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The Crystal and Molecular Structure of *cis*-2,2,4,4-Tetramethyl-1,3-cyclobutanediol

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$C_8H_{16}O_2$; orthorhombic, $Pna2_1$; $Z=8$; $a=10{\cdot}395$ (2), $b=16{\cdot}556$ (1), $c=10{\cdot}166$ (1) Å; $D_o=1{\cdot}09$, $D_c=1{\cdot}09$ g cm^{-3}. The structure has two molecules in the asymmetric unit. The cyclobutane rings are non-planar, with dihedral angles of 19·0 (7) and 16·0 (7)°.

A 1:1 mixture of *cis*- and *trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediol (Matheson, Coleman & Bell Laboratories, Cincinnati, Ohio) was dissolved in ethyl acetate and the solution was allowed to evaporate slowly. This resulted in the formation of two morphologically distinct crystal types (Soltzberg, 1969). One set of crystals, hexagonally shaped, was found to be the *trans* isomer (Margulis, 1969). The other set has been postulated to be the *cis* isomer (Soltzberg, 1969).

After several recrystallizations from ethyl acetate of the postulated *cis* isomer, NMR and the melting point (Hasek, Elam, Martin & Nations, 1961) verified that it was indeed a pure sample of *cis*-2,2,4,4-tetramethyl-1,3-cyclobutanediol. A small crystal, 0·50 × 0·40 × 0·35 mm, was mounted in a thin-walled Lindemann capillary tube. The 0·50 mm axis (b) was parallel to the walls of the capillary tube.

Approximate cell dimensions, systematic absences ($0kl$: $k+l$ odd; $hk0$: h odd), and orthorhombic symmetry were noted from photographic and preliminary diffractometer data. The photographic data were taken with nickel-filtered Cu $K\alpha$ radiation. The possible space groups were $Pnma$ and $Pna2_1$. This information is consistent with the results of Soltzberg (1969).

With vanadium-filtered Cr $K\alpha$ radiation ($\lambda=2{\cdot}2916$ Å), 13 reflection angles with high 2θ values were accurately measured. The lattice constants were determined by a least-squares fit (Williams, 1964) using the extrapolation function of Nelson & Riley (1945). The values obtained for room temperature (23 °C) were $a=10{\cdot}395$ (2), $b=16{\cdot}556$ (1) and $c=10{\cdot}166$ (1) Å. The volume of the unit cell is 1749·56 Å^3, and the calculated density for eight molecules of $C_8H_{16}O_2$ (F.W. 144·22) is 1·09 g cm^{-3}.

The intensities of 1196 independent reflections, up to $2\theta=45°$, were measured using zirconium-filtered Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å). Intensities were measured with a Siemens manual diffractometer using the θ–2θ scan technique with a scan rate of 2° min^{-1}. The background was measured graphically. The take-off angle was 3·0° and the receiving slit was 4 × 4 mm. A check of the intensities of several reflections selected as standards showed them to remain constant within statistical and instrumental fluctuations during the data collection. The Lorentz and polarization corrections were made in the usual manner. For Mo $K\alpha$ X-rays, the linear absorption coefficient of this compound is 0·81 cm^{-1}. No absorption correction was made. The standard deviation of each intensity measurement was estimated by the formula:

$$\sigma^2(I)=CT+CB+(0{\cdot}05CT)^2+(0{\cdot}05CB)^2,$$

where CT is the total counts and CB is the background counts. The error in the structure factor, $\sigma(F_o)$, was calculated from $\sigma(I)$ by the finite difference method (Williams & Rundle, 1964). If $CT \le CB$, then F_o was set to zero. In the least-squares refinement the weight of a reflection was $1/[\sigma(F_o)]^2$.

The observed systematic absences do not lead to a positive identification of the space group; $Pnma$ and $Pna2_1$ are both possibilities. Soltzberg (1969) attempted structural solution in the centric space group, $Pnma$, but was unsuccessful and he suggests $Pna2_1$ as the correct space group.

The structure factors were scaled by Wilson's method (Wilson, 1942) and were converted to normalized structure factors by *FAME* (Dewar, 1970) for use in the phase determination. The statistical distribution of the normalized structure factors from the Wilson plot strongly indicates the presence of the acentric space group $Pna2_1$. The selection of $Pna2_1$ implies that there are two independent molecules of *cis*-2,2,4,4-tetramethyl-1,3-cyclobutanediol per asymmetric unit.

