

Fig. 4. Projection de la structure de la bromo-3-décalone-2 sur le plan xOz .

Références

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program*. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
COREY, E. J. & SNEEN, R. A. (1955). *J. Amer. Chem. Soc.* **77**, 2505.

IBERS, A. (1969). *Acta Cryst.* **B25**, 1667.
LAPASSET, J. & FALGUEIRETTES, J. (1971). *Acta Cryst.* **B27**, 108.
MION, L. (1969). Thèse, No. 852, C.N.R.S. AO 3428.
ROMERS, C. (1956). *Rec. Trav. Chim. Pays-Bas*, **75**, 956.
Tables of Interatomic Distances and Configurations in Molecules and Ions (1965). Ed. L. E. SUTTON. London: The Chemical Society.

Acta Cryst. (1971). **B27**, 630

The Crystal and Molecular Structure of Cyclopropane-1,1-dicarboxylic Acid

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Cyclopropane-1,1-dicarboxylic acid forms triclinic crystals of space group $P\bar{1}$ with cell constants $a = 12.045$, $b = 13.822$, $c = 5.286$ Å, $\alpha = 137.53$, $\beta = 92.22$, $\gamma = 89.88^\circ$, $Z = 4$. X-ray intensities were measured with the help of a Nonius automatic single-crystal diffractometer. The structure was solved by means of the Patterson technique and refined by a block-diagonal least-squares procedure. The final discrepancy index was 4.3% for 1669 independent reflexions. The molecules have intramolecular O...O hydrogen bonds of 2.563 Å and are arranged in strings along the y axis by means of O...O hydrogen bonds of 2.641 Å. The length of the bond of the cyclopropane group opposite to the carboxylic groups is 1.462 Å and the other two bonds of this ring are 1.531 and 1.538 Å. The e.s.d.'s in the bond lengths are approximately 0.004 Å.

Introduction

In dicarboxylic acids a large value of the ratio of the first and second dissociation constants K_1/K_2 is an indication of intramolecular hydrogen bonding. For instance fumaric acid, which has a K_1/K_2 ratio of 23.2 cannot form an intramolecular hydrogen bond on

sterical grounds. Maleic acid on the other hand has a K_1/K_2 ratio of 20200 and in this acid the COOH groups are so situated that intramolecular hydrogen bonding may take place.

Cyclopropane-1,1-dicarboxylic acid has a K_1/K_2 ratio of 40600, which suggests a strong intramolecular hydrogen bond. In accordance with this the mechanism

of the isomerization of this acid could only be interpreted by assuming intramolecular hydrogen bonding (Bus, 1967).

The object of this investigation was to verify the presence of intramolecular hydrogen bonding in the solid state.

Experimental

Crystals of cyclopropanedicarboxylic acid are triclinic of space group $P\bar{1}$. The unit cell was chosen such that the cell dimensions are

$$\begin{aligned} a &= 12.045 (1) \text{ \AA} & \alpha &= 137.53 (1)^\circ \\ b &= 13.822 (1) & \beta &= 92.22 (5) \\ c &= 5.286 (1) & \gamma &= 89.88 (3) \\ Z &= 4, D_m = 1.43, D_c = 1.46 \text{ g.cm}^{-3}. \end{aligned}$$

The calculation of the cell constants was carried out by means of a least-squares procedure with data measured from three zero-layer Weissenberg diagrams taken at room temperature with Cu $K\alpha$ radiation and calibrated with Al powder lines.

The intensities were collected by means of a Nonius automatic single-crystal diffractometer using Cu $K\alpha$ radiation and the θ - 2θ scan mode with a maximum θ -value of 68.5° , high intensities were reduced by using attenuation filters. The background intensity was measured at each side of a reflexion for half the scanning time. A reflexion was considered significant if the net count was greater than twice the standard deviation. In the reduction of intensities to structure factors the absorption correction was ignored because of the small size of the crystal.

