Discussion. Fig. 1 shows the high thermal motion (especially of the aromatic ring) of molecule 2. Because of this thermal motion, and also because of the rather small number of reflections collected from a weakly diffracting crystal, the precision of molecular dimensions is rather low. Despite this, a highly significant difference in conformation between the two molecules is observed (Figs. 2 and 3). The C(1)—C(2)—C(3)—C(4)—C(5)—C(11) rings show sofa and half-chair conformations for molecule 1 and 2 respectively [mean absolute deviations from the ideal values of Bucourt & Hainaut (1965) are 2 and 4°]. The C(6)—C(6a)—C(10a)—C(1)—C(11)—C(5) rings are not close to ideal conformations, for molecule 1 being between half-chair (7°) and sofa (9°), for molecule 2 between sofa (9°) and 1,3-diplanar (9°) (mean absolute deviations in parentheses). The pharmacological implications of this will be discussed elsewhere.

The packing diagram (Fig. 2) shows a striking similarity to Org.6582 (Jones *et al.*, 1979), with a belt of anions running parallel to **b**. Six short N···Cl contacts (3·15–3·25 Å), interpreted as N—H···Cl hydrogen bonds, are observed.

All programs used were written by GMS. We thank Dr M. B. Hursthouse, Queen Mary College, University of London, for data collection, Organon Laboratories Ltd, for a sample of Org.6997 and the Verband der Chemischen Industrie for financial support.

References

BUCOURT, R. & HAINAUT, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.
JONES, P. G., KENNARD, O. & HORN, A. S. (1979). *Acta Cryst.* B35, 1512–1515.
KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.

Acta Cryst. (1982). B**38**, 3107–3110

3,3,6,6-Tetramethoxy-1,2,4,5-tetramethyl-1,4-cyclohexadiene

BY LEIF NØRSKOV-LAURITSEN, SINE LARSEN AND MARTIN G. ETTLINGER

Chemical Laboratories II *and* IV, *University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken* 5, *DK*-2100 *Copenhagen Ø, Denmark*

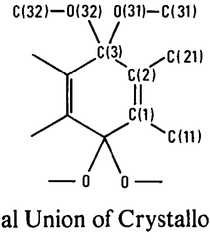
AND JERZY W. JAROSZEWSKI

Department of Chemistry BC, Royal Danish School of Pharmacy, Universitetsparken 2, *DK*-2100 *Copenhagen Ø, Denmark*

(*Received* 4 *January* 1982; *accepted* 23 *April* 1982)

Abstract. $C_{14}H_{24}O_4$, monoclinic, $C2/c$, $a = 14{\cdot}043$ (3), $b = 11{\cdot}506$ (2), $c = 8{\cdot}851$ (3) Å, $\beta = 104{\cdot}94$ (2)°, $V = 1381{\cdot}8$ (6) Å^3, $D_x = 1{\cdot}232$ Mg m^{-3}, $Z = 4$. For the 3055 data measured at *ca* 90 K the final R is 0·072, being 0·046 for the 2231 reflections with $I > 2\sigma(I)$. The conformation of the dimethyl acetal groups is *anti,anti* rather than that favoured by the anomeric effect. The O–C–O angle is 99°.

Introduction. The geometries of acetals, in particular the coupling between torsion angles, bond lengths and bond angles, are of especial interest in connection with the anomeric effect (Szarek & Horton, 1979; Tvaroška & Bleha, 1979). Of the possible spatial arrangements of the acetal group, the *anti,anti* arrangement is the rarest, having been hitherto encountered only in molecules in which the acetal group is adjacent to C atoms bearing a high density of negative charge (Jackson–Meisenheimer complexes: Destro, Gramaccioli & Simonetta, 1968; Ueda, Sakabe, Tanaka & Furusaki, 1968; Messmer & Palenik, 1971) or is conformationally fixed by being part of a bicyclic system (Norrestam, Bock & Thøgersen, 1981; Zheng, Qin, Gu & Zheng, 1981). The discovery that the *anti,anti* conformation can be realized in quinone bisacetals by appropriate substitution of the 1,4-cyclohexadiene ring (Jaroszewski, 1979) provided us with an opportunity of investigating the geometry of the *anti,anti* dimethyl acetal group in a relatively nonpolar environment (Ettlinger, Jaroszewski, Nørskov-Lauritsen & Watson, 1982). This paper describes the crystal structure of one such compound, 3,3,6,6-tetramethoxy-1,2,4,5-tetramethyl-1,4-cyclohexadiene.



