# The Crystal Structure of *trans*-1,2-Cyclobutanedicarboxylic Acid

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*trans*-1,2-Cyclobutanedicarboxylic acid, $C_6H_8O_4$, crystallizes in the monoclinic system; the space group is $C2/c$ with $a = 5 \cdot 52$, $b = 10 \cdot 74$, $c = 11 \cdot 90$ Å, $\beta = 90° 55'$. There are four molecules per unit cell. The crystal structure has been determined from counter data with the use of close-packing criteria. The cyclobutane ring is found to be puckered with a dihedral angle near $150°$. The structure consists of rows of molecules in the $a - c$ directions. The ketonic oxygen atom is synplanar with respect to a C–C bond of the ring.

## Introduction

Recently, considerable attention has been given to the study of the structure of four-membered rings. According to a number of different researches, the non-planar conformation of these rings is more favorable than the planar conformation. Several cyclobutane rings in simple derivatives have been found to be planar; these include tetraphenylcyclobutane (Dunitz, 1949), octahydroxycyclobutane (Bock, 1967), *trans*-1,3-cyclobutanedicarboxylic acid (Margulis & Fisher, 1967), and tetracyanocyclobutane (Greenberg & Post, 1968). It is worth noting that all of these molecules have a center of symmetry which is retained in the crystal state as a crystallographic element of symmetry. On the other hand, puckered cyclobutane rings have also been reported in the crystalline state for molecules such as octachlorocyclobutane (Owen & Hoard, 1951), the *cis* and *trans* isomers of 1,2-dibromo-1,2-dimethoxy-carbonylcyclobutane (Karle, Karle & Britts, 1966) and *cis*-1,3 and *cis*-1,2-cyclobutanedicarboxylic acid (Adman & Margulis, 1967 and Van der Helm, Sims & Seigler, 1967 respectively). An interesting case has recently been described for the disodium salt of *trans*-1,3-cyclobutanedicarboxylic acid (Adman & Margulis, 1968) which crystallizes with two neutral acid molecules of crystallization. The neutral acid, previously found to have a planar conformation when crystallized by itself, is now found to be puckered while the dianion of the acid has a planar ring.

A rather large number of studies have been devoted to the investigation of the structure of cyclobutane by other techniques such as infrared and Raman spectra. The vibrational spectra of $C_4H_8$ (Wilson, 1943; Rathjens, Freeman, Gwinn & Pitzer, 1953; Schaffer, 1961; Krainov, Prokofiev & Sverdlov, 1964; Aleksanyan, Kuziyants, Lukina, Zotova & Vostokova, 1968) and $C_4D_8$ (Lord & Nakagawa, 1963) have been inten-

sively studied. The results of such studies show better agreement with the non-planar model for the cyclobutane ring, but the final conclusions depend to a marked extent on the adequacy of the interpretation of the spectrum of the fundamental vibrations of the molecule.

To gain more information on the structure of cyclic compounds in the crystalline state we have recently undertaken a systematic study on the conformation of dicarboxylic acids of cyclohexanes (Benedetti, Corradini, Pedone & Post, 1968, 1969) cyclopentanes and cyclobutanes. We now report on the crystal structure of *trans*-1,2-cyclobutanedicarboxylic acid.

## Experimental

Single crystals of *trans*-1,2-cyclobutanedicarboxylic acid, $C_6H_8O_4$, suitable for X-ray diffraction analysis were kindly provided by Dr R. F. Winter. From the irregularly shaped crystal ($0 \cdot 2 \times 0 \cdot 3 \times 0 \cdot 6$ mm) selected for this investigation, preliminary Weissenberg photographs taken with Cu $K\alpha$ radiation indicate the monoclinic system with $C2/c$ or $Cc$ as possible space groups (extinctions of $hkl$ reflections for $h + k = 2n + 1$ and $h0l$ for $h = 2n + 1$ and $l = 2n + 1$). The crystal was carefully centered on a Picker four circle automated diffractometer equipped with a PDP-8 digital computer. The unit-cell parameters were determined from a least-square fitting of the setting angles $(2\theta, \omega, \chi)$ of twelve high angle reflections $(2\theta > 90°)$. The parameters obtained are reported in Table 1. The density calculated, $d_{calc} = 1 \cdot 36$ g.cm$^{-3}$ on the basis of four molecules per unit cell (M.W. $= 144 \cdot 13$) agreed reasonably well with the experimental value $d_{exp} = 1 \cdot 35$ g.cm$^{-3}$ (flotation method).

Integrated intensities were measured with the $\theta$–$2\theta$ scan mode using Ni-filtered Cu $K\alpha$ radiation ($\alpha = 1 \cdot 5418$ Å), pulse height analysis to reduce unwanted background and a scintillation counter. A scan range of $1 \cdot 67°$ was found to be sufficient in the range of $2\theta$ examined ($0$–$130°$) with a scan speed of $1°$ min$^{-1}$. The

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## Table 1. *Crystal data*

*trans*-1,2-Cyclobutanedicarboxylic acid, $C_6H_8O_4$, M.W. 144·13.
Monoclinic, space group $C2/c$, $Z=4$, $F(000)=304$

$$a= 5·519 \pm 0·004 \text{ Å}$$
$$b=11·899 \pm 0·006$$
$$c=10·742 \pm 0·006$$
$$\beta=90°\,55' \pm 10'$$
$$d_{calc}=1·36 \text{ g.cm}^{-3}$$

take-off angle of the tube was 3·0° and a counter aperture, 4·0×4·0 mm, was placed 30 cm from the crystal. Two stationary-crystal stationary-counter background counts of 10 sec were taken at the two ends of each scan. A total of 553 non-zero independent reflections were collected. One standard reflection was measured every 20 reflections (every 45 min) during data collection in order to check the electronic stability of the instrument and any deterioration of the crystal. The fluctuations in the intensity of this reflection were within 4% over the data collection time (20 hours). The integrated intensities from which the background counts were subtracted were then corrected for the Lorentz and polarization effects in the usual way.