Structure determination

The first attempt to solve the structure was made by means of the symbolic addition method (Karle &

Karle, 1966) with half-automatic computer programs (Schenk, 1969). The intensities exhibited a hypercentric distribution, but we thought to overcome this difficulty by using only very high triplet probabilities. Five symbols were chosen in order that the search for new signs should be sufficiently rapid. A careful consistency analysis led to a classification of the 32 solutions in order of reliability. E maps of the six best solutions were computed, but none of them gave a chemically consistent set of peaks.

An E^2 Patterson map was then computed and a very strong maximum at $u=0.500$, $v=0.870$ and $w=0.360$ with a height of half the origin value confirmed the hypercentric statistics and we concluded that there was a pseudo centre between the two crystallographically independent molecules. In order to obtain information about the vectors between nearest and next-nearest neighbours, spheres of radii 1.5 and 2.5 Å about the origin were plotted in a stereographic projection. The spheres showed the plane of the molecules and the direction of the bonds in this plane. Besides this information the 2.5 Å sphere showed two maxima, which could only be interpreted as intermolecular hydrogen bonds. Next a plane through the strong peak at 0.500, 0.870, 0.360 parallel to the plane of the molecule revealed rough positions for the carboxylic groups and their connecting carbon atoms. The coordinates of the remaining cyclopropane carbon atoms were derived on the assumption that the plane through the approximately coplanar carboxylic groups is a mirror plane for the molecule. A structure factor calculation with scale and temperature factors taken from a Wilson plot resulted in $R=53\%$.

Refinement

After two cycles of Fourier refinement ($R=35\%$) a

Table 1. *The final parameters of the heavy atoms and their e.s.d.'s, in brackets*

The positional parameters are given in fractions multiplied by 10^4 and the thermal parameters U_{ij} in Å² multiplied by 10^4 . The thermal parameters are based on the expression $\exp \left\{ -2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} h_i h_j a_i^* a_j^* \right\}$ where a_i^* are the reciprocal cell constants and h_i the Laue indices.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
O(1)	3111 (1)	0015 (2)	6332 (5)	500 (09)	582 (09)	929 (12)	166 (14)	1326 (21)	245 (16)
C(1)	2641 (2)	0940 (2)	6925 (6)	380 (10)	420 (11)	524 (12)	067 (16)	0768 (21)	130 (17)
O(2)	1606 (1)	1198 (2)	7863 (6)	414 (08)	763 (11)	1137 (15)	283 (15)	1601 (25)	548 (18)
C(2)	3208 (1)	1809 (2)	6645 (5)	307 (08)	355 (09)	436 (10)	057 (14)	0633 (18)	083 (15)
C(3)	2538 (2)	2806 (2)	7008 (6)	413 (10)	388 (10)	454 (11)	094 (17)	0675 (20)	051 (17)
O(3)	1572 (1)	3031 (2)	7852 (5)	404 (08)	662 (10)	863 (12)	368 (14)	1259 (21)	288 (15)
O(4)	3079 (1)	3440 (2)	6419 (5)	565 (09)	585 (09)	829 (11)	204 (15)	1253 (20)	229 (16)
O(1')	1900 (1)	5269 (2)	7262 (5)	546 (09)	615 (10)	851 (12)	035 (15)	1312 (20)	037 (16)
C(1')	2382 (2)	5868 (2)	6709 (6)	387 (10)	368 (10)	465 (11)	016 (15)	0659 (20)	066 (16)
O(2')	3422 (1)	5588 (2)	5768 (5)	411 (08)	553 (09)	830 (12)	190 (14)	1090 (20)	123 (15)
C(2')	1827 (2)	6902 (2)	6984 (6)	313 (09)	392 (10)	478 (11)	019 (15)	0719 (20)	014 (15)
C(3')	2508 (2)	7692 (2)	6649 (6)	391 (10)	386 (10)	483 (11)	052 (16)	0691 (20)	016 (17)
O(3')	3478 (1)	7444 (2)	5851 (5)	404 (08)	606 (09)	856 (12)	047 (14)	1183 (20)	270 (15)
O(4')	1977 (1)	8676 (2)	7280 (5)	491 (08)	583 (09)	909 (12)	054 (14)	1307 (20)	149 (16)
C(7)	4213 (2)	1135 (3)	4203 (7)	437 (11)	557 (13)	701 (15)	319 (19)	1052 (26)	437 (21)
C(8)	4415 (2)	2289 (3)	8262 (7)	345 (10)	562 (13)	783 (16)	082 (18)	1120 (27)	120 (20)
C(8')	0624 (2)	6457 (3)	5291 (7)	342 (10)	654 (14)	788 (16)	182 (19)	1261 (29)	214 (20)
C(7')	0814 (2)	7614 (3)	9388 (7)	399 (10)	614 (14)	761 (16)	257 (19)	1173 (28)	340 (21)