0567-7408/82/123107-04$01.00

The compound (m.p. 478 K) was synthesized by anodic oxidation of 1,4-dimethoxy-2,3,5,6-tetramethylbenzene and crystallized from diethyl ether (Ettlinger *et al.*, 1982). It was found unnecessary to mount the crystals in glass capillaries. Weissenberg and precession photographs provided preliminary cell dimensions, and the systematic absences (*hkl*, $h + k$ odd, *h0l*, *l* odd) characterized the space group as *Cc* or *C*2/*c*. Data collection and determination of final cell parameters were performed at *ca* 90 K on a Picker FACS-1 diffractometer, equipped with a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å) and a modified (Hope, 1979) Nonius low-temperature device, using a crystal of 0·35 × 0·20 × 0·15 mm. The temperature was constant to within ±1 K during data collection. The intensities of six standard reflections measured after every 100 reflections showed an isotropic decay of 10% due to crystal deterioration or instrumental instability. Corrections of the intensity measurements were made using a linear rescale function based on the standard intensities. One hemisphere of reflections ($h \geq 0$) was measured, giving a total of 5912 reflections with $\theta < 35°$. The symmetry-related reflections were averaged to yield 3057 unique ones, of which 2231 have $I > 2\sigma(I)$. Corrections for Lorentz and polarization effects were made, but absorption ($\mu = 0·095$ mm^{-1}) was ignored.

The structure was solved by direct methods using the *MULTAN* 77 programs (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Although the correct space group was later proved to be *C*2/*c*, attempts to solve the structure in this space group were fruitless. Reduction of the symmetry to *Cc* immediately produced the correct solution corresponding to *C*2/*c*. The full-matrix refinement (XRAY system, 1976) was based on the *C*2/*c* symmetry. H atoms were found from a difference synthesis, and their positional and individual thermal parameters were included in the final cycles of least squares, where anisotropic temperature factors were used for the non-H atoms. In a refinement cycle based on 2231 'observed' [$I > 2\sigma(I)$] reflections, the maximum shift was 0·023σ with $R = 0·046$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0·051$. The final refinement, based on all unique reflections except 200 and $2\bar{2}\bar{2}$, since there were indications that these suffer from extinction, gave $R = 0·072$ and $R_w = 0·051$ for 3055 data.* Owing to the presence of a large proportion of high-order reflections, the weighting factors $w = [1 + 2\sigma(F_o)^2 - 2\sin\theta/\lambda + 0·01|F_o| + 0·0005|F_o|^2]^{-1}$ were chosen to minimize variations in $\langle w(|F_o| - |F_c|)^2\rangle$ as a function of $|F_o|$ and $\sin\theta/\lambda$. The scattering factors were taken from Cromer & Mann (1968) for the non-H atoms, and from Stewart, Davidson & Simpson (1965) for the H atoms. Atomic coordinates and isotropic thermal parameters are given in Table 1.