## Structure determination

The structure was determined by a relatively straightforward application of the close-packing criteria that we have used in recent studies (Benedetti, Corradini, Pedone & Post, 1968, 1969). The presence in the lattice of hydrogen-bonded rows of molecules with the hydrogen bonds across symmetry centers between carboxyl groups of different molecules was the starting assumption. Thus, the occurrence of 4 molecules in the

$C2/c$ space group which requires that the $C_2$ symmetry of the molecule should be retained in the structure as a crystallographic element of symmetry, dictates that three translations: $c$, $a+c$ or $a-c$ could be compatible with the identity period of the row. The choice was made on the basis of packing considerations; in fact only the $a-c$ possibility gave rise to acceptable van der Waals contacts between atoms of neighboring molecules. The starting planar model after four cycles of full-matrix isotropic least-square refinement, brought the reliability index $R$

$$(R=\sum ||F_o| - |F_c||/\sum |F_o|)$$

from 40 to 17%. The introduction of anisotropic temperature factors resulted in a decrease of the $R$ index to 12%. The hydrogen atoms were then introduced in their sterically expected positions ($d_{C-H}=$ 1·08 Å, $d_{O-H}=1·00$ Å, H–C–H = 109·5°, C–O–H = 120°). Their atomic parameters were held fixed and the isotropic temperature factor was assigned equal to the average of the $B_{ii}$ values of the carbon atom to which the hydrogen atom is bonded. Two additional cycles of full-matrix least-squares gave an $R$ index of 0·088 for the 553 measured reflections. At this point the maximum shifts of either positional or thermal parameters for the heavy atoms were smaller than $\frac{1}{5}$ of the corresponding standard deviation. The weighting scheme suggested by Cruickshank (Cruickshank & Pilling, 1961):

$$w(hkl) = 1/[aF_o^2(hkl) + bF_o(hkl) + c] ,$$

was adopted in the final stage of the least-square refinement process. A list of the observed and calculated structure factors (×10) is reported in Table 2. In Table 3 the fractional coordinates and the thermal
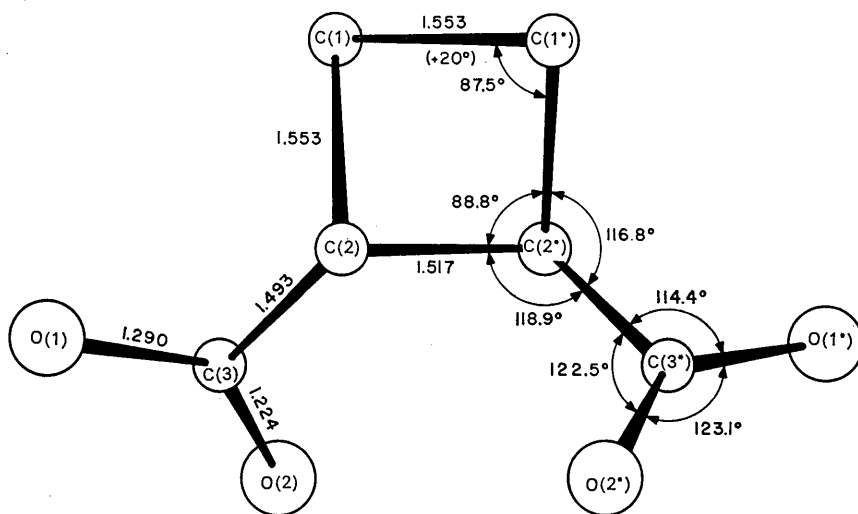


Fig. 1. Molecular model of *trans*-1,2-cyclobutanedicarboxylic acid. Bond lengths (in Å) and angles (in degrees) are reported; their average standard deviations are 0·004 Å and 0·2° respectively. The average internal rotation angle in the ring is also indicated for C(2)–C(1)–C(1*)–C(2*).

Table 2. *Observed and calculated structure factors* ($\times 10$)

