(2*R*,3*R*)-2,3-epoxybutane and *cis*-2,3-epoxybutane. In order that an analysis of the reaction mechanism could be made, it was imperative that the identity of each isomer be established unequivocally. The constitution of (I) was inferred from its optical activity. One of the other two isomers was isolated from the product mixture as a solid, m.p. 79-–80·5°, and we have subjected it to single-crystal *X*-ray analysis to determine its configuration We here report the results of this analysis.

EXPERIMENTAL

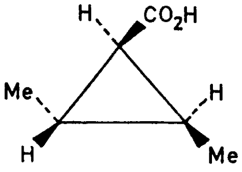
Crystal Data.—$C_6H_{10}O_2$, m.p. 79—80·5°, $M = 114{\cdot}1$. Monoclinic, $a = 6{\cdot}39(1)$, $b = 10{\cdot}98(2)$, $c = 9{\cdot}76(2)$ Å, $\beta = 105{\cdot}6(2)°$, $U = 660$ Å^3, $D_m = 1{\cdot}14$, $Z = 4$, $D_c = 1{\cdot}148$, $F(000) = 248$. Cu-K_α radiation $\lambda = 1{\cdot}542$ Å, $\mu(\text{Cu-}K_\alpha) = 7{\cdot}1$ cm^{-1}. Space group $P2_1/c$ (C_{2h}^5) from systematic absences: $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$.

Crystallographic Measurements.—The crystals have a tendency to sublime at room temperature, and so those used for the data collection were sealed in thin-walled glass capillaries. Unit-cell dimensions were evaluated from

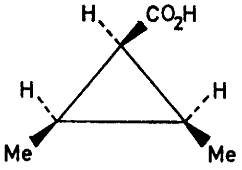
---

[1] R. G. Ghirardelli and R. A. Izydore, personal communication.

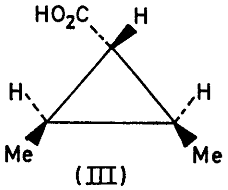
precession photographs taken with Mo-K_α ($\lambda = 0{\cdot}7107$ Å) radiation. Intensities were estimated visually from equi-inclination multiple-film Weissenberg photographs of the layers 0—6*kl* taken with Cu-K_α radiation. Spot-shape corrections and the usual Lorentz and polarization factors were applied, and 638 independent observed structure amplitudes were obtained. No allowance was made for absorption.



(I)



(II)



(III)

Structure Analysis.—The structure was solved by direct phase-determining methods.[2] Initially, three origin-defining reflections were assigned phases, 2,2,1, $|E| = 2{\cdot}48$, $\phi = 0$; 1,3,2, $|E| = 2{\cdot}47$, $\phi = 0$; 4,7,$\bar{2}$, $|E| = 2{\cdot}46$, $\phi = 0$, and one further reflection 4,11,$\bar{1}$, $|E| = 2{\cdot}25$ was assigned $\phi = a$. These four reflections were expanded into a set of ten reflections for which $|E_H{\cdot}E_K{\cdot}E_{H-K}| > 10{\cdot}0$. By use of a local version of the iterative program of Drew[3] as amended by Larson and Motherwell[4] the tangent formula[5] was applied to this basis set to generate the phases for other reflections. The phase a was allowed to assume values of 0 and π and the largest 120 $|E|$ values were refined for four cycles and 200 were refined for five cycles. In any cycle a phase assignment was rejected if the consistency index, $t = \sqrt{A^2 + B^2}/\Sigma_K|E_K{\cdot}E_{H-K}|$ was $<0{\cdot}30$ and the value of $\alpha = |E_H|\sqrt{A^2 + B^2}$ was $<3{\cdot}0$. A summary of the results of the refinement are presented in Table 1, which shows that the set with $a = 0$ has a markedly lower R_K [$= \Sigma_H|E_H|_{\text{obs}} - |E_H|_{\text{calc}}|/\Sigma_H|E_H|_{\text{obs}}$] value. In the E-map computed by use of the phases derived from the set with R_K 0·04, all non-hydrogen atoms appeared in chemically reasonable positions. The E-map based on the other set contained no recognizable features. The approximate atomic positions derived from the E-map, all with B 3·5 Å^2, were used to compute structure factors for which R was 0·378. The positional and isotropic thermal parameters were then refined for seven cycles of full-matrix least-squares calculations which reduced R to 0·176. Calculation of a three-dimensional difference electron-density map indicated that there was significant density at all positions calculated for the hydrogen atoms assuming C–H 1·07 and O–H 1·0 Å. The ten hydrogen atoms were included, with B 5·0 Å^2 in the next eight rounds of least-squares calculations during which carbon and oxygen atomic positional and anisotropic thermal parameters were adjusted. These decreased R to 0·094. In a further three least-squares cycles the hydrogen positional and isotropic thermal parameters were varied, and the refinement converged at R 0·085.

