3,3,6,6-Tetramethoxy-1,4-cyclohexadiene

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Dedicated to Professor H. Nowotny on the occasion of his birthday

Abstract. $C_{10}H_{16}O_4$, triclinic, $P\bar{1}$, $a=6\cdot592$ (8), $b=6\cdot891$ (8), $c=6\cdot487$ (8) Å, $\alpha=114\cdot19$ (5), $\beta=99\cdot63$ (4), $\gamma=86\cdot61$ (4)°, $U=264\cdot9$ Å^3, $Z=1$, F.W. 200·3, $D_x=1\cdot251$ g cm^{-3}, $F(000)=108$. The counter technique was used and the structure solved by the Patterson superposition method. Because of sublimation (m.p. 43 ~ 44°C), the measurements were made at -50°C. At this temperature for 1195 reflexions a final $R=0\cdot055$ was obtained. The molecule has almost $2/m$ symmetry. The conformation of the 1,4-cyclohexadiene ring shows slight deviations from planarity.

Introduction. The structure determination of 3,3,6,6-tetramethoxy-1,4-cyclohexadiene (TMCH) is of interest because of the question of the preferred conformation of 1,4-cyclohexadiene and its derivatives. Both the boat and planar conformations have been suggested from n.m.r. data (Marshall, Ohrig & Jenkins, 1972; Paschal & Rabideau, 1974) and electron diffraction measurements (Dallinga & Toneman, 1967). On the other hand, two derivatives of 1,4-cyclohexadiene, whose crystal structures have been determined by X-rays (Jandacek & Simonsen, 1969; Bennett, Purdham, Takada & Masamune, 1971), show an almost planar conformation of the ring. The conformation was also considered in relation to the strong antagonism of 1,4-cyclohexadiene-1-alanine to phenylalanine (Shoulders, Gipson, Jandacek, Simonsen & Shive, 1968).

TMCH is obtained by anodical oxidation of *p*-dimethoxybenzene in methanol containing sodium methoxide (Belleau & Weinberg, 1963; Margaretha & Tissot, 1975). The transparent, white crystals are unstable at room temperature. Storage and single-crystal studies were therefore done at low temperatures. Diffraction measurements at -50°C with an automatic Philips PW 1100 diffractometer, equipped with a low-temperature device (Leybold-Heraeus), allowed the determination of a triclinic space group with $Z=1$, for which 1526 intensities ($1195\geq3\sigma$) were collected (ω–2θ scan,

Mo $K\alpha$ radiation, $\lambda=0\cdot7107$ Å, graphite monochromator).

The data were adjusted to an absolute scale by a Wilson plot and normalized structure factors were derived from the K curve ($K=I/\langle I\rangle$). The cumulative distribution indicated the presence of a centre of symmetry. *LSAM* (Main, Woolfson & Germain, 1972) was used to determine the phases of the reflexions. The resulting E maps however did not reveal the correct atom positions. Consequently Patterson methods were used to solve the structure. The failure of *LSAM* is probably due to the multiple overlap of interatomic vectors. After the structure was solved, the latest version of the computer program *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) became available to the authors. This program actually solved the structure but only after several unsuccessful trials. It appears that the number of E values for which phases had to be calculated is the most critical input parameter (2000 triple relationships, 240 E values > 1·4).

The least-squares refinement was carried out with *CRYLSQ* (X-RAY System, 1972). The function minimized was $\sum\omega\Delta F^2$ where $\omega=1/\sigma^2$ (F_o). Scattering factors computed from Hartree–Fock wave functions (Cromer & Mann, 1968) were used.* In the preliminary stages of refinement the data set was limited to sin θ/$\lambda<0\cdot3$ Å^{-1}. Atomic positions and anisotropic thermal parameters of the heavy atoms (Table 1) were refined by full-matrix least-squares calculations with all the data. All the H atoms were found from a difference map and their positional and isotropic thermal parameters (Table 2) simultaneously refined. The final cycle gave $R=\sum|\Delta F|/\sum|F_o|=0\cdot055$ for 1195 reflexions with $I\geq3\sigma$.

