

The Crystal Structure of *cis*-Cyclobut-1-ene-3,4-dicarboxylic Acid

BY ETTORE BENEDETTI AND MARIA ROSARIA CIAJOLO

Laboratorio di Chimica Generale, Istituto Chimico, Università di Napoli, Via Mezzocannone 4, 80134 Napoli, Italy

AND JEAN PAUL DECLERCQ AND GABRIEL GERMAIN

Laboratoire de Chimie Physique et Cristallographie, Bâtiment Lavoisier, Université de Louvain, Place L. Pasteur 1, Louvain-la-Neuve, Belgium

(Received 3 July 1974; accepted 23 July 1974)

cis-3,4-Cyclobut-1-ene-3,4-dicarboxylic acid (CBDA), $C_6H_6O_4$, crystallizes in the monoclinic system, space group $P2_1/n$, with $a=11.332$, $b=6.978$, $c=8.106$, $\beta=102.62^\circ$ and four molecules per unit cell. The structure has been solved by a straightforward application of direct methods and refined by a least-squares procedure to a final R value of 0.087 for 950 reflexions measured by the counter technique (Cu $K\alpha$). The geometry and the conformation of the molecule are discussed with relation to the strains present in it. The cyclobutene ring as well as the two crystallographically independent pairs of facing carboxyl groups are almost planar. Long rows of hydrogen-bonded molecules extend along the c - b direction.

Introduction

Recently, considerable attention has been given by some of us to the solid-state study of small ring compounds (Benedetti, Corradini & Pedone, 1972; Pedone, Benedetti & Allegra, 1970; Benedetti, Claverini & Pedone, 1973, and references therein). A number of different researches have been reported in order to gain more information on the structure and the conformation of such molecules with particular attention to the cyclobutane ring (Benedetti, Corradini & Pedone, 1970, and references therein). Generally, simple derivatives of such cyclic molecules have been used such as, for example, dicarboxylic acids. We now report the crystal structure of *cis*-cyclobut-1-ene-3,4-dicarboxylic acid (CBDA) as a continuation of previous studies.

Experimental

Single crystals of CBDA, $C_6H_6O_4$, suitable for X-ray diffraction analysis were kindly supplied by Dr R. F. Winter. From preliminary Weissenberg and rotation photographs taken with Cu $K\alpha$ radiation, the crystals were found to belong to the monoclinic system, space group $P2_1/n$ (systematic extinctions of $h0l$ with $h+l=2n+1$ and $0k0$ with $k=2n+1$). The unit-cell parameter determination and the data collection were carried out by one of us (E.B.) at the Polytechnic Institute of Brooklyn with the X-ray equipment of the Chemistry Department. A crystal was centred on a Picker four-circle automated diffractometer equipped with a PDP-8 digital computer. The unit-cell dimensions were determined and refined from a least-squares fitting of the setting angles (2θ , χ , φ) of 12 high-angle reflexions ($2\theta > 80^\circ$). The physical data for CBDA are reported in Table 1. The data collection was carried out in the θ - 2θ scan mode with Ni-filtered Cu $K\alpha$ radiation,

pulse-height analysis and a scintillation counter. A scan range of 1.67° was used for the whole range of 2θ examined ($2-130^\circ$), with a scan speed of 1°min^{-1} . Two background counts of 10 s were taken at both ends of each scan. 950 independent reflexions were collected. One standard reflexion was measured every 45 min (every 20 reflexions) during the data collection to monitor the electronic stability of the instrument and any crystal deterioration and/or misalignment. The fluctuations in the intensity of this reflexion were within 6%. The integrated intensities were then corrected for Lorentz and polarization effects in the usual way.

Table 1. *Physical data*

Molecular formula	$C_6H_6O_4$
M.W.	142.1 a.m.u.
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	4 molecules/unit cell
a	$11.332 \pm 0.002 \text{ \AA}$
b	$6.978 \pm 0.001 \text{ \AA}$
c	$8.106 \pm 0.002 \text{ \AA}$
β	$102.62^\circ \pm 0.20^\circ$
V	625.5 \AA^3
Density (calculated)	1.508 g cm^{-3}
Radiation	Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$ (Ni-filtered)
Temperature	$25^\circ \pm 3^\circ$
Number of independent reflexions	950

Structure determination and refinement

An overall temperature factor ($B=3.24 \text{ \AA}^2$) and scale factor were evaluated and used to compute normalized structure factors, E . The structure was determined by a straightforward application of direct methods using the multisolution technique in the form programmed by Germain, Main & Woolfson (1971). For the 100 largest