| H | K | L | FO | FC |
|---|---|---|---|---|
| 0 | 0 | 0 | **** | 3040 |
| 0 | 2 | 0 | 131 | -136 |
| 0 | 4 | 0 | 524 | -520 |
| 0 | 6 | 0 | 327 | -274 |
| 0 | 8 | 0 | 12 | -11 |
| 0 | 10 | 0 | 87 | -79 |
| 0 | 12 | 0 | 22 | 17 |
| 0 | 12 | 1 | 51 | -50 |
| 0 | 10 | 1 | 63 | 61 |
| 0 | 8 | 1 | 44 | 43 |
| 0 | 6 | 1 | 36 | -27 |
| 0 | 4 | 1 | 228 | -206 |
| 0 | 2 | 1 | 516 | 576 |
| 0 | 0 | 2 | 279 | -269 |
| 0 | 2 | 2 | 558 | -651 |
| 0 | 4 | 2 | 71 | 63 |
| 0 | 6 | 2 | 230 | 231 |
| 0 | 8 | 2 | 189 | 187 |
| 0 | 12 | 2 | 57 | -56 |
| 0 | 10 | 2 | 40 | 41 |
| 0 | 12 | 3 | 31 | -33 |
| 0 | 10 | 3 | 108 | 107 |
| 0 | 8 | 3 | 33 | -33 |
| 0 | 6 | 3 | 123 | -120 |
| 0 | 4 | 3 | 390 | -407 |
| 0 | 2 | 3 | 641 | 751 |
| 0 | 0 | 4 | 355 | -358 |
| 0 | 2 | 4 | 522 | 520 |
| 0 | 4 | 4 | 86 | 92 |
| 0 | 6 | 4 | 194 | -181 |
| 0 | 8 | 4 | 207 | -205 |
| 0 | 10 | 4 | 57 | 51 |
| 0 | 12 | 4 | 28 | 28 |
| 0 | 8 | 5 | 111 | -116 |
| 0 | 6 | 5 | 86 | 88 |
| 0 | 4 | 5 | 117 | 105 |
| 0 | 2 | 5 | 196 | 173 |
| 0 | 0 | 6 | 652 | -670 |
| 0 | 2 | 6 | 161 | 169 |
| 0 | 4 | 6 | 52 | 55 |
| 0 | 6 | 6 | 105 | 101 |
| 0 | 8 | 6 | 23 | -33 |
| 0 | 10 | 6 | 7 | 4 |
| 0 | 10 | 7 | 13 | -11 |
| 0 | 8 | 7 | 6 | 4 |
| 0 | 6 | 7 | 5 | 8 |
| 0 | 4 | 7 | 49 | 35 |
| 0 | 2 | 7 | 303 | -297 |
| 0 | 2 | 8 | 20 | -22 |
| 0 | 4 | 8 | 25 | -33 |
| 0 | 6 | 8 | 64 | 65 |
| 0 | 8 | 8 | 19 | 24 |
| 0 | 10 | 8 | 81 | -70 |
| 0 | 8 | 9 | 55 | 50 |
| 0 | 6 | 9 | 17 | -23 |
| 0 | 4 | 9 | 89 | 95 |
| 0 | 0 | 10 | 161 | 161 |
| 0 | 2 | 10 | 64 | -61 |
| 0 | 4 | 10 | 23 | 23 |
| 0 | 6 | 10 | 38 | -40 |
| 0 | 8 | 10 | 16 | 15 |
| 0 | 6 | 11 | 18 | -18 |
| 0 | 4 | 11 | 45 | -38 |
| 0 | 2 | 11 | 23 | -31 |
| 0 | 2 | 12 | 53 | -58 |
| 0 | 4 | 12 | 43 | 38 |
| 0 | 6 | 12 | 16 | -17 |
| 0 | 4 | 13 | 7 | -8 |
| 0 | 2 | 13 | 16 | -14 |
| -1 | 1 | 13 | 2 | -4 |
| -1 | 3 | 13 | 88 | -81 |
| -1 | 5 | 12 | 112 | 99 |
| -1 | 3 | 12 | 8 | 4 |
| -1 | 1 | 12 | 127 | -114 |
| -1 | 1 | 11 | 28 | 17 |
| -1 | 3 | 11 | 57 | 56 |
| -1 | 5 | 11 | 15 | -14 |
| -1 | 7 | 10 | 83 | -76 |
| -1 | 5 | 10 | 12 | 2 |
| -1 | 3 | 10 | 12 | 13 |
| -1 | 1 | 10 | 101 | 89 |
| -1 | 1 | 9 | 90 | -76 |
| -1 | 3 | 9 | 211 | 190 |
| -1 | 5 | 9 | 69 | -72 |
| -1 | 9 | 9 | 48 | -43 |
| -1 | 9 | 9 | 16 | -11 |
| -1 | 9 | 8 | 22 | 16 |
| -1 | 7 | 8 | 120 | 115 |
| -1 | 5 | 8 | 42 | -19 |
| -1 | 3 | 8 | 11 | 9 |
| -1 | 1 | 8 | 133 | -120 |
| -1 | 1 | 7 | 159 | -135 |
| -1 | 3 | 7 | 116 | 92 |
| -1 | 5 | 7 | 102 | -84 |
| -1 | 7 | 7 | 17 | 4 |
| -1 | 9 | 7 | 15 | 5 |
| -1 | 11 | 6 | 49 | 39 |
| -1 | 9 | 6 | 14 | -25 |
| -1 | 7 | 6 | 96 | 15 |
| -1 | 5 | 6 | 281 | -245 |
| -1 | 3 | 6 | 179 | 153 |
| -1 | 1 | 6 | 130 | 103 |
| -1 | 1 | 5 | 379 | 341 |
| -1 | 3 | 5 | 54 | 34 |
| -1 | 5 | 5 | 72 | 12 |
| -1 | 7 | 5 | 35 | -17 |
| -1 | 7 | 5 | 37 | -13 |
| -1 | 11 | 5 | 21 | -14 |
| -1 | 11 | 4 | 20 | 8 |
| -1 | 9 | 4 | 37 | 12 |
| -1 | 7 | 4 | 80 | 77 |
| -1 | 5 | 4 | 194 | -174 |
| -1 | 3 | 4 | 80 | -45 |
| -1 | 1 | 4 | 180 | 146 |
| -1 | 1 | 3 | 368 | 333 |
| -1 | 3 | 3 | 551 | -528 |
| -1 | 5 | 3 | 121 | 98 |
| -1 | 7 | 3 | 36 | 39 |
| -1 | 9 | 3 | 51 | 38 |
| -1 | 11 | 3 | 27 | -19 |
| -1 | 11 | 2 | 65 | -63 |
| -1 | 9 | 2 | 74 | 61 |
| -1 | 7 | 2 | 160 | 133 |
| -1 | 5 | 2 | 201 | 162 |
| -1 | 3 | 2 | 469 | -437 |
| -1 | 1 | 2 | 364 | -322 |
| -1 | 1 | 1 | 449 | -429 |
| -1 | 5 | 1 | 328 | 317 |
| -1 | 7 | 1 | 87 | 85 |
| -1 | 9 | 1 | 61 | -60 |
| -1 | 11 | 1 | 9 | -1 |
| 1 | 9 | 0 | 35 | -27 |
| 1 | 7 | 0 | 365 | -352 |
| 1 | 5 | 0 | 113 | 109 |
| 1 | 1 | 0 | 428 | 447 |
| 1 | 1 | 1 | 574 | 649 |