block-diagonal least-squares refinement was started which minimized the function $\sum w_i(F_o - F_c)^2$. The weights w_i were calculated from the expression $w_i = 1/(2 + |F_o| + 0.036 |F_o|^2)$ (Cruickshank, 1961), and the atomic form factors were those from *International Tables for X-ray Crystallography* (1962). The discrepancy index R defined by the expression $R = \sum |F_o - F_c| / \sum |F_o| \times 100\%$ rapidly dropped to 9%. At this stage all hydrogen atoms were found from a difference map with peak heights between 0.4 and 0.6 e.Å⁻³.

In the later cycles positional parameters for all atoms, anisotropic thermal parameters for the heavy atoms and isotropic thermal parameters for the hydrogen atoms were refined. The final R value was 4.3% for 1669 independent reflexions. A final difference synthesis showed a residual density between -0.2 and 0.2 e.Å⁻³.

The positional and thermal parameters of the atoms are given in Tables 1 and 2 together with their estimated standard deviations, as calculated from the least-squares refinement. A list of structure factors can be obtained from this laboratory.

Table 2. Final hydrogen atom parameters with their e.s.d.'s, in brackets

The positional parameters x , y and z are given in fractions multiplied by 10³ and the isotropic thermal parameter B in Å². The thermal parameter B is taken from $\exp \{-B \sin^2 \theta / \lambda^2\}$.

	x	y	z	B
H(11')	041 (2)	545 (3)	403 (08)	2.9 (0.5)
H(12')	042 (2)	673 (3)	412 (07)	1.9 (0.5)
H(10')	074 (2)	857 (3)	067 (08)	2.9 (0.6)
H(9')	073 (2)	736 (3)	061 (08)	3.4 (0.6)
H(5)	136 (3)	193 (4)	815 (10)	5.2 (0.8)
H(6)	263 (3)	404 (4)	663 (10)	6.5 (0.9)
H(6')	243 (3)	909 (4)	701 (10)	6.1 (0.9)
H(5')	364 (3)	625 (4)	565 (09)	4.3 (0.7)
H(9)	428 (2)	009 (3)	270 (08)	3.2 (0.6)
H(10)	428 (2)	136 (3)	283 (08)	2.8 (0.6)
H(11)	466 (2)	201 (3)	949 (08)	2.7 (0.6)
H(12)	460 (3)	325 (3)	947 (09)	3.7 (0.7)

Table 3. Bond lengths of two crystallographically independent molecules

Equivalent lengths are on the same line. The e.s.d.'s (in brackets) are given in units of the last digit.

C(1)-O(1)	1.214 (4) Å	C(1')-O(1')	1.217 (5) Å
C(1)-O(2)	1.309 (3)	C(1')-O(2')	1.314 (3)
C(1)-C(2)	1.485 (5)	C(1')-C(2')	1.485 (5)
C(2)-C(3)	1.483 (4)	C(2')-C(3')	1.483 (5)
C(3)-O(3)	1.218 (3)	C(3')-O(3')	1.218 (3)
C(3)-O(4)	1.309 (5)	C(3')-O(4')	1.309 (4)
C(2)-C(7)	1.531 (3)	C(2')-C(7')	1.531 (3)
C(2)-C(8)	1.535 (3)	C(2')-C(8')	1.540 (3)
C(7)-C(8)	1.456 (4)	C(7')-C(8')	1.467 (4)
O(2)-H(5)	0.96 (6)	O(2')-H(5')	1.00 (6)
O(4)-H(6)	0.92 (6)	O(4')-H(6')	0.88 (6)
C(7)-H(9)	1.01 (4)	C(7')-H(9')	0.95 (6)
C(7)-H(10)	0.98 (5)	C(7')-H(10')	0.95 (4)
C(8)-H(11)	1.00 (5)	C(8')-H(11')	1.02 (4)
C(8)-H(12)	0.98 (5)	C(8')-H(12')	0.96 (5)