A total of 271 reflections with $E \geq 1{\cdot}20$ were used in *MULTAN* (Germain, Main & Woolfson, 1970). From one of the E maps, all twenty of the non-hydrogen atoms could be found among the top 23 peaks.

Isotropic least-squares refinement of these positions using a modification of the full-matrix program of Busing, Martin & Levy (1962) resulted in an R of 0·134 for all data. The function minimized in the least-squares calculations was $\sum(F_o-|F_c|/K)^2/\sigma^2(F_o)$. The scattering factors of Hanson, Herman, Lea & Skillman (1964) were used for O and C.

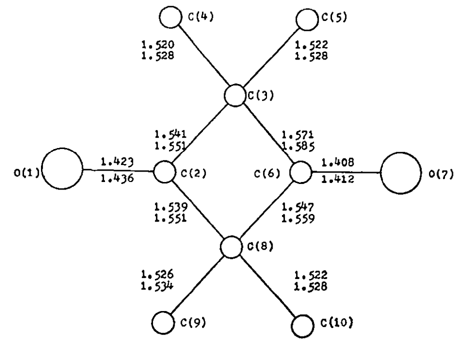
After several cycles of least squares using anisotropic temperature factors, R dropped to 0·103. A difference

Table 1. *Final atomic parameters and anisotropic thermal vibrational parameters* ($\times 10^4$), *and their estimated standard deviations*

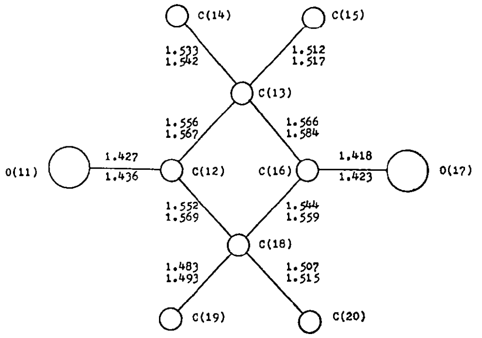
$$T=\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)\right].$$