| 1 | 3 | 1 | 183 | -173 |
| 1 | 5 | 1 | 79 | -52 |
| 1 | 7 | 1 | 34 | -18 |
| 1 | 9 | 1 | 103 | 100 |
| 1 | 11 | 1 | 20 | -15 |
| 1 | 11 | 2 | 27 | 30 |
| 1 | 9 | 2 | 84 | 85 |
| 1 | 7 | 2 | 43 | -39 |
| 1 | 5 | 2 | 426 | 419 |
| 1 | 3 | 2 | 326 | 333 |
| 1 | 1 | 2 | 797 | -1048 |
| 1 | 1 | 3 | 132 | 87 |
| 1 | 3 | 3 | 460 | -455 |
| 1 | 5 | 3 | 274 | 298 |
| 1 | 7 | 3 | 27 | -27 |
| 1 | 9 | 3 | 79 | -89 |
| 1 | 11 | 3 | 26 | 21 |
| 1 | 11 | 4 | 45 | 39 |
| 1 | 9 | 4 | 132 | -131 |
| 1 | 7 | 4 | 112 | -114 |
| 1 | 5 | 4 | 178 | -171 |
| 1 | 3 | 4 | 283 | 286 |
| 1 | 1 | 4 | 220 | 189 |
| 1 | 1 | 5 | 318 | -293 |
| 1 | 3 | 5 | 160 | -170 |
| 1 | 5 | 5 | 252 | 257 |
| 1 | 7 | 5 | 101 | 102 |
| 1 | 9 | 5 | 117 | -115 |
| 1 | 11 | 5 | 8 | 9 |
| 1 | 11 | 6 | 26 | -23 |
| 1 | 7 | 6 | 311 | 317 |
| 1 | 5 | 6 | 102 | -95 |
| 1 | 3 | 6 | 200 | -187 |
| 1 | 1 | 6 | 64 | -43 |
| 1 | 1 | 7 | 160 | -155 |
| 1 | 3 | 7 | 37 | 25 |
| 1 | 5 | 7 | 187 | -193 |
| 1 | 7 | 7 | 56 | 63 |
| 1 | 9 | 7 | 34 | 33 |
| 1 | 9 | 8 | 15 | -16 |
| 1 | 7 | 8 | 18 | 16 |
| 1 | 5 | 8 | 126 | -137 |
| 1 | 3 | 8 | 44 | -50 |
| 1 | 1 | 8 | 212 | 208 |
| 1 | 1 | 9 | 81 | 75 |
| 1 | 3 | 9 | 202 | 210 |
| 1 | 5 | 9 | 85 | -89 |
| 1 | 9 | 9 | 43 | 38 |
| 1 | 7 | 10 | 58 | -59 |
| 1 | 5 | 10 | 26 | 30 |
| 1 | 3 | 10 | 37 | 41 |
| 1 | 1 | 10 | 78 | -70 |
| 1 | 1 | 11 | 22 | -14 |
| 1 | 3 | 11 | 42 | -47 |
| 1 | 5 | 11 | 15 | -19 |
| 1 | 7 | 11 | 47 | -43 |
| 1 | 5 | 12 | 35 | 30 |
| 1 | 3 | 12 | 25 | 22 |
| 2 | 2 | 13 | 28 | 28 |
| 2 | 0 | 12 | 122 | 113 |
| 2 | 4 | 12 | 27 | -27 |
| 2 | 6 | 11 | 24 | 29 |
| 2 | 4 | 11 | 14 | -12 |
| 2 | 2 | 11 | 151 | -151 |
| 2 | 0 | 10 | 125 | -112 |
| 2 | 2 | 10 | 93 | -96 |
| 2 | 4 | 10 | 115 | 119 |
| 2 | 4 | 9 | 127 | 124 |
| 2 | 2 | 9 | 18 | 11 |
| 2 | 0 | 8 | 45 | -19 |
| 2 | 2 | 8 | 87 | 80 |
| 2 | 4 | 8 | 129 | 136 |
| 2 | 6 | 8 | 142 | -143 |
| 2 | 8 | 8 | 71 | -72 |
| 2 | 8 | 7 | 68 | 73 |
| 2 | 6 | 7 | 172 | -178 |
| 2 | 4 | 7 | 29 | -26 |
| 2 | 2 | 7 | 130 | 133 |
| 2 | 0 | 6 | 250 | -224 |
| 2 | 4 | 6 | 86 | -102 |
| 2 | 6 | 6 | 101 | 115 |
| 2 | 8 | 6 | 92 | 95 |
| 2 | 10 | 6 | 12 | -10 |
| 2 | 8 | 5 | 28 | 26 |
| 2 | 6 | 5 | 47 | -58 |
| 2 | 4 | 5 | 37 | -37 |
| 2 | 2 | 5 | 210 | 216 |
| 2 | 0 | 4 | 361 | 311 |
| 2 | 2 | 4 | 307 | 304 |
| 2 | 4 | 4 | 354 | -370 |
| 2 | 8 | 4 | 29 | -35 |
| 2 | 10 | 4 | 27 | -31 |
| 2 | 10 | 3 | 9 | 7 |
| 2 | 8 | 3 | 125 | -134 |
| 2 | 6 | 3 | 158 | 168 |
| 2 | 4 | 3 | 68 | -50 |
| 2 | 2 | 3 | 24 | -22 |
| 2 | 2 | 2 | 102 | -100 |
| 2 | 4 | 2 | 105 | -112 |
| 2 | 6 | 2 | 87 | 89 |
| 2 | 8 | 2 | 64 | 65 |
| 2 | 10 | 2 | 50 | 50 |
| 2 | 10 | 1 | 36 | 31 |
| 2 | 8 | 1 | 21 | -23 |
| 2 | 6 | 1 | 193 | 203 |
| 2 | 4 | 1 | 205 | -207 |
| 2 | 2 | 1 | 264 | -270 |
| 2 | 0 | 0 | 310 | 315 |
| 2 | 2 | 0 | 277 | -281 |
| 2 | 4 | 0 | 232 | 226 |
| 2 | 6 | 0 | 109 | -109 |
| 2 | 8 | 0 | 25 | -22 |
| 2 | 10 | 0 | 35 | 37 |
| -2 | 10 | 1 | 42 | 39 |
| -2 | 8 | 1 | 57 | -54 |
| -2 | 6 | 1 | 46 | -45 |
| -2 | 2 | 1 | 129 | 125 |
| -2 | 0 | 2 | 447 | 444 |
| -2 | 2 | 2 | 197 | -212 |
| -2 | 4 | 2 | 182 | 186 |
| -2 | 6 | 2 | 67 | -69 |
| -2 | 8 | 2 | 45 | -58 |
| -2 | 10 | 2 | 51 | -43 |
| -2 | 10 | 3 | 50 | 47 |
| -2 | 8 | 3 | 60 | -50 |
| -2 | 6 | 3 | 98 | 112 |
| -2 | 4 | 3 | 175 | -174 |
| -2 | 2 | 3 | 191 | 177 |
| -2 | 0 | 4 | 581 | -572 |
| -2 | 2 | 4 | 140 | -122 |
| -2 | 4 | 4 | 157 | 145 |
| -2 | 6 | 4 | 183 | 180 |
| -2 | 8 | 4 | 28 | 25 |
| -2 | 10 | 4 | 15 | -7 |
| -2 | 6 | 5 | 78 | 87 |
| -2 | 4 | 5 | 147 | -147 |
| -2 | 2 | 5 | 61 | 65 |
| -2 | 0 | 6 | 147 | -147 |