Discussion

In Tables 3 and 4 the bond lengths and angles are given. All corresponding values of the two independent molecules are equal within the limits of accuracy. Therefore in the Figures the indicated lengths and angles are the mean values.

Hydrogen bonding and packing

Each molecule has an intramolecular hydrogen bond of 2.563 Å, with an O-H bond length of 0.98 Å and an O...H distance of 1.63 Å. The angle O...H-O is 150°.

The molecules are arranged in infinite strings along the y axis by means of intermolecular hydrogen bonds of 2.641 Å (see Fig. 1). The two molecules in the asym-

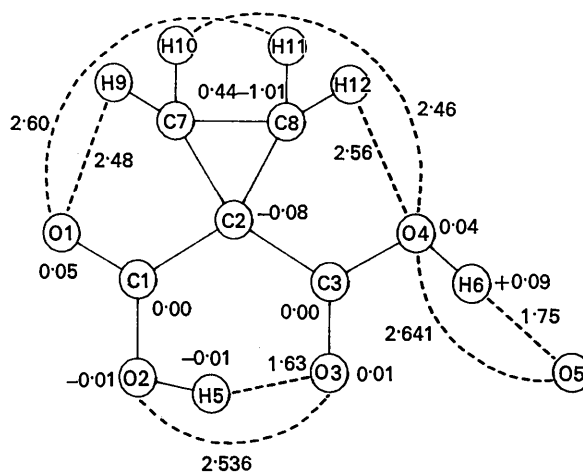


Fig. 1. Short distances between non-bonded atoms; each distance is indicated with a dotted line. The numbers near the atoms give the distances of these atoms from the best plane through both the carboxylic groups and C(2). All numbers in this Figure are mean values of the corresponding values in the two independent molecules. Atom O(1') is indicated as O(5).

metric unit are in a relative pseudocentric position with respect to a point halfway along the intermolecular hydrogen bridge. Two strings running through the cell are related to each other by the true centres of symmetry; their carboxyl groups are in approximately the same plane, which makes an angle of 15° with the xy plane. These double strings have only a few short contacts (see Fig. 3).

The sets of double strings are packed by translations along the x and z axes in a two-dimensional array. The shortest hydrogen-hydrogen contact there is 2.36 \AA .

Molecular conformation

The planar COOH groups of both molecules make an angle of 6° with each other. The cyclopropane group

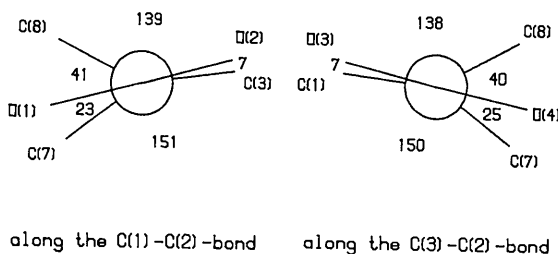


Fig. 2. Newman projection along the two bonds between the carboxylic groups and the central carbon atom.

is nearly perpendicular to the best plane through both COOH-groups (see Figs. 2 and 3).

From the Newman projections of Fig. 2 it can be seen that the dihedral angles between the carboxylic group and C(7) and C(8) are about 24 and 40° respectively; this shows that the plane through the carboxylic groups is not a mirror plane of the molecule.

Bond lengths

The carboxylic groups show normal bond lengths, and the C-H and O-H distances [see Fig. 4(a)] are equal to those normally found from X-ray experiments.