TABLE 1

Summary of output from tangent refinement

a	t	α	R_K	No. of Σ_2 values	No. of phases assigned
0	0·87	58	0·04	2211	185
π	0·77	48	0·15	2029	176

For all the structure-factor calculations, scattering factors for neutral atoms were taken from ref. 6. The weighting scheme for the least-squares calculations was $\sqrt{w} = 1$ for $|F_o| \leqslant 5{\cdot}5$ and $\sqrt{w} = |F_o|/5{\cdot}5$ for $|F_o| > 5{\cdot}5$, and $\Sigma w\Delta^2$ was minimized. At the conclusion of the refinement, analysis of $\langle w\Delta^2\rangle$ in ranges of $|F_o|$ and sin θ indicated the adequacy of this scheme.

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20527 (6 pp., 1 microfiche).*

RESULTS AND DISCUSSION

This X-ray analysis defines (III) as the constitution of the acid studied, whence the third isomeric acid must have configuration (II).

TABLE 2

Fractional atomic co-ordinates * ($\times 10^4$) and temperature factor parameters, with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
C(1)	7185(7)	2532(4)	3385(4)	†
C(2)	6792(8)	1445(4)	4250(5)	†
C(3)	4966(8)	2261(4)	3579(5)	†
C(4)	8401(8)	3582(4)	4091(5)	†
C(5)	7011(10)	169(5)	3738(7)	†
C(6)	3140(11)	1844(6)	2364(9)	†
O(7)	9767(5)	4055(3)	3472(3)	†
O(8)	8134(5)	4003(3)	5217(3)	†
H(1)	749(9)	229(5)	267(5)	3(1)
H(2)	740(8)	159(4)	503(5)	2(1)
H(3)	465(9)	281(5)	417(5)	3(1)
H(5α)	629(13)	−40(7)	421(8)	8(2)
H(5β)	628(12)	14(7)	282(7)	6(2)
H(5γ)	852(12)	1(6)	392(6)	6(2)
H(6α)	212(13)	259(7)	156(7)	8(2)
H(6β)	170(11)	140(6)	276(7)	5(2)
H(6γ)	370(12)	139(6)	182(7)	5(2)
H(7)	1056(8)	472(4)	391(4)	2(1)

* Hydrogen atoms are labelled according to their bonded atom, and have co-ordinates $\times 10^3$.

† For these atoms anisotropic temperature factors of the form $B \sin^2 \theta/\lambda^2 = b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl$ were employed with parameters $b_{ij} \times 10^4$.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	256(12)	77(4)	121(5)	−66(11)	152(12)	−18(7)
C(2)	327(14)	81(4)	135(5)	−76(12)	176(13)	−19(8)
C(3)	240(12)	76(4)	176(6)	−89(11)	152(13)	−73(8)
C(4)	230(11)	71(3)	115(5)	−4(11)	107(11)	12(7)
C(5)	436(18)	78(4)	221(8)	−59(15)	220(18)	−31(10)
C(6)	332(20)	110(6)	284(11)	−84(17)	31(25)	−83(13)
O(7)	348(9)	86(3)	164(3)	−126(8)	274(8)	−48(6)
O(8)	321(9)	92(3)	132(3)	−117(8)	193(8)	−42(6)

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[2] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[3] See, *e.g.*, M. G. B. Drew, D. H. Templeton, and A. Zalkin, *Acta Cryst.*, 1969, *B*, 25, 261.

[4] See *e.g.*, O. Kennard, D. L. Wampler, J. C. Coppola, W. D. S. Motherwell, D. G. Watson, and A. C. Larson, *Acta Cryst.*, 1971, *B*, **27**, 1116.

[5] J. Karle and H. Hauptmann, *Acta Cryst.*, 1956, **9**, 635.

[6] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

Final atomic co-ordinates and temperature-factor parameters are in Table 2, and the molecular dimensions derived from these are in Table 3. The crystal structure projected along the *b*-axis is shown in the Figure. In the crystal the acid molecules exist as centrosymmetric hydrogen-bonded dimers with O–H · · · O 2·65 Å. The dimers are separated from each other by normal van der Waals distances with the closest interdimer separation at 3·45 Å occurring between a carboxyl oxygen atom of the reference molecule and a methyl carbon atom of a molecule related by the *c* glide plane operation.