| -2 | 2 | 6 | 365 | 374 |
| -2 | 4 | 6 | 48 | 9 |
| -2 | 6 | 6 | 106 | -107 |
| -2 | 8 | 6 | 139 | -139 |
| -2 | 10 | 6 | 11 | 3 |
| -2 | 10 | 7 | 37 | 34 |
| -2 | 8 | 7 | 31 | 23 |
| -2 | 6 | 7 | 86 | 98 |
| -2 | 4 | 7 | 27 | 34 |
| -2 | 2 | 7 | 197 | -200 |
| -2 | 0 | 8 | 227 | -226 |
| -2 | 2 | 8 | 25 | -21 |
| -2 | 4 | 8 | 60 | -65 |
| -2 | 6 | 8 | 85 | 100 |
| -2 | 8 | 8 | 96 | 104 |
| -2 | 6 | 9 | 9 | 9 |
| -2 | 4 | 9 | 20 | -26 |
| -2 | 2 | 9 | 51 | 51 |
| -2 | 0 | 10 | 162 | -165 |
| -2 | 0 | 10 | 319 | 326 |
| -2 | 4 | 10 | 86 | -101 |
| -2 | 6 | 10 | 63 | -60 |
| -2 | 6 | 11 | 31 | -46 |
| -2 | 4 | 11 | 50 | 56 |
| -2 | 2 | 11 | 74 | 84 |
| -2 | 0 | 12 | 37 | -45 |
| -2 | 2 | 12 | 92 | -95 |
| -2 | 4 | 12 | 12 | 14 |
| -2 | 2 | 13 | 53 | 53 |
| -3 | 3 | 12 | 88 | -93 |
| -3 | 1 | 12 | 46 | 46 |
| -3 | 3 | 11 | 85 | -116 |
| -3 | 1 | 11 | 13 | 22 |
| -3 | 5 | 11 | 80 | 86 |
| -3 | 3 | 10 | 37 | 41 |
| -3 | 1 | 10 | 13 | 12 |
| -3 | 1 | 9 | 196 | -204 |
| -3 | 3 | 9 | 12 | -12 |
| -3 | 5 | 9 | 12 | -8 |
| -3 | 7 | 9 | 10 | 15 |
| -3 | 7 | 8 | 20 | 21 |
| -3 | 5 | 8 | 61 | 62 |
| -3 | 3 | 8 | 154 | 174 |
| -3 | 1 | 8 | 262 | -273 |
| -3 | 1 | 7 | 117 | 120 |
| -3 | 3 | 7 | 119 | 137 |
| -3 | 5 | 7 | 68 | -72 |
| -3 | 9 | 7 | 34 | 29 |
| -3 | 9 | 6 | 90 | -93 |
| -3 | 7 | 6 | 60 | -71 |
| -3 | 5 | 6 | 110 | -130 |
| -3 | 3 | 6 | 144 | 154 |
| -3 | 1 | 6 | 100 | 103 |
| -3 | 1 | 5 | 354 | 349 |
| -3 | 3 | 5 | 26 | -12 |
| -3 | 5 | 5 | 87 | -100 |
| -3 | 7 | 5 | 73 | -79 |
| -3 | 9 | 5 | 47 | 50 |
| -3 | 9 | 4 | 43 | 46 |
| -3 | 7 | 4 | 227 | 234 |
| -3 | 5 | 4 | 44 | 55 |
| -3 | 3 | 4 | 221 | -233 |
| -3 | 1 | 4 | 87 | -85 |
| -3 | 1 | 3 | 191 | 190 |
| -3 | 3 | 3 | 65 | -85 |
| -3 | 5 | 3 | 122 | 140 |
| -3 | 7 | 3 | 45 | -43 |
| -3 | 9 | 3 | 29 | -22 |
| -3 | 11 | 2 | 23 | -26 |
| -3 | 9 | 2 | 14 | 19 |
| -3 | 7 | 2 | 127 | -139 |
| -3 | 5 | 2 | 89 | -104 |
| -3 | 3 | 2 | 154 | -157 |
| -3 | 1 | 2 | 424 | 438 |
| -3 | 1 | 1 | 220 | -236 |
| -3 | 3 | 1 | 106 | -115 |
| -3 | 5 | 1 | 63 | 65 |
| -3 | 7 | 1 | 24 | 16 |
| -3 | 9 | 1 | 56 | -57 |
| -3 | 11 | 1 | 31 | 31 |
| 3 | 9 | 0 | 118 | 125 |
| 3 | 7 | 0 | 54 | -49 |
| 3 | 5 | 0 | 102 | -98 |
| 3 | 3 | 0 | 69 | -72 |
| 3 | 1 | 0 | 99 | -109 |
| 3 | 1 | 1 | 255 | 241 |
| 3 | 3 | 1 | 155 | -163 |
| 3 | 5 | 1 | 18 | 30 |
| 3 | 7 | 1 | 78 | -94 |
| 3 | 9 | 1 | 26 | 23 |
| 3 | 11 | 1 | 49 | 49 |
| 3 | 11 | 2 | 11 | 11 |
| 3 | 9 | 2 | 32 | -31 |
| 3 | 7 | 2 | 50 | -51 |
| 3 | 5 | 2 | 12 | 13 |
| 3 | 1 | 3 | 67 | 67 |
| 3 | 1 | 3 | 188 | 184 |
| 3 | 3 | 3 | 21 | 27 |
| 3 | 5 | 3 | 89 | 99 |
| 3 | 7 | 3 | 39 | -45 |
| 3 | 9 | 3 | 64 | -60 |
| 3 | 9 | 4 | 64 | -77 |
| 3 | 7 | 4 | 56 | 60 |
| 3 | 5 | 4 | 39 | -29 |
| 3 | 3 | 4 | 64 | 64 |
| 3 | 1 | 4 | 41 | -46 |
| 3 | 1 | 5 | 25 | -20 |
| 3 | 3 | 5 | 20 | 19 |
| 3 | 5 | 5 | 76 | -93 |
| 3 | 7 | 5 | 46 | 49 |
| 3 | 9 | 5 | 9 | 7 |
| 3 | 9 | 6 | 23 | -26 |
| 3 | 7 | 6 | 46 | 48 |
| 3 | 3 | 6 | 85 | 86 |
| 3 | 1 | 6 | 133 | -130 |
| 3 | 1 | 7 | 108 | -104 |
| 3 | 3 | 7 | 32 | 41 |
| 3 | 5 | 7 | 27 | -28 |
| 3 | 7 | 7 | 28 | 39 |
| 3 | 9 | 7 | 15 | -20 |
| 3 | 7 | 8 | 46 | -53 |
| 3 | 5 | 8 | 24 | -18 |
| 3 | 3 | 8 | 47 | 56 |
| 3 | 1 | 8 | 32 | 17 |
| 3 | 1 | 9 | 8C | -86 |
| 3 | 5 | 9 | 58 | 61 |
| 3 | 7 | 9 | 13 | 12 |
| 3 | 5 | 10 | 21 | 17 |
| 3 | 3 | 10 | 64 | -71 |
| 3 | 1 | 10 | 7 | 3 |
| 3 | 3 | 11 | 8 | -4 |
| 3 | 1 | 11 | 40 | -47 |
| 4 | 0 | 10 | 65 | 67 |
| 4 | 2 | 10 | 44 | 52 |
| 4 | 4 | 9 | 26 | -29 |
| 4 | 2 | 9 | 22 | 17 |
| 4 | 0 | 8 | 12 | 9 |
| 4 | 2 | 8 | 17 | -21 |