E 's the Σ_2 relationships were determined from which the reliabilities α_h of the phases to be expected from the tangent formula refinement were estimated. The α_h 's were then used to select the best starting set by the 'convergence' procedure. The starting set of phases was:

h	k	l	E	Phase
7	2	4	3.21	+
9	1	3	2.96	+
8	1	6	2.77	+
6	3	4	3.92	+, -
2	5	5	3.23	+, -
1	6	-2	2.48	+, -
3	4	3	2.41	+, -
2	2	-1	1.84	+, -

This phase information was extended by iterative weighted tangent-formula refinement to yield the phases of all the 100 strongest E 's. Of the 32 calculated sets of phases only two sets had significantly better figures of merit. The automatic chemical interpretation program (Declercq, Germain, Main & Woolfson, 1973) revealed the positions of all the atoms of the molecule (except the hydrogen atoms) in the E map corresponding to the set of phases having the highest figure of merit. The structure was then refined by least-squares procedure with anisotropic thermal factors for the heavy atoms (C and O). The hydrogen atoms were clearly detected on a difference Fourier map and their atomic positions were refined in the last cycles, assuming for each hydrogen atom an isotropic thermal factor equal to that of the heavy atom to which it is bonded. The final R value is 0.087 for the 950 measured reflexions. The final atomic parameters (fractional coordinates and thermal factors) together with their estimated standard deviations are reported in Table 2. The calculations were performed at the Computing Center of the University of Louvain (IBM 370/155) and partially at the Centro di Calcolo Elettronico della Facoltà di Scienze of the University of Napoli (IBM 360/44 PS).

Results and discussion

In Fig. 1 the molecular model of CBDA is reported; bond angles, bond lengths and internal rotation angles are given in Table 3. Bond angles and bond lengths in the cyclobutene ring are comparable with literature data. In particular the values for bond lengths in the ring, which is highly strained, are quite normal except for the C(3)-C(4) bond distance which has a significantly larger value of 1.578 Å. Other four-membered-ring molecules have been found to present a similar abnormally long bond (Dunitz & Schomaker, 1952; Lemain & Livingston, 1952; Owen & Hoard, 1951; Goldish, Hedberg & Schomaker, 1956; Greenberg & Post, 1968; Adman & Margulis, 1968). The slightly larger values for bond angles on the sp^2 -hybridized carbon atoms C(1) and C(2) and the slight decrease of

the angles on the sp^3 -hybridized carbon atoms C(3) and C(4) also follow a similar trend found in molecules having the cyclobutene residue (Goldish, Hedberg & Schomaker, 1956; Karle, Britts & Brenner, 1964; Wong,

Table 2. Final atomic parameters

(a) Fractional coordinates (e.s.d.'s in uni of the last significant figure)

	x/a	y/b	z/c
O(1)	0.9950 (3)	0.3885 (5)	0.2963 (4)
O(2)	0.8721 (3)	0.5923 (5)	0.3893 (4)
O(3)	0.9899 (3)	0.7854 (5)	0.0934 (4)
O(4)	0.8544 (3)	0.9185 (5)	-0.1151 (5)
C(1)	0.6801 (4)	0.5304 (7)	0.0964 (7)
C(2)	0.6805 (4)	0.6502 (6)	-0.0300 (6)
C(3)	0.8098 (4)	0.6099 (6)	-0.0376 (5)
C(4)	0.8091 (4)	0.4637 (6)	0.1096 (6)
C(5)	0.8944 (4)	0.7781 (6)	-0.0102 (6)
C(6)	0.8956 (4)	0.4895 (6)	0.2775 (6)
H-O(1)*	1.036 (6)	0.404 (9)	0.393 (9)
H-O(4)	0.905 (6)	1.010 (10)	-0.105 (9)
H-C(1)	0.620 (5)	0.493 (10)	0.162 (9)
H-C(2)	0.616 (5)	0.743 (9)	-0.102 (9)
H-C(3)	0.818 (5)	0.553 (9)	-0.152 (9)
H-C(4)	0.812 (5)	0.320 (8)	0.081 (8)

* H-X(n) stands for hydrogen atom bonded to the atom X(n).

(b) Thermal parameters. Temperature factor in the form: $T = \exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{23}kl + 2\beta_{13}hl + 2\beta_{12}hk] \times 10^{-4}$.