TABLE 3

Interatomic distances (Å) and angles (deg.), with estimated standard deviations in parentheses

(*a*) Intramolecular distances

C(1)–C(2)	1·522(7)	C(1)–H(1)	0·82(5)
C(1)–C(3)	1·510(7)	C(2)–H(2)	0·78(5)
C(1)–C(4)	1·456(6)	C(3)–H(3)	0·89(5)
C(2)–C(3)	1·478(7)	C(5)–H(5α)	0·96(8)
C(2)–C(5)	1·507(7)	C(5)–H(5β)	0·89(7)
C(3)–C(6)	1·495(9)	C(5)–H(5γ)	0·95(7)
C(4)–O(7)	1·296(6)	C(6)–H(6α)	1·20(8)
C(4)–O(8)	1·246(5)	C(6)–H(6β)	1·19(7)
		C(6)–H(6γ)	0·87(7)
C(2) · · · O(8)	3·01	O(7)–H(7)	0·92(4)
C(3) · · · O(8)	2·93		
C(5) · · · C(6)	3·09		

(*b*) Valency angles

C(2)–C(1)–C(3)	58·3(3)	C(1)–C(2)–H(2)	106(4)
C(2)–C(1)–C(4)	120·4(4)	C(3)–C(2)–H(2)	116(4)
C(3)–C(1)–C(4)	119·8(4)	C(5)–C(2)–H(2)	117(4)
C(1)–C(2)–C(3)	60·4(3)	C(1)–C(3)–H(3)	109(4)
C(1)–C(2)–C(5)	120·1(4)	C(2)–C(3)–H(3)	114(4)
C(3)–C(2)–C(5)	123·3(5)	C(6)–C(3)–H(3)	117(4)
C(1)–C(3)–C(2)	61·2(3)	C(2)–C(5)–H(5α)	110(5)
C(1)–C(3)–C(6)	121·3(5)	C(2)–C(5)–H(5β)	107(5)
C(2)–C(3)–C(6)	121·4(4)	C(2)–C(5)–H(5γ)	107(4)
C(1)–C(4)–O(7)	116·0(4)	H(5α)–C(5)–H(5β)	106(7)
C(1)–C(4)–O(8)	122·0(4)	H(5α)–C(5)–H(5γ)	113(6)
O(7)–C(4)–O(8)	122·1(4)	H(5β)–C(5)–H(5γ)	115(6)
		H(6α)–C(6)–H(6β)	99(5)
C(2)–C(1)–H(1)	109(4)	H(6α)–C(6)–H(6γ)	116(6)
C(3)–C(1)–H(1)	119(4)	H(6β)–C(6)–H(6γ)	103(6)
C(4)–C(1)–H(1)	117(4)	C(4)–O(7)–H(7)	117(3)

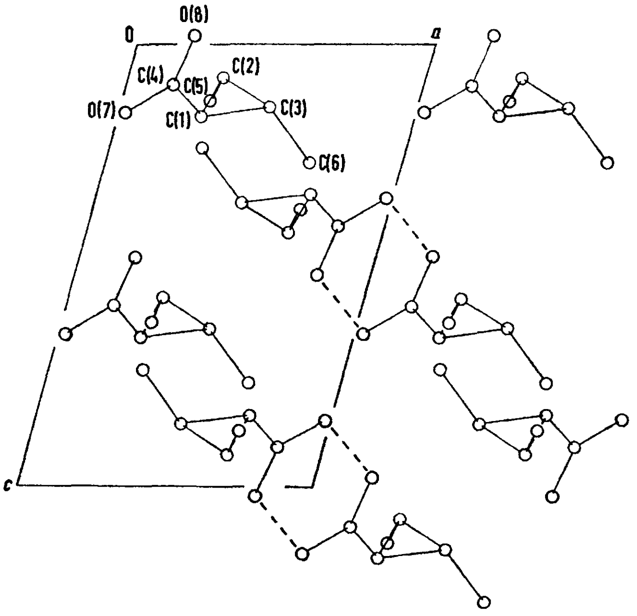
(*c*) Intermolecular distances ⩽3·6 Å

O(7) · · · O(8$^{\mathrm{I}}$)	2·66	O(7) · · · C(6$^{\mathrm{III}}$)	3·56
C(4) · · · O(8$^{\mathrm{I}}$)	3·40	O(7) · · · C(5$^{\mathrm{IV}}$)	3·57
O(8) · · · C(6$^{\mathrm{II}}$)	3·45	O(7) · · · O(7$^{\mathrm{I}}$)	3·58
C(4) · · · O(7$^{\mathrm{I}}$)	3·50		

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 2:

I	$2 - x, 1 - y, 1 - z$	III	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
II	$1 + x, \frac{1}{2} - y, \frac{1}{2} + z$	IV	$2 - x, \frac{1}{2} + y, \frac{1}{2} - z$