| 4 | 4 | 8 | 26 | 24 |
| 4 | 6 | 8 | 29 | -30 |
| 4 | 4 | 7 | 27 | -22 |
| 4 | 6 | 7 | 69 | 73 |
| 4 | 2 | 7 | 24 | 22 |
| 4 | 0 | 6 | 21 | -7 |
| 4 | 4 | 6 | 78 | 69 |
| 4 | 4 | 6 | 5 | -6 |
| 4 | 6 | 6 | 64 | -67 |
| 4 | 8 | 6 | 6 | 4 |
| 4 | 8 | 5 | 70 | 70 |
| 4 | 6 | 5 | 50 | -46 |
| 4 | 4 | 5 | 105 | -103 |
| 4 | 2 | 5 | 12 | -8 |
| 4 | 0 | 4 | 76 | -72 |
| 4 | 2 | 4 | 22 | 17 |
| 4 | 4 | 4 | 120 | -117 |
| 4 | 6 | 4 | 90 | 95 |
| 4 | 8 | 4 | 60 | 52 |
| 4 | 8 | 3 | 17 | -14 |
| 4 | 6 | 3 | 96 | 97 |
| 4 | 2 | 3 | 49 | 47 |
| 4 | 0 | 2 | 182 | 142 |
| 4 | 2 | 2 | 84 | 77 |
| 4 | 4 | 2 | 101 | -100 |
| 4 | 6 | 2 | 40 | 46 |
| 4 | 2 | 2 | 64 | -69 |
| 4 | 8 | 1 | 92 | -90 |
| 4 | 6 | 1 | 121 | 122 |
| 4 | 4 | 1 | 49 | -52 |
| 4 | 2 | 1 | 187 | -204 |
| 4 | 0 | 0 | 258 | -221 |
| 4 | 2 | 0 | 149 | -173 |
| 4 | 4 | 0 | 162 | 174 |
| 4 | 6 | 0 | 61 | 67 |
| 4 | 8 | 0 | 11 | 13 |
| -4 | 8 | 1 | 39 | 40 |
| -4 | 6 | 1 | 38 | -37 |
| -4 | 4 | 1 | 68 | -77 |
| -4 | 2 | 1 | 6 | 6 |
| -4 | 0 | 2 | 87 | 83 |
| -4 | 2 | 2 | 31 | 12 |
| -4 | 4 | 2 | 210 | 220 |
| -4 | 6 | 2 | 189 | -198 |
| -4 | 8 | 2 | 113 | -113 |
| -4 | 8 | 3 | 59 | -60 |
| -4 | 6 | 3 | 176 | 181 |
| -4 | 4 | 3 | 9 | -7 |
| -4 | 2 | 3 | 191 | -165 |
| -4 | 0 | 4 | 46 | -59 |
| -4 | 2 | 4 | 120 | -107 |
| -4 | 6 | 4 | 62 | 66 |
| -4 | 8 | 4 | 80 | 82 |
| -4 | 8 | 5 | 69 | -65 |
| -4 | 6 | 5 | 104 | 110 |
| -4 | 4 | 5 | 42 | -49 |
| -4 | 2 | 5 | 117 | -118 |
| -4 | 0 | 6 | 203 | 180 |
| -4 | 2 | 6 | 118 | 105 |
| -4 | 4 | 6 | 215 | -210 |
| -4 | 6 | 6 | 21 | 19 |
| -4 | 8 | 6 | 12 | 15 |
| -4 | 6 | 7 | 25 | -27 |
| -4 | 4 | 7 | 19 | -14 |
| -4 | 2 | 7 | 118 | 107 |
| -4 | 0 | 8 | 57 | -48 |
| -4 | 2 | 8 | 82 | 65 |
| -4 | 4 | 8 | 89 | -82 |
| -4 | 6 | 8 | 19 | 26 |
| -4 | 2 | 9 | 69 | 59 |
| -4 | 0 | 10 | 104 | -80 |
| -4 | 4 | 10 | 60 | 50 |
| -5 | 1 | 9 | 40 | -42 |
| -5 | 3 | 8 | 16 | 13 |
| -5 | 1 | 8 | 59 | 44 |
| -5 | 1 | 7 | 28 | -28 |
| -5 | 3 | 7 | 66 | -56 |
| -5 | 5 | 7 | 34 | 37 |
| -5 | 5 | 6 | 9 | 5 |
| -5 | 3 | 6 | 33 | 35 |
| -5 | 1 | 6 | 70 | -57 |
| -5 | 1 | 5 | 56 | 42 |
| -5 | 3 | 5 | 72 | -69 |
| -5 | 5 | 5 | 73 | 73 |
| -5 | 7 | 4 | 42 | -46 |
| -5 | 5 | 4 | 54 | 61 |
| -5 | 3 | 4 | 79 | 77 |
| -5 | 1 | 4 | 105 | -99 |
| -5 | 1 | 3 | 125 | 112 |
| -5 | 3 | 3 | 111 | 13 |
| -5 | 5 | 3 | 38 | -37 |
| -5 | 7 | 3 | 12 | -11 |
| -5 | 7 | 2 | 76 | -81 |
| -5 | 5 | 2 | 28 | 21 |
| -5 | 1 | 2 | 51 | 51 |
| -5 | 3 | 2 | 73 | 62 |
| -5 | 3 | 1 | 95 | 101 |
| -5 | 5 | 1 | 110 | -119 |
| 5 | 7 | 0 | 77 | 84 |
| 5 | 5 | 0 | 35 | 34 |
| 5 | 3 | 0 | 140 | -150 |
| 5 | 1 | 0 | 32 | 29 |
| 5 | 1 | 1 | 86 | 82 |
| 5 | 3 | 1 | 68 | -83 |
| 5 | 5 | 2 | 22 | -17 |
| 5 | 7 | 1 | 9 | -7 |
| 5 | 5 | 2 | 67 | -76 |
| 5 | 1 | 2 | 36 | -38 |
| 5 | 3 | 3 | 149 | 135 |
| 5 | 5 | 3 | 169 | 138 |
| 5 | 3 | 3 | 75 | 82 |
| 5 | 5 | 3 | 52 | -54 |
| 5 | 7 | 3 | 15 | 12 |
| 5 | 5 | 4 | 21 | 25 |
| 5 | 3 | 4 | 70 | 61 |
| 5 | 1 | 4 | 129 | -104 |
| 5 | 1 | 5 | 35 | -33 |
| 5 | 5 | 5 | 57 | -62 |
| 5 | 5 | 6 | 24 | -24 |
| 5 | 3 | 6 | 87 | 77 |
| 5 | 1 | 7 | 57 | -46 |
| 5 | 3 | 7 | 50 | 51 |
| 5 | 3 | 8 | 32 | -33 |
| 5 | 1 | 8 | 27 | -24 |
| 6 | 0 | 4 | 105 | -99 |
| 6 | 2 | 4 | 8 | 8 |
| 6 | 0 | 2 | 70 | -63 |
| 6 | 2 | 2 | 39 | 43 |
| 6 | 4 | 2 | 17 | 21 |
| 6 | 4 | 1 | 25 | -27 |
| 6 | 2 | 1 | 67 | 79 |
| 6 | 0 | 0 | 28 | 21 |
| 6 | 2 | 0 | 12 | -16 |
| 6 | 4 | 0 | 9 | -8 |
| -6 | 4 | 1 | 23 | 18 |
| -6 | 0 | 2 | 21 | -23 |
| -6 | 2 | 2 | 82 | 83 |
| -6 | 4 | 2 | 60 | -49 |
| -6 | 4 | 2 | 7 | -12 |
| -6 | 4 | 3 | 52 | -47 |
| -6 | 0 | 4 | 90 | 75 |