Molecule *A*	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	1176 (4)	2345 (3)	1365	98 (5)	38 (2)	108 (5)	−22 (3)	8 (5)	−7 (3)
H(1)	1800	2700	700						
C(2)	647 (6)	1725 (4)	562 (8)	74 (7)	25 (2)	90 (4)	−5 (4)	9 (6)	−10 (4)
H(2)	1400	1300	100						
C(3)	−242 (6)	1975 (4)	−580 (8)	73 (6)	32 (3)	71 (7)	−9 (4)	9 (6)	−1 (4)
C(4)	−807 (7)	2821 (4)	−489 (10)	98 (8)	26 (2)	158 (11)	−2 (4)	7 (8)	0 (5)
H(4*a*)	−945	3068	480						
H(4*b*)	−1800	2900	−700						
H(4*c*)	−301	3300	−959						
C(5)	304 (8)	1838 (6)	−1952 (8)	149 (11)	60 (5)	117 (11)	−11 (6)	40 (10)	−17 (5)
H(5*a*)	797	1395	−2334						
H(5*b*)	−550	1809	−2671						
H(5*c*)	824	2250	−2202						
C(6)	−1191 (6)	1292 (3)	−123 (8)	64 (6)	27 (3)	85 (7)	−3 (3)	4 (6)	−8 (4)
H(6)	−1581	802	−660						
O(7)	−2507 (4)	1491 (2)	−80 (7)	67 (4)	32 (2)	128 (6)	2 (2)	4 (5)	6 (3)
H(7)	−3196	1075	−29						
C(8)	−436 (7)	1218 (4)	1182 (9)	99 (8)	23 (3)	122 (10)	−4 (4)	−2 (8)	4 (4)
C(9)	−1077 (7)	1612 (5)	2370 (9)	69 (8)	66 (4)	91 (8)	−10 (5)	12 (7)	17 (5)
H(9*a*)	−2000	1500	2700						
H(9*b*)	−539	1629	3179						
H(9*c*)	−1200	2300	2100						
C(10)	−80 (8)	350 (5)	1512 (13)	126 (10)	37 (3)	308 (19)	−5 (5)	−77 (13)	46 (8)
H(10*a*)	806	729	974						
H(10*b*)	200	300	2300						
H(10*c*)	−810	−149	132						
Molecule *B*									
O(11)	1035 (5)	4811 (3)	869 (7)	123 (6)	43 (2)	109 (6)	25 (3)	22 (5)	27 (3)
H(11)	567	4545	1681						
C(12)	574 (7)	5617 (4)	716 (8)	117 (8)	25 (3)	71 (7)	3 (4)	−10 (7)	1 (4)
H(12)	900	6000	1500						
C(13)	−761 (6)	5735 (4)	53 (9)	106 (8)	26 (3)	86 (7)	4 (4)	−2 (7)	3 (4)
C(14)	−1791 (8)	6097 (5)	958 (9)	140 (11)	56 (4)	133 (11)	30 (5)	21 (9)	22 (5)
H(14*a*)	−2092	5752	1737						
H(14*b*)	−2500	6200	300						
H(14*c*)	−1700	6600	1500						
C(15)	−1270 (8)	4992 (4)	−636 (9)	144 (10)	40 (3)	129 (10)	−22 (5)	−18 (9)	14 (5)
H(15*a*)	−691	4759	−1257						
H(15*b*)	−1811	4592	−204						
H(15*c*)	−1916	5175	−1236						
C(16)	−90 (6)	6372 (4)	−857 (8)	97 (8)	24 (2)	82 (8)	8 (4)	0 (7)	−3 (4)
H(16)	−500	6800	−300						
O(17)	−382 (5)	6319 (3)	−2216 (7)	158 (7)	40 (2)	85 (6)	−11 (3)	−31 (6)	11 (3)
H(17)	−465	6847	−2854						
C(18)	1257 (7)	6110 (4)	−378 (8)	81 (7)	41 (3)	80 (8)	−2 (4)	−16 (7)	5 (4)
C(19)	2106 (9)	6779 (6)	58 (12)	140 (11)	91 (6)	171 (13)	−55 (7)	−27 (12)	11 (8)
H(19*a*)	2762	6663	927						
H(19*b*)	1700	7000	700						
H(19*c*)	2911	7000	−286						
C(20)	1921 (9)	5590 (5)	−1387 (10)	155 (11)	54 (4)	131 (10)	42 (5)	42 (9)	29 (6)
H(20*a*)	2089	5985	−2183						
H(20*b*)	2700	5400	−1300						
H(20*c*)	1300	5000	−1700						

Fourier map then revealed the 32 hydrogen atoms. The hydrogen atoms were included in the least-squares refinement with an isotropic temperature factor of 4·5 Å^2.



Molecule *A*



Molecule *B*

Fig. 1. The bond distances (Å), uncorrected (upper) and corrected (lower). The bond distances for C–C have an estimated standard deviation of 0·009 Å; for C–CH$_3$ the estimated standard deviation is 0·010 Å; and for C–O the estimated standard deviation is 0·008 Å.

Their coordinates and temperature factors were not allowed to vary in the least-squares refinement. The scattering factors of Stewart, Davidson & Simpson (1965) were used for hydrogen. After five cycles of full-matrix least-squares refinement, the final *R* was 0·072. In the final least-squares cycle, all of the parameters varied less than $0\cdot1\sigma$.*

A difference Fourier map was prepared from the final model. The values on this map varied in an apparent random fashion from 0·276 to −0·073 e Å^{-3}. The final atomic parameters are listed in Table 1 together with their estimated standard deviations.

Discussion

The bond distances corrected and uncorrected for thermal motion are given in Fig. 1. The thermally corrected bond distances were computed using the method of Cruickshank (1961). The screw tensor was assumed to be near zero. The bond angles are given in Table 2.* Fig. 2 shows the orientation of the thermal ellipsoids as plotted by *ORTEP* (Johnson, 1965).

The cyclobutane rings in both molecules *A* and *B* are non-planar. For molecule *A* the dihedral angle between the normals to the planes of C(3),C(2),C(8) and C(3),C(6),C(8) is 19·0 (7)°. In molecule *B* the dihedral angle between the normals to the planes of C(13), C(12),C(18) and C(13),C(16),C(18) is 16·0 (7)°. These values are consistent with the dihedral angles reported in other simple non-planar cyclobutane compounds which range from 19 to 31° (Shirrell & Williams, 1973; Cotton & Frenz, 1974).

