trans-2,5-Dimethylcyclopentane-1,1-dicarboxylic Acid

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Abstract. $C_9H_{14}O_4$, triclinic, $a = 10.742$ (3), $b = 7.658$ (2), $c = 7.150$ (2) Å, $\alpha = 58.51$ (3), $\beta = 85.80$ (4), $\gamma = 78.42$ (4)°, $Z = 2$, space group $P\bar{1}$. The crystal structure consists of infinite chains of molecules along the x axis, held together by hydrogen bonds. The conformation of the molecule is similar to that of its *cis* isomer.

Introduction. Approximately 1550 independent reflections were measured by means of a Nonius CAD-4 diffractometer using monochromatized Cu $K\alpha$ radiation. Of these, 1472 were above the significance level of 3σ. Intensity statistics point to a centrosymmetric space group.

The structure determination has been tackled by the interactive direct-methods program system *SIMPEL* (Schenk, Overbeek & van der Putten, 1976). However, the negative-quartet criterion (Schenk, 1974), the Harker–Kasper criterion (Schenk & de Jong, 1973) and the Σ_2 consistency index selected only those Σ_2 solutions in which all hhl reflections were signed minus and all $h\bar{h}l$ reflections plus. Ignoring these incorrect solutions, from those remaining the Harker–Kasper criterion indicated the correct solution.

The structure has been refined by a conventional block-diagonal least-squares procedure in the course of which the H atoms were located. The final R value was

Table 1. *Fractional coordinates* ($\times 10^4$, *for* H $\times 10^3$)

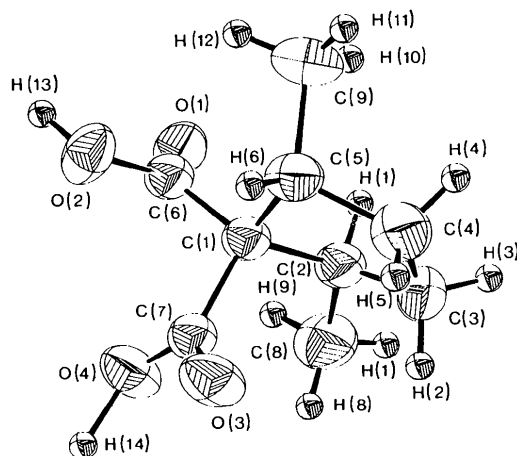|	x	y	z
C(1)	2493 (2)	8796 (3)	−1542 (3)
C(2)	2344 (2)	10026 (3)	−330 (3)
C(3)	3352 (2)	8687 (4)	1545 (3)
C(4)	3479 (2)	6450 (4)	2139 (4)
C(5)	2708 (2)	6477 (3)	387 (3)
C(6)	1360 (2)	9340 (3)	−3009 (3)
C(7)	3629 (2)	9278 (3)	−3023 (3)
C(8)	2421 (2)	12318 (4)	−1689 (4)
C(9)	1458 (2)	5733 (3)	1258 (4)
O(1)	394 (1)	10585 (2)	−3208 (2)
O(2)	1513 (1)	8286 (2)	−4011 (3)
O(3)	4700 (1)	8157 (2)	−2352 (2)
O(4)	3404 (1)	10910 (2)	−4928 (2)
H(1)	151 (2)	992 (4)	29 (4)
H(2)	416 (2)	909 (4)	112 (4)
H(3)	305 (2)	891 (4)	278 (4)
H(4)	306 (3)	580 (5)	352 (5)
H(5)	442 (3)	572 (4)	213 (5)
H(6)	322 (2)	560 (3)	−11 (3)
H(7)	223 (2)	1289 (4)	−74 (4)
H(8)	326 (2)	1253 (4)	−230 (4)
H(9)	165 (2)	1316 (4)	−292 (4)
H(10)	96 (2)	668 (4)	172 (4)
H(11)	162 (3)	446 (4)	248 (5)
H(12)	101 (2)	583 (4)	4 (4)
H(13)	78 (3)	861 (4)	−490 (5)
H(14)	423 (4)	1135 (7)	−619 (8)

5·0% with isotropic thermal parameters for the H atoms and anisotropic for the others. Table 1 contains the positional parameters.* The atom numbering is in Fig. 1.

Discussion. In dicarboxylic acids a large value for the ratio of the dissociation constants K_1/K_2 is an indication of intramolecular hydrogen bonding. The ratios for *cis*- and *trans*-2,5-dimethyl-cyclopentane-1,1-dicarboxylic acid are 5.4×10^6 and 2.5×10^3 respectively (Verbrugge, 1969). However, in monoclinic crystals of the *cis* isomer only intermolecular hydrogen bonds were found (Kops & Schenk, 1974). The present

Fig. 1. Numbering of the atoms.

study was carried out in order to determine the hydrogen-bond scheme of the *trans* compound and the similarities between the conformations of both isomers.