	B_{150}	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
O(1)	3.77	64	23	13	22	-11	56
O(2)	4.01	89	199	127	-4	-24	66
O(3)	4.11	78	203	131	91	-78	-53
O(4)	4.57	74	224	189	170	-78	-19
C(1)	3.74	61	196	155	-34	0	-28
C(2)	3.52	60	164	134	-19	-40	0
C(3)	3.32	62	168	92	-17	-29	4
C(4)	3.05	63	146	127	-10	-22	-21
C(5)	2.96	58	172	99	24	-15	8
C(6)	3.17	60	148	120	32	-7	10

	B_{150}	B_{150}	
H-O(1)	3.77	H-C(2)	3.52
H-O(4)	4.57	H-C(3)	3.32
H-C(1)	3.74	H-C(4)	3.05

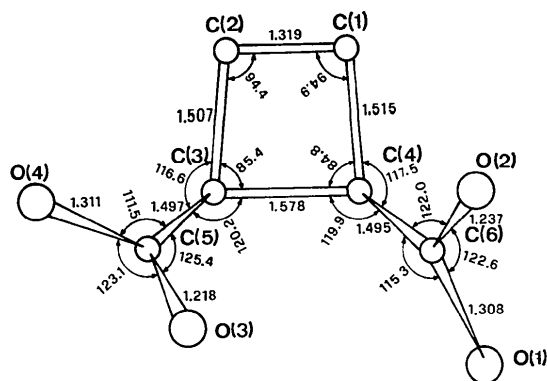


Fig. 1. Molecular model of CBDA. Some of the bond distances and bond angles are reported (cf. Table 3).

Marsh & Schomaker, 1964; Karle & Britts, 1965). Furthermore, the bond angles C(6)–C(4)–C(3) and C(5)–C(3)–C(4) present larger values with respect to the tetrahedral value (119.9 and 120.2° respectively). The reason for this increase is found in the need for the molecule to release the intramolecular contacts between atoms separated by four or more bonds. In fact by increasing these angles the contacts between the atoms of the two carboxylic groups are released: the shorter intramolecular distances are C(6)···O(3), O(3)···O(1) and O(3)···O(2) which have values of 2.89, 3.21 and 3.28 Å respectively.

The cyclobutene ring is almost planar: the r.m.s. distance of the atoms C(1), C(2), C(3) and C(4) from the best plane passing through them is 0.008 Å. The two carboxyl groups are in the *cis* conformation (the internal rotation angle C(5)–C(3)–C(4)–C(6) is 2°); they also maintain a quasi synplanar conformation with respect to the C–C bonds of the ring (Bürgi & Dunitz, 1968). In fact the O(2)–C(6)–C(4)–C(1) and O(3)–C(5)–C(3)–C(4) internal rotation angles are –14 and 26° respectively. These values depart from a perfectly synplanar conformation and this probably reflects the tendency to balance the preference to achieve this conformation with the need to release the intramolecular interactions between non-bonded atoms.

The atoms of the two crystallographically independent pairs of facing carboxyl groups (through centres of symmetry) are very nearly coplanar. The equations of the corresponding least-squares planes (referred to the crystallographic axes) through C(3), C(5), O(3), O(4) and C(4), C(6), O(1), O(2) and their centrosymmetrically related atoms are, respectively:

$$-0.6145X + 0.4165Y + 0.7881Z = 4.0578$$

$$-0.5641X - 0.7721Y + 0.4088Z = 7.4088$$

The r.m.s. distances of the eight atoms of each of the two carboxyl groups from the best plane passing through them is 0.041 and 0.052 Å, respectively.

Finally, Figs. 2 and 3 show views of the molecular packing along the **b** and **a** directions. Some of the shorter intermolecular contacts are also indicated. Long rows of hydrogen-bonded molecules extend along the **c**–**b** direction. The symmetry of the molecular row in the crystal is *ti* according to the classification of the possible symmetry of rows given by Corradini (1960). The hydrogen-bond distances have normal values: O(4)···O(3) and O(2)···O(1) distances are 2.697 (5) and 2.663 (5), respectively.

We wish to thank the National Research Council of Italy for partial support of the present investigation.