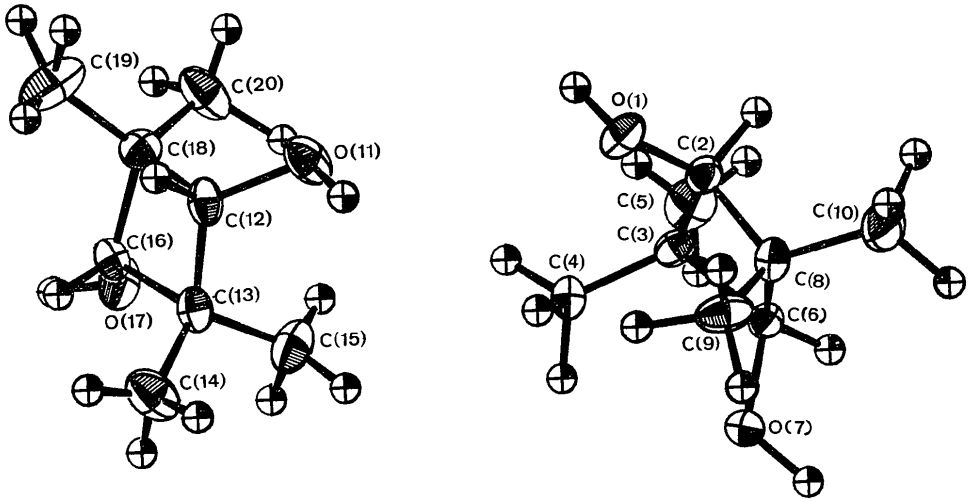


Fig. 2. The molecular structure. The thermal ellipsoids enclose a probability density of 0·30. For clarity the hydrogen atoms have been plotted as small spheres.

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* Tables 2 and 3 and a list of the structure factors (Table 4) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31536 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

No structures have been reported with a dihedral angle in the range 1–15°. Cotton & Frenz (1974) deduce from this fact that the steric and electronic natures of substituents on cyclobutane rings have a limited effect on ring non-planarity. In other words, they conclude that ring non-planarity is caused primarily by intermolecular interactions. We think that this question is not resolved for two reasons. The first is that future studies may turn up dihedral angles in the range 1–15°. The second is that the observed range of 19–31° in the dihedral angles could be caused by differences in steric and electronic substituent effects, as well as differences in intermolecular effects.

The equations for the best least-squares planes are for the cyclobutane ring in molecule *A*:

$$-0{\cdot}4564X+0{\cdot}7518Y+0{\cdot}4759Z=2{\cdot}2034; \quad (1)$$

and for the cyclobutane ring in molecule *B*:

$$-0{\cdot}0940X+0{\cdot}7645Y+0{\cdot}6378Z=7{\cdot}4421\,. \quad (2)$$

The mean deviation of the cyclobutane ring atoms from these least-squares planes is 0·09 Å for equation (1) and 0·075 Å for equation (2). For both molecules, the direction of puckering is such that the transannular O···O distance is increased. Thus the direction of puckering may be understood in terms of van der Waals and Coulombic repulsions between the oxygen substituents.

The bond distances in the rings give an average value of 1·552 Å without correction for thermal motion and 1·566 Å with correction. Both values are somewhat longer than the usual value of 1·537 Å for a C–C single bond (Sutton, 1965). However, this is not unusual since most C–C bonds in simple cyclobutane compounds have bond lengths which normally lie in the region 1·547–1·58 Å (see Table 2; Shirrell & Williams, 1973). A rationale for these long bonds was given by Dunitz & Schomaker (1952). The C–CH_3 and C–O bond lengths are within the ranges for their expected values. The C–H bonds, uncorrected for thermal motion, have an average value of 1·03 Å.

Fig. 2 shows the approximately eclipsed conformation of the methyl hydrogens in both molecules *A* and *B*, corresponding to H···H non-bonded contacts with an average value of 2·96 Å. The shortest transannular H···H contact is 2·10 Å.

The crystal structure contains a three-dimensional network of hydrogen bonds. Each hydroxyl unit is hydrogen bonded to two other hydroxyl units. Thus, a single molecule is hydrogen bonded to four other molecules. As can be seen in Table 3,* the O···H distances are 1·72 and 1·83 Å. The O–H···O distances are 2·77, 2·78, 2·78 and 2·81 Å. This type of molecular packing is also observed for the *trans* isomer of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (Margulis, 1969).

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* See previous footnote.

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