The molecules are arranged in infinite strings along the *x* axis and are held together by intermolecular hydrogen bonds [2·643 (2) and 2·645 (2) Å] between molecules related by inversion centres at (0·0, 1·0, −0·5) and (0·5, 1·0, −0·5) respectively.

The bond lengths of the *trans* isomer are equal, within the limits of accuracy, to those of the *cis* isomer. The lengths C(1)—C(2) and C(1)—C(5) are rather large probably as a result of the steric interactions of the substituents at C(1), C(2) and C(5) (see Table 2). Bond angles are in Table 3.

The dihedral angles in the cyclopentene ring are 40, −30, 9, 16 and −35° for C(1)—C(2), C(2)—C(3) *etc.*, indicating that the ring is in a conformation between an envelope and a half-chair. Similar dihedral angles were found in the *cis* isomer (Kops & Schenk, 1974).

Table 2. *Bond lengths* (Å) *with standard deviations*

C(1)—C(2)	1·561 (4)	C(5)—H(6)	0·97 (2)
C(1)—C(5)	1·560 (2)	C(6)—O(1)	1·220 (2)
C(1)—C(6)	1·510 (3)	C(6)—O(2)	1·314 (4)
C(1)—C(7)	1·526 (2)	C(7)—O(3)	1·243 (2)
C(2)—C(3)	1·533 (3)	C(7)—O(4)	1·274 (2)
C(2)—C(8)	1·515 (3)	C(8)—H(7)	0·98 (4)
C(2)—H(1)	0·97 (3)	C(8)—H(8)	0·98 (2)
C(3)—C(4)	1·512 (4)	C(8)—H(9)	1·08 (2)
C(3)—H(2)	0·96 (3)	C(9)—H(10)	1·00 (3)
C(3)—H(3)	1·01 (3)	C(9)—H(11)	0·90 (2)
C(4)—C(5)	1·541 (4)	C(9)—H(12)	0·97 (3)
C(4)—H(4)	0·97 (3)	O(2)—H(13)	0·95 (3)
C(4)—H(5)	1·05 (3)	O(4)—H(14)	1·18 (5)
C(5)—C(9)	1·526 (3)		

Table 3. *Bond angles* (°) *of the non-hydrogen atoms*

C(2)—C(1)—C(5)	102·8 (2)	C(3)—C(4)—C(5)	107·3 (2)
C(2)—C(1)—C(6)	114·0 (1)	C(1)—C(5)—C(4)	104·1 (2)
C(2)—C(1)—C(7)	109·9 (2)	C(1)—C(5)—C(9)	112·2 (1)
C(5)—C(1)—C(6)	112·0 (2)	C(4)—C(5)—C(9)	111·8 (2)
C(5)—C(1)—C(7)	112·2 (1)	C(1)—C(6)—O(1)	123·9 (2)
C(6)—C(1)—C(7)	106·1 (1)	C(1)—C(6)—O(2)	112·7 (2)
C(1)—C(2)—C(3)	102·3 (2)	O(1)—C(6)—O(2)	123·4 (2)
C(1)—C(2)—C(8)	117·4 (2)	C(1)—C(7)—O(3)	120·9 (1)
C(3)—C(2)—C(8)	114·7 (2)	C(1)—C(7)—O(4)	115·6 (1)
C(2)—C(3)—C(4)	107·4 (2)	O(3)—C(7)—O(4)	123·5 (2)

The carboxylic group C(6)O(1)O(2) has the usual conformation, the C=O bond eclipsing a bond of the ring. For the other COOH group this conformation is sterically impossible and O(3) is rotated by 20° out of the eclipsed position. In the *cis* isomer this rotation is 30° indicating a somewhat larger steric hindrance.

References

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Diaveridine: 2,4-Diamino-5-(3',4'-dimethoxybenzyl)pyrimidine*

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Abstract. $C_{13}H_{16}N_4O_2$, $M_r = 260\cdot92$, crystallizes from wet ethanol in the monoclinic space group $C2/c$, $a = 18\cdot140$ (5), $b = 12\cdot796$ (3), $c = 12\cdot332$ (3) Å, $\beta = 114\cdot78$ (1)°. D_c (for eight molecules in the cell of volume $2598\cdot93$ Å^3) $= 1\cdot169$ g cm^{-3}. The structure was solved with *MULTAN* and refined by full-matrix least-squares techniques based upon 1838 unique F_o^2 terms to yield agreement factors $R = 0\cdot057$ and $R_w = 0\cdot089$. The pyrimidine bases are linked together in infinite ribbons by hydrogen bonds involving the amino groups and ring-nitrogen atoms. Both methyl C atoms are approximately coplanar with the phenyl ring. The ether O atom bound to C(3') is positioned 3·47 Å