Table 3. *Atomic parameters*

E.s.d.'s in units of the last digit are given in parentheses.

(a) Positional parameters

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| C(1) | 0·1024 (11) | 0·0747 (4) | 0·2060 (5) |
| C(2) | 0·1271 (6) | −0·0676 (3) | 0·2266 (3) |
| C(3) | 0·1791 (6) | −0·1466 (3) | 0·1266 (3) |
| O(1) | 0·3888 (5) | −0·1277 (3) | 0·0833 (2) |
| O(2) | 0·0333 (6) | −0·2221 (3) | 0·0886 (2) |
| H(1)C(1)† | 0·260 | 0·129 | 0·230 |
| H(2)C(1) | 0·044 | 0·101 | 0·122 |
| H(1)C(2) | 0·259 | −0·085 | 0·292 |
| H(1)O(1) | 0·441 | −0·177 | 0·016 |

(b) Anisotropic thermal parameters (Å²)

$$T = \exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right].$$

| | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| C(1) | 7·8 (3) | 3·9 (2) | 6·4 (2) | −0·5 (1) | 2·7 (2) | −0·4 (1) |
| C(2) | 3·3 (1) | 4·2 (2) | 3·0 (1) | −0·1 (1) | 0·5 (1) | −0·6 (1) |
| C(3) | 3·5 (1) | 4·2 (1) | 2·8 (1) | −0·0 (1) | 0·3 (1) | 0·1 (1) |
| O(1) | 4·5 (1) | 7·1 (2) | 5·1 (1) | −1·6 (1) | 1·9 (1) | −2·2 (1) |
| O(2) | 5·0 (1) | 6·5 (2) | 4·8 (1) | −1·9 (1) | 1·7 (1) | −2·3 (1) |

† $H(a)X(b)$ stands for hydrogen number (a) bonded to atom X(b).

factors $B_{ij}$ are reported together with their estimated standard deviations.

## Results and discussion

In Fig. 1 a molecular model of the *trans*-1,2-cyclobutanedicarboxylic acid is presented with bond lengths and angles; in Table 4 the internal rotation angles are reported.

Table 4. *Internal rotation angles*

| | |
|---|---|
| C(3)—C(2)-C(2*)-C(3*) | 99·1° |
| C(3)—C(2)-C(2*)-C(1*) | 140·7 |
| C(3)—C(2)-C(1)—C(1*) | −142·6 |
| C(2)—C(1)-C(1*)-C(2*) | 20·1 |
| C(1*)-C(1)-C(2)—C(2*) | −20·2 |
| O(1)—C(3)-C(2)—C(2*) | −170·8 |
| O(2)—C(3)-C(2)—C(2*) | 8·6 |
| O(1)—C(3)-C(2)—C(1) | 66·2 |
| O(2)—C(3)-C(2)—C(1) | −113·1 |
| C(1)—C(2)-C(2*)-C(1*) | +20·1 |

The four-membered ring is found to be non-planar. The dihedral angle between the planes defined by C(1), C(2), C(2*) and C(1), C(1*), C(2*) is 149±2° with an internal rotation angle (average of 3 determinations) of 20±5° (*trans* conformation = 180°). Deviations from planarity for other cyclobutane rings have been reported from researches conducted by means of X-ray diffraction, electron diffraction and microwave absorption: the dihedral angle being in the range 145–180°. In the crystalline state packing forces must evidently play an important role in fixing the conformation of this four-membered ring consistent with the estimated fairly low potential barrier (about 1 kcal.mole⁻¹) between the puckered and the planar conformations of cyclobutane in the gas phase

(Rathjens, Freeman, Gwinn & Pitzer, 1963). In the crystalline state the preferred conformation of the carboxyl groups in the molecule is 'quasi' diequatorial, analogous to the diequatorial conformation found in the case of *trans*-1,2-cyclohexanedicarboxylic acids (Benedetti, Corradini, Pedone & Post, 1968, 1969). The internal rotation angle C(3)–C(2)–C(2*)–C(3*) is 99°.

The length (1·553 Å) of two C–C bonds of the ring [C(1)–C(2) and C(1)–C(1*)] is somewhat greater than normal C–C values (1·537 Å) in good agreement with similar observations reported for the other derivatives of cyclobutanes (C–C in the range 1·547 to 1·57 Å) (Greenberg & Post, 1968; Adman & Margulis, 1968). In spite of the fact that the weight of evidence is toward longer C–C bonds in puckered rings, in the present investigation a rather short distance [C(2)–C(2*) = 1·517 Å] is observed. The difference between the two observed bond lengths equals six estimated standard deviations and is therefore statistically significant.

The carboxyl group is found to occur in its unsymmetrical conformation (Dunitz & Strickler, 1968) in such a way that the C=O bond is synplanar with respect to the C(2)–C(2*) bond, the internal rotation angle O(2)–C(3)–C(2)–C(2*) being 8°. This conformation, recently described as 'preferred' (Dunitz & Strickler, 1968), has been observed by us in the case of the *trans* and *cis* isomers of 1,2-cyclohexanedicarboxylic acids (Benedetti, Corradini, Pedone & Post, 1968, 1969; Benedetti, Pedone & Allegra, 1970). The atoms of the carboxyl group forming hydrogen bonds across symmetry centers are essentially planar. The equation of the mean-square plane passing through:

$$
\begin{array}{ccc}
 & \text{O(1)......O(2*)} & \\
 \diagup & & \diagdown \\
\text{C(2)-C(3)} & & \text{C(3*)-C(2*)} \\
 \diagdown & & \diagup \\
 & \text{O(2)......O(1*)} &
\end{array}
$$
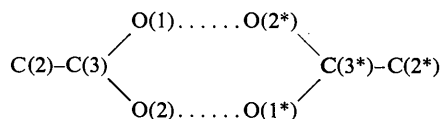
is $0.3792x - 0.6936y + 0.6064z - 2.3856 = 0$, with a mean-square distance of $0.017$ Å.

The shortest intramolecular contacts between atoms separated by four or more bonds are 3·56, 3·69 and 3·86 Å for C(3)–C(3*), C(3)–O(2*) and O(2)–O(2*) respectively. The mode of packing is determined by the formation of hydrogen-bonded rows of molecules (Fig. 2) with the shortest intermolecular contacts between atoms belonging to different molecular rows of 3·78, 3·53 and 3·70 Å for C–C, C–O and O–O respectively. The symmetry of the molecular row in the crystal is $t\ i\ c$ according to the classification of the possible symmetries of rows given by Corradini (1960). Such symmetry allows the repetition of molecules having $C_2$ symmetry and in agreement with our recent studies the packing of such molecular rows is best obtained by centering the '$c$' face in a monoclinic unit-cell ($b$ unique axis).