Table 1. *Positional and thermal parameters of the heavy atoms* ($\times 10^4$)

The temperature factors are in the form $\exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klc^*b^* + 2U_{13}hla^*c^*)\}$.
E.s.d.'s are in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	682 (3)	2126 (3)	1288 (3)	299 (10)	315 (11)	328 (11)	−86 (9)	16 (9)	117 (9)
C(2)	−1893 (3)	−818 (3)	102 (3)	259 (10)	359 (11)	367 (11)	−76 (8)	43 (8)	161 (9)
C(3)	−1359 (3)	1473 (3)	1600 (3)	256 (9)	353 (11)	298 (11)	−17 (8)	40 (8)	146 (9)
C(4)	−2785 (4)	1241 (5)	4717 (5)	470 (14)	607 (17)	426 (15)	33 (12)	202 (12)	252 (13)
C(5)	−2959 (5)	4884 (4)	2255 (6)	589 (18)	389 (15)	611 (19)	50 (13)	−103 (15)	144 (14)
O(1)	−1126 (2)	1938 (2)	3976 (2)	349 (8)	482 (9)	299 (8)	−17 (7)	52 (6)	188 (7)
O(2)	−3040 (2)	2631 (2)	966 (2)	306 (8)	368 (8)	355 (8)	12 (6)	8 (6)	149 (7)

Table 2. *Positional and thermal parameters of the hydrogen atoms* ($\times 10^3$)

Isotropic temperature factors are expressed as
$\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$.
E.s.d.'s are in parentheses.

	x	y	z	U
H(C1)	107 (3)	356 (3)	223 (3)	31 (5)
H(C2)	327 (3)	128 (3)	−14 (3)	38 (6)
H(C4)	−272 (3)	−36 (4)	435 (4)	60 (7)
H'(C4)	−420 (3)	154 (3)	399 (4)	48 (6)
H''(C4)	−258 (3)	196 (4)	−367 (4)	54 (7)
H(C5)	428 (3)	448 (3)	−118 (4)	51 (6)
H'(C5)	204 (4)	458 (4)	−174 (5)	88 (10)
H''(C5)	217 (4)	463 (4)	−362 (4)	73 (8)

0·007 (2) Å were found. If, however, only the four olefinic C atoms are considered, deviations of 0·020 (2) Å for the two methylenic C atoms were found. These deviations towards the chair form are small but most probably significant. The same symmetry conditions were found for *anti*-1,2,4,5-tetraphenyl-3,6-dimethoxy-carbonyl-1,4-cyclohexadiene (Bennett, Purdham, Takada & Masamune, 1971). For this compound a least-squares plane through the central six atoms showed deviations of approximately 0·01 Å, and of 0·03 Å for the two methylenic C atoms, if a least-squares plane through the four olefinic C atoms was considered.

Discussion. In agreement with the close-packing theory (Kitaigorodsky, 1961) one molecule of TMCH is found in the unit cell of space group $P\bar{1}$ (Fig. 1). Therefore the olefinic C atoms have to lie in a plane whereas the two methylene C atoms have to be centrosymmetrically related. These conditions are fulfilled by a planar or chair conformation; the boat form can thus be excluded.

The deviations of different sets of atoms from least-squares planes are given in Table 3. Taking the atoms of the cyclohexadiene ring as reference, deviations of

Table 3. *Deviations* (Å) *from least-squares planes through different sets of atoms*

An asterisk indicates a centrosymmetrically related atom, for which a deviation is not listed.