The cyclopropane ring dimensions accord well with those for other similar systems studied by *X*-ray diffraction. In cyclopropanecarbohydrazide,[7] cyclopropanecarboxamide,[8] and cyclopropane-1,1-dicarboxylic acid,[9] the endocyclic angle at the carbon atom bearing the substituent is smaller than at the other two which are not significantly different, and, correspondingly, the bond length opposite the smallest angle is the shortest. This situation holds true also in (III), for the internal angle at C(1) is 58·3° and C(2)–C(3) 1·478 Å, significantly smaller than the mean (1·516 Å) for the other ring bonds. The mean cyclopropane C–C distance (1·503 Å) is smaller than the normal length in saturated hydrocarbons[10] [1·537(5) Å], but is in excellent agreement with the corresponding mean in other crystalline simple cyclopropane derivatives studied (1·50 in cyclopropanecarbohydrazide[7] and cyclopropanecarboxamide,[8] 1·510 in cyclopropane-1,1-dicarboxylic acid,[9] and 1·507 Å in bicyclopropyl[11] at –105 °C), and only slightly shorter than the 1·518 Å in *cis*-1,2,3-tricyanocyclopropane.[12] The cyclopropane C–C length from an electron diffraction study[13] is 1·510 Å. There have been numerous discussions in the literature to account for the physical and chemical properties of cyclopropane and its derivatives with either the Coulson–Moffitt[14] ' bent ' bond model or Walsh's[15] π-electron model being favoured.



The crystal structure viewed in projection along the *b* axis. Hydrogen bonds are denoted by broken lines

The dihedral angle between the planar carboxy-group and the cyclopropane ring is 85°, similar to the values of 88·0 and 88·3° in two crystallographically independent molecules of cyclopropanecarboxamide,[8] 88·5° in cyclopropanecarbohydrazide,[7] and 86·2, 86·7, 87·6, and 88·6° at the carboxy-groups in two molecules of cyclopropane-1,1-dicarboxylic acid.[9] In the carboxy-group the identity of the carbonyl oxygen atom, O(8), is consistently

---

[7] D. B. Chesnut and R. E. Marsh, *Acta Cryst.*, 1958, **11**, 413.

[8] R. E. Long, H. Maddox, and K. N. Trueblood, *Acta Cryst.*, 1969, *B*, **25**, 2083.

[9] M. A. M. Meester, H. Schenk, and C. H. MacGillavry, *Acta Cryst.*, 1971, *B*, **27**, 630.

[10] *Chem. Soc. Special Publ.*, No. 18, 1965.

[11] J. Eraker and C. Rømming, *Acta Chem. Scand.*, 1967, **21**, 2721.

[12] A. Hartman and F. L. Hirshfeld, *Acta Cryst.*, 1966, **20**, 80.

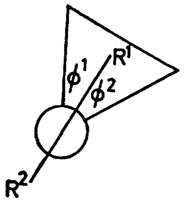
[13] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Cryst.*, 1964, **17**, 538.

[14] C. A. Coulson and W. E. Moffit, *Phil. Mag.*, 1949, **40**, 1; C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 1962, 2851.

[15] A. D. Walsh, *Trans. Faraday Soc.*, 1949, **45**, 179.

TABLE 4

Torsion angles (deg.) around exocyclic C–C bonds in some cyclopropane derivatives



R^1	R^2	ϕ^1	ϕ^2	Ref.
O	$NH{\cdot}NH_2$	38	30	7
O	NH_2	41	27	8
		38	29	
O	OH	41	22	9
		42	22	
OH	O	41	24	9
		42	24	
O	OH	42	27	Present work

established[16] from the short C(4)–O(8) bond length, the pattern of angles around C(4), and the location of the hydroxy-hydrogen atom 0·92 Å from O(7). The carbonyl oxygen atom lies over the cyclopropane ring, but it is not equidistant from C(2) and C(3) (Table 3). A survey of the torsion angles around the exocyclic C–C bonds in simple cyclopropane derivatives (Table 4) shows that in all of these the torsion angles are unequal and there is a significant departure from C_s symmetry. Electron diffraction patterns of cyclopropanecarbaldehyde[17] have been interpreted on the basis of about 50% population of the C_s-*cis*-configuration in the vapour phase.

We thank Drs. R. G. Ghirardelli and R. A. Izydore for suggesting this problem and for crystals, and the Army Research Office, Durham, for partial support of this work. All calculations were performed on the IBM 370/165 computer located at the Triangle Universities Computation Centre, Research Triangle Park, North Carolina.

[2/1678 *Received*, 17*th July*, 1972]

---

[16] See *e.g.*, J. D. Dunitz and P. Strickler in 'Structural Chemistry and Molecular Biology,' eds. A. Rich and N. Davidson, Freeman, San Francisco, 1968, p. 595.

[17] L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, 1965, **43**, 647.