The mean bond length in the cyclopropane ring is 1.510 \AA in good agreement with the value normally found (see Long, Maddox & Trueblood, 1969). However the individual lengths within the ring show remarkable differences. Those involving the carbon atom which connects the carboxylic groups are 1.531 and 1.538 \AA and the 'back' ring bond is 1.462 \AA . In cyclopropane carboxamide (Long, Maddox & Trueblood, 1969) and the corresponding hydrazide (Chesnut & Marsh, 1958) the bond between the unsubstituted carbon atoms is also the smaller one (1.481 and 1.478 \AA respectively).

From the Newman projections of Fig. 2 it can be seen that the oxygen atoms O(1) and O(4) are pointing

Table 4. Important angles in the two independent molecules

Corresponding angles are on the same line. E.s.d.'s are given in brackets.

O(1)—C(1)—O(2)	119.8 (3) ^o	O(1')—C(1')—O(2')	120.0 (3) ^o
O(1)—C(1)—C(2)	122.0 (2)	O(1')—C(1')—C(2')	122.1 (2)
O(2)—C(1)—C(2)	118.3 (3)	O(2')—C(1')—C(2')	117.8 (3)
O(3)—C(3)—O(4)	123.0 (3)	O(3')—C(3')—O(4')	123.0 (3)
O(3)—C(3)—C(2)	122.6 (3)	O(3')—C(3')—C(2')	122.8 (3)
O(4)—C(3)—C(2)	114.3 (2)	O(4')—C(3')—C(2')	114.2 (2)
C(1)—C(2)—C(3)	118.3 (2)	C(1')—C(2')—C(3')	118.4 (2)
C(1)—C(2)—C(7)	115.7 (2)	C(1')—C(2')—C(7')	116.0 (3)
C(1)—C(2)—C(8)	115.1 (3)	C(1')—C(2')—C(8')	114.5 (2)
C(3)—C(2)—C(7)	119.2 (3)	C(3')—C(2')—C(7')	118.9 (2)
C(3)—C(2)—C(8)	117.2 (2)	C(3')—C(2')—C(8')	117.3 (3)
C(7)—C(2)—C(8)	56.7 (1)	C(7')—C(2')—C(8')	57.1 (2)
C(2)—C(7)—C(8)	61.8 (2)	C(2')—C(7')—C(8')	61.7 (2)
C(2)—C(8)—C(7)	61.5 (1)	C(2')—C(8')—C(7')	61.2 (2)
C(1)—O(2)—H(5)	109 (3)	C(1')—O(2')—H(5')	105 (2)
C(3)—O(4)—H(6)	111 (3)	C(3')—O(4')—H(6')	109 (3)
O(2)—H(5)—O(3)	150 (4)	O(2')—H(5')—O(3')	157 (3)
O(4)—H(6)—O(5)	178 (4)	O(4')—H(6')—O(5')	172 (4)
C(2)—C(7)—H(9)	112 (2)	C(2')—C(7')—H(9')	110 (2)
C(2)—C(7)—H(10)	113 (2)	C(2')—C(7')—H(10')	113 (2)
C(8)—C(7)—H(9)	121 (3)	C(8')—C(7')—H(9')	116 (1)
C(8)—C(7)—H(10)	119 (1)	C(8')—C(7')—H(10')	118 (3)
H(9)—C(7)—H(10)	117 (3)	H(9')—C(7')—H(10')	122 (3)
C(2)—C(8)—H(11)	113 (2)	C(2')—C(8')—H(11')	111 (2)
C(2)—C(8)—H(12)	112 (2)	C(2')—C(8')—H(12')	114 (2)
C(7)—C(8)—H(11)	117 (1)	C(7')—C(8')—H(11')	117 (2)
C(7)—C(8)—H(12)	118 (3)	C(7')—C(8')—H(12')	117 (1)
H(11)—C(8)—H(12)	120 (3)	H(11')—C(8')—H(12')	121 (3)

towards the cyclopropane ring. The same has been found for the oxygen atom in each of the two compounds mentioned above, whilst Bartell (Bartell & Guillory, 1965; Bartell, Guillory & Parks, 1965) found similar conformations in several compounds in the vapour phase.