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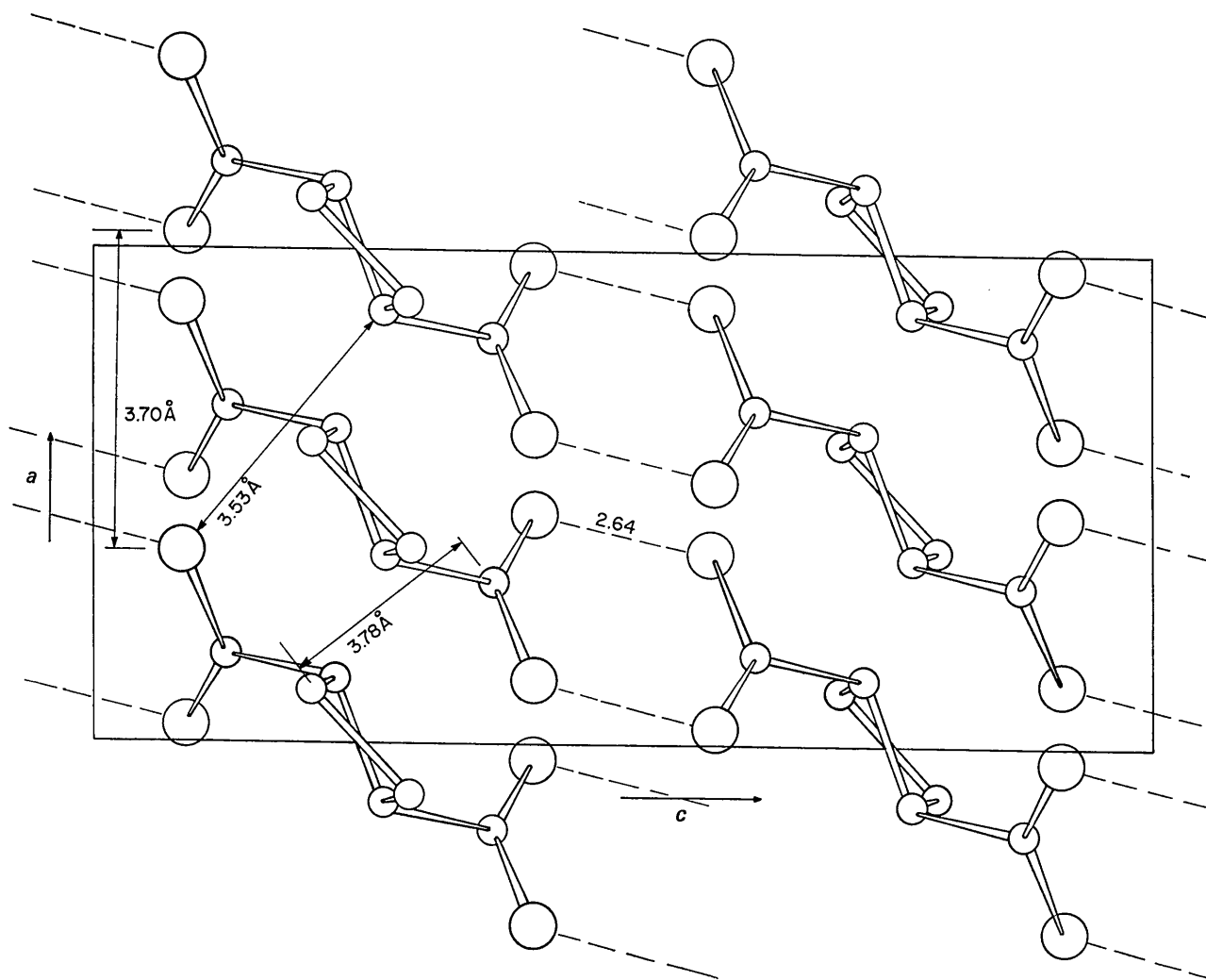


Fig. 2. Mode of packing of *trans*-1,2-cyclobutanedicarboxylic acid along (010). The shortest C–C, C–O and O–O intermolecular contacts are indicated, together with the O–O H-bonded distance.

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# The Crystal and Molecular Structure of *p*-Methylaminophenol Sulphate (Metol)

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A three-dimensional X-ray study of *p*-methylaminophenol sulphate (metol) has been accomplished by Patterson and Fourier methods. The crystals are monoclinic (space group $C2/c$ or $Cc$) with four molecules in the unit cell of dimensions: $a = 23.16$ (6), $b = 5.87$ (1), $c = 14.71$ (4) Å. Without considering the hydrogen atoms, two models of the structure, based on the two possible space groups, can be postulated: both give $R = 11.5\%$. The location of the hydrogen atoms is possible only with the model based on the $C2/c$ space group, in which there is a disordered arrangement of the $SO_4^{2-}$ group; the introduction of the hydrogen atoms improves the $R$ value to $10.5\%$. Packing and hydrogen bonding are discussed.

## Introduction

*p*-Methylaminophenol sulphate (metol) is a compound largely used in photographic work as a reducing agent. Although it is very common in X-ray laboratories, the available information on its crystal structure concerns only the morphological and optical properties and preliminary X-ray powder diffraction data (McCrone, Cook, Whitney, Corvin & Tull, 1948). The X-ray structural analysis of this compound was started in our laboratory as long ago as 1955, in order to study the hydrogen bonding system formed by the protonated methylamino and the hydroxyl phenolic groups with the oxygen atoms of the anion. This work was interrupted owing to the difficulties found in the solution of the two-dimensional structure. The three-dimensional analysis taken up recently showed that the trouble was due to the existence of two models, which are equivalent apart from the $SO_4^{2-}$ situation, both giving nearly equal $R$ values.

## Experimental

Single crystals suitable for X-ray work were grown by slow cooling from aqueous solutions of the commercial product. In this way monoclinic prisms elongated along the *b* axis were obtained. Cell constants, determined from Weissenberg and rotation photographs, are as follows:

$(C_7H_9ON)_2 \cdot H_2SO_4$; $M = 344.4$

$a = 23.16 \pm 0.06$, $b = 5.87 \pm 0.01$, $c = 14.71 \pm 0.04$ Å

$\beta = 126°42' \pm 7'$

$V = 1603$ Å³, $Z = 4$, $D_x = 1.422$, $D_m = 1.416$ g.cm⁻³,

$\mu = 22.3$ cm⁻¹ (Cu $K\alpha$).

Space group $C2/c$ or $Cc$ (from systematic absences). These data agree well with those previously given in the literature if the crystal axes are changed according to the trasformation matrix: $\overline{1}0\overline{1}/010/001$.

A set of intensity data was obtained up to the 5th layer around [010] and up to the 13th layer around [001] on an integrating Weissenberg camera by means of the multiple-film technique and Ni-filtered Cu $K\alpha$ radiation. 1764 independent reflexions were collected out of the 1976 possible ones contained in the limiting sphere; 333 were too weak to be measured. For the photographs taken around [010] the crystal used was a prism with nearly rectangular cross-section (0·014 × 0·021 cm), while for the data taken around [001] a