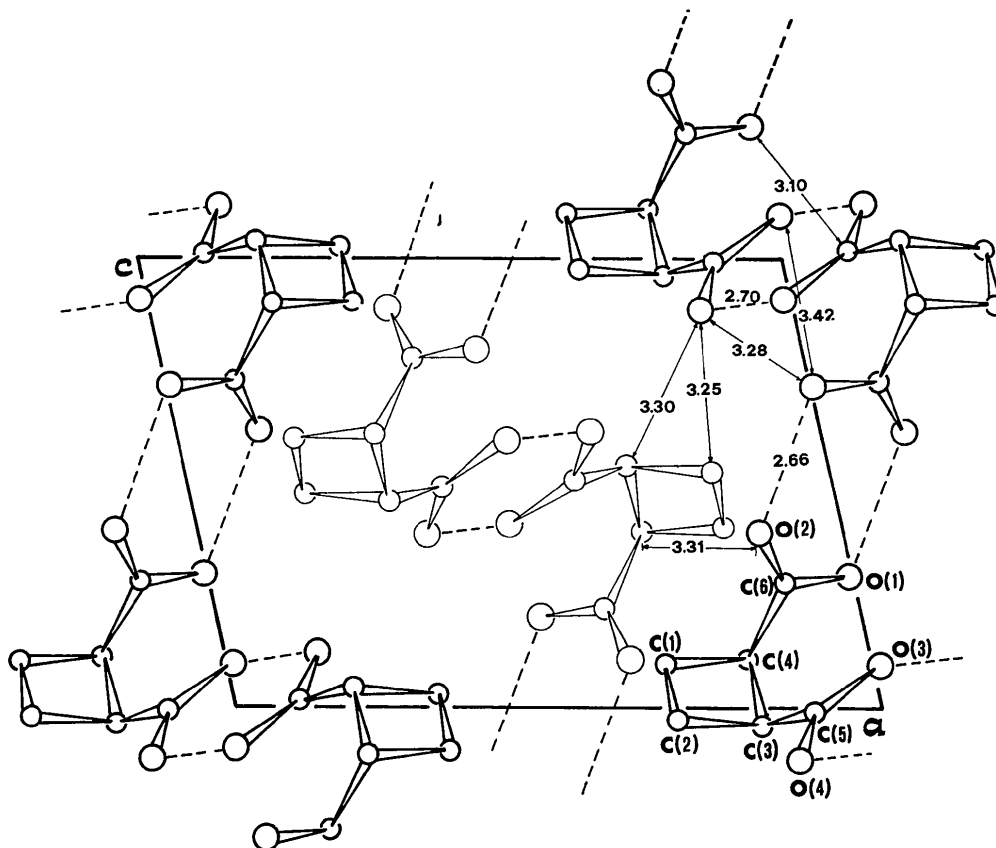


Fig. 2. Mode of packing of the molecules along the **b** direction. Some of the shortest intermolecular contacts are reported. Hydrogen bonds are indicated with a dashed line.

Table 3. Bond lengths, bond angles and torsion angles

(a) Bond lengths in Å (e.s.d.'s in units of the last significant figure)

O(1)-C(6)	1.308 (5)	C(3)-C(5)	1.497 (6)
O(2)-C(6)	1.237 (6)	C(4)-C(6)	1.495 (6)
O(3)-C(5)	1.218 (6)	C(1)-HC(1)	1.00 (6)
O(4)-C(5)	1.311 (6)	C(2)-HC(2)	0.96 (6)
C(1)-C(2)	1.319 (7)	C(3)-HC(3)	1.01 (7)
C(1)-C(4)	1.515 (6)	C(4)-HC(4)	0.99 (6)
C(2)-C(3)	1.507 (6)	O(1)-HO(1)	0.78 (7)
C(3)-C(4)	1.578 (6)	O(4)-HO(4)	0.97 (7)

(b) Bond angles in degrees

O(1)-C(6)-O(2)	122.6 (4)	C(4)-C(1)-C(2)	94.9 (4)
O(3)-C(5)-O(4)	123.1 (4)	C(6)-O(1)-HO(1)	111 (5)
O(1)-C(6)-C(4)	115.3 (4)	C(5)-O(4)-HO(4)	111 (4)
O(2)-C(6)-C(4)	122.0 (4)	C(4)-C(1)-HC(1)	137 (4)
O(3)-C(5)-C(3)	125.4 (4)	C(2)-C(1)-HC(1)	128 (4)
O(4)-C(5)-C(3)	111.5 (4)	C(3)-C(2)-HC(2)	134 (4)
C(6)-C(4)-C(1)	117.5 (4)	C(1)-C(2)-HC(2)	132 (4)
C(6)-C(4)-C(3)	119.9 (4)	C(6)-C(4)-HC(4)	105 (4)
C(5)-C(3)-C(4)	120.2 (4)	C(1)-C(4)-HC(4)	112 (4)
C(5)-C(3)-C(2)	116.6 (4)	C(2)-C(4)-HC(4)	123 (4)
C(1)-C(2)-C(3)	94.9 (4)	C(5)-C(3)-HC(3)	104 (4)
C(2)-C(3)-C(4)	85.4 (3)	C(4)-C(3)-HC(3)	114 (4)
C(3)-C(4)-C(1)	84.8 (3)	C(2)-C(3)-HC(3)	117 (4)