Plane 1: C(1), C(1)*, C(2), C(2)*, C(3), C(3)*
C(1) −0·0064; C(2) −0·0064; C(3) −0·0056;
H(C1) −0·014; H(C2) −0·081
Plane 2: C(1), C(1)*, C(2), C(2)*
C(1) −0; C(2) −0; C(3) −0·020; H(1) −0·026,
H(2) −0·069
Plane 3: C(3), C(3)*, O(1), O(1)*, O(2), O(2)*
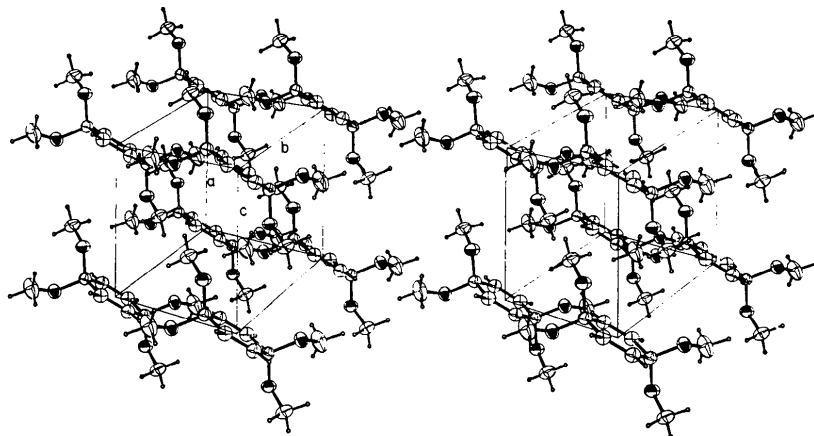C(3) −0·006; O(1) −0·002; O(2) −0·002

Fig. 1. Stereo view of the arrangement of TMCH molecules. Eight molecules at the origin of the triclinic cell are shown (*ORTEP*, Johnson, 1971).
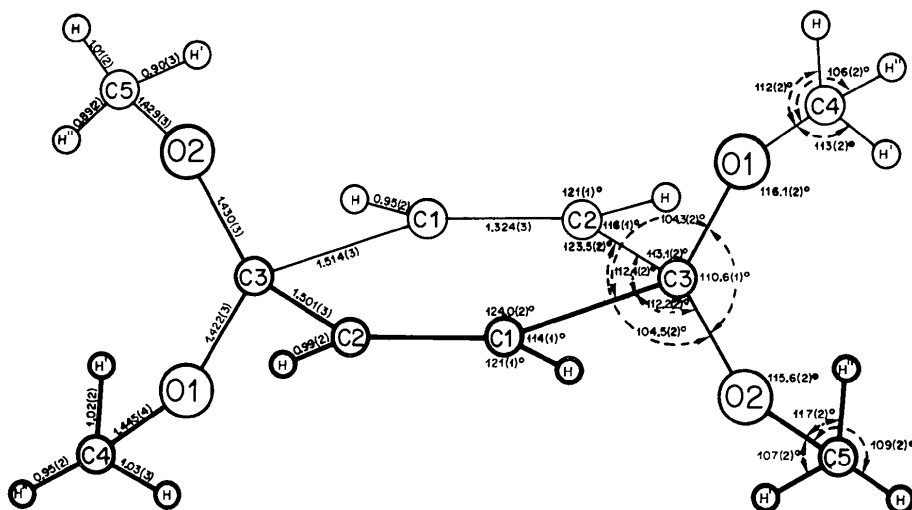
Fig. 2. The molecule, the numbering scheme, the intramolecular distances and the angles in TMCH. The estimated standard deviations for the distances and angles are given in parentheses.

For the third least-squares plane the four O atoms and the two methylenic C atoms of the ring were taken as reference. A dihedral angle of 84·3° with the least-squares plane of the cyclohexadiene ring was found. This deviation from 90° could be due to bulkiness of the substituents.

Further unexpected differences in bond distances and angles are seen in Fig. 2, for example between C(5)–O(2) (1·429 Å) and C(4)–O(1) (1·445 Å), or between C(1)–C(3)–O(1) (104·3°) and C(1)–C(3)–O(2) (112·2°). The value of 112·4° for C(2)–C(3)–C(1) in the 1,4-cyclohexadiene ring is smaller than the one reported for comparable compounds.

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