Though Long *et al.* questioned the significance of the shortening of the 'back' ring bond with respect to the average ring bond length in cyclopropane carboxamide and -hydrazide (both 0.019 Å), our results indicate that this is too pessimistic. For in cyclopropane-1,1-dicarboxylic acid, where two oxygen atoms are pointing towards the cyclopropane ring, we find a shortening of 0.048 Å. This is approximately twice the difference in the amide and hydrazide, where only one oxygen atom is in this conformation. A probable conclusion from our results could be that a correlation exist between the bond lengths in the cyclopropane ring and the proximity of the polar CO-group.

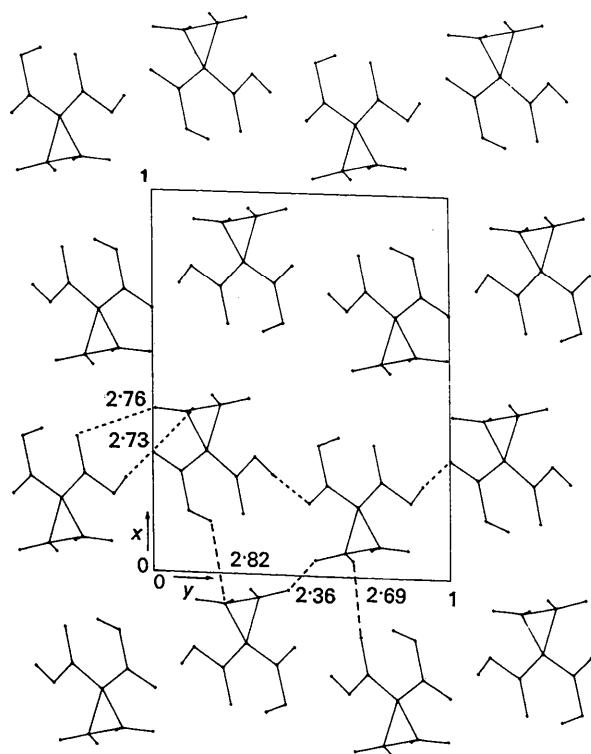


Fig. 3. Projection of the crystal structure along the z axis. Short intermolecular distances are indicated (see also Table 4).

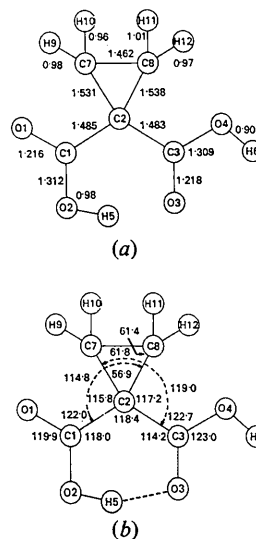


Fig. 4. Mean values of the corresponding bond lengths (a) and bond angles (b) of the two crystallographically independent molecules.

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References

- BARTELL, L. S. & GUILLORY, J. P. (1965). *J. Chem. Phys.* **43**, 647.
 BARTELL, L. S., GUILLORY, J. P. & PARKS, A. T. (1965). *J. Phys. Chem.* **69**, 3043.
 BUS, J. (1967). Dissertation (Amsterdam).
 CHESNUT, D. B. & MARSH, R. E. (1958). *Acta Cryst.* **11**, 413.
 CRUICKSHANK, D. W. J. (1961). In *Computing Methods and The Phase Problem in X-ray Crystallography*, p. 45, Oxford: Pergamon Press.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
 LONG, R. E., MADDOX, H. & TRUEBLOOD, K. N. (1969). *Acta Cryst.* **B25**, 2083.
 SCHENK, H. (1969). *Automation of the Symbolic Addition Method. Verhandel. Koninkl. Ned. Akad. Wetenschap., Afdel. Natuurk., eerste reeks, deel XXV, no. 5*, Amsterdam-London: North Holland.