(c) Internal rotation angles in degrees

O(2)-C(6)-C(4)-C(1)	-14
O(2)-C(6)-C(4)-C(3)	86
O(1)-C(6)-C(4)-C(1)	164
O(1)-C(6)-C(4)-C(3)	264
C(6)-C(4)-C(1)-C(2)	122
C(6)-C(4)-C(3)-C(2)	240
C(4)-C(1)-C(2)-C(3)	-1
C(4)-C(3)-C(5)-O(3)	25
C(4)-C(3)-C(2)-C(1)	1
C(4)-C(3)-C(5)-O(4)	204
C(1)-C(4)-C(3)-C(2)	-1
C(1)-C(2)-C(3)-C(5)	240
C(1)-C(4)-C(3)-C(5)	117
C(2)-C(1)-C(4)-C(3)	1
C(2)-C(3)-C(5)-O(3)	126
C(2)-C(3)-C(5)-O(4)	-55
C(5)-C(3)-C(4)-C(6)	-2

One of us (J.P.D.) is indebted to the Fonds National de la Recherche Scientifique for a research fellowship.

References

- ADMAN, E. & MARGULIS, T. N. (1968). *J. Amer. Chem. Soc.* **90**, 4717-4521.
 BENEDETTI, E., CLAVERINI, R. & PEDONE, C. (1973). *Gazz. Chim. Ital.* **103**, 525-535.
 BENEDETTI, E., CORRADINI, P. & PEDONE, C. (1970). *Acta Cryst.* **B26**, 493-498.
 BENEDETTI, E., CORRADINI, P. & PEDONE, C. (1972). *J. Phys. Chem.* **76**, 790-797.

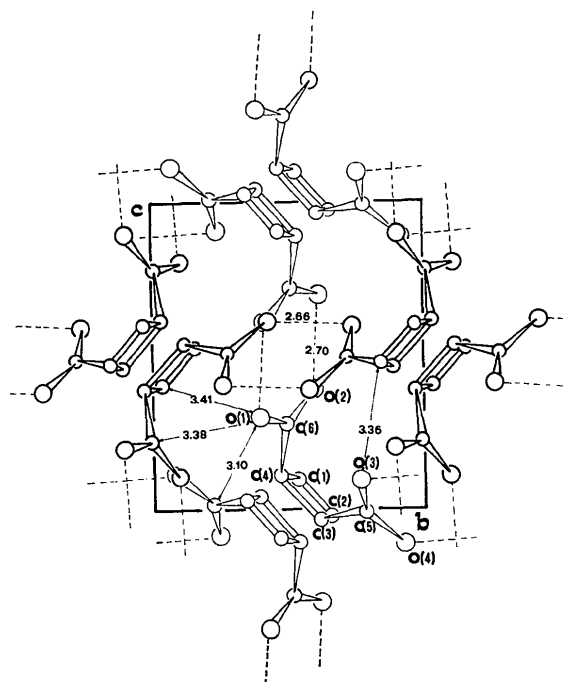


Fig. 3. Mode of packing of the molecules along the a direction. Some of the shortest intermolecular contacts are reported. Hydrogen bonds are indicated with a dashed line.

- BÜRGI, H. B. & DUNITZ, J. D. (1968). *Helv. Chim. Acta*, **51** 1514-1526.
 CORRADINI, P. (1960). *Atti Accad. Nazl. Lincei, Rend. Classe. Sci. Fis. Mat. Nat.* **24**, 8-17.
 DECLERQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* **A29**, 231.
 DUNITZ, J. D. & SCHOMAKER, V. (1952). *J. Chem. Phys.* **20**, 1703-1709.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368-376.
 GOLDISH, E., HEDBERG, K. & SCHOMAKER, V. (1956). *J. Amer. Chem. Soc.* **78**, 2714-2716.
 GREENBERG, B. & POST, B. (1968). *Acta Cryst.* **B24**, 918-924.
 KARLE, I. L. & BRITTS, K. (1965). *Z. Kristallogr.* **121**, 190-203.
 KARLE, I. L., BRITTS, K. & BRENNER, S. (1964). *Acta Cryst.* **18**, 1506-1510.
 LEMAIN, H. P. & LIVINGSTON, R. L. (1952). *J. Amer. Chem. Soc.* **74**, 5732-5736.
 OWEN, T. B. & HOARD, J. L. (1951). *Acta Cryst.* **4**, 172-176.
 PEDONE, C., BENEDETTI, E. & ALLEGRA, G. (1970). *Acta Cryst.* **B26**, 933-937.
 WONG, C., MARSH, R. E. & SCHOMAKER, V. (1964). *Acta Cryst.* **17**, 131-137.