Table 1. *Atomic coordinates and isotropic temperature coefficients*

The other half of the molecule (atoms designated by primed numbers in Table 2) is generated by $x' = 0·5 - x$, $y' = 0·5 - y$ and $z' = -z$. $U_{\rm iso} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm iso}$(Å^2)
C(1)	0·33507 (6)	0·22852 (6)	−0·05956 (8)	0·0126 (2)
C(2)	0·31428 (6)	0·15023 (6)	0·03982 (8)	0·0128 (2)
C(3)	0·22796 (6)	0·16479 (6)	0·11153 (8)	0·0126 (2)
C(11)	0·42013 (7)	0·21815 (8)	−0·13324 (11)	0·0198 (2)
C(21)	0·37289 (8)	0·04043 (8)	0·08893 (11)	0·0224 (2)
O(31)	0·26168 (5)	0·16335 (6)	0·27894 (6)	0·0173 (2)
O(32)	0·16879 (5)	0·06222 (5)	0·08974 (7)	0·0171 (2)
C(31)	0·32432 (8)	0·25745 (8)	0·34544 (9)	0·0208 (2)
C(32)	0·11976 (7)	0·03627 (7)	−0·06883 (10)	0·0189 (2)
H(111)	0·400 (2)	0·202 (2)	−0·242 (3)	0·054 (6)
H(112)	0·459 (2)	0·287 (2)	−0·122 (3)	0·055 (6)
H(113)	0·464 (2)	0·157 (2)	−0·090 (3)	0·052 (6)
H(211)	0·366 (2)	0·015 (2)	0·186 (3)	0·048 (5)
H(212)	0·349 (2)	−0·021 (2)	0·017 (3)	0·048 (5)
H(213)	0·444 (2)	0·051 (2)	0·097 (2)	0·046 (5)
H(311)	0·388 (1)	0·254 (2)	0·317 (2)	0·030 (4)
H(312)	0·293 (1)	0·331 (2)	0·315 (2)	0·033 (4)
H(313)	0·334 (1)	0·247 (1)	0·455 (2)	0·027 (4)
H(321)	0·077 (1)	0·099 (1)	−0·116 (2)	0·026 (4)
H(322)	0·166 (1)	0·022 (2)	−0·130 (2)	0·032 (4)
H(323)	0·077 (1)	−0·032 (2)	−0·068 (2)	0·033 (4)

Discussion. The molecular geometry is illustrated by the *ORTEP* (Johnson, 1965) drawing in Fig. 1, and selected bond lengths, bond angles and torsion angles are given in Table 2. It is notable that the symmetry-related acetal groups in this molecule adopt the *anti,anti* conformation (O–C–O–C torsion angles close to 180°) with an O–C–O angle of only 99°. The presence of the *anti,anti* conformation with its small central angle is apparently due to the steric effect of the methyl groups attached to the ring, since in 3,3,6,6-tetramethoxy-1,4-cyclohexadiene the acetal groups

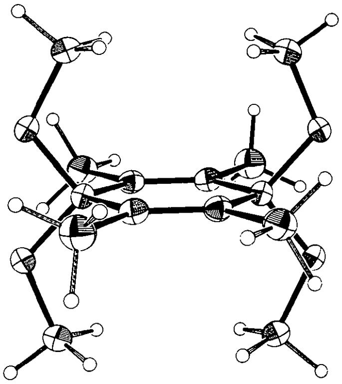


Fig. 1. Perspective view of 3,3,6,6-tetramethoxy-1,2,4,5-tetramethyl-1,4-cyclohexadiene. Thermal ellipsoids have been scaled to enclose regions of 50% probability, while H atoms are represented by spheres with radii of 0·07 Å.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36848 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond lengths* (Å), *bond angles and torsion angles* (°)

C–H bond distances lie in the range 0·94–0·99 (2) Å.

C(1)–C(2)	1·3426 (11)	C(3)–O(31)	1·4346 (10)
C(1)–C(3′)	1·5140 (11)	C(3)–O(32)	1·4275 (10)
C(1)–C(11)	1·5059 (14)	O(31–C(31)	1·4232 (11)
C(2)–C(3)	1·5155 (13)	O(32)–C(32)	1·4264 (11)
C(2)–C(21)	1·5092 (12)		
C(2)–C(1)–C(3′)	122·28 (8)	C(1′)–C(3)–O(32)	110·79 (6)
C(2)–C(1)–C(11)	124·15 (7)	O(31)–C(3)–O(32)	98·95 (5)
C(3′)–C(1)–C(11)	113·55 (7)	C(3)–O(31)–C(31)	115·00 (6)
C(1)–C(2)–C(3′)	122·19 (7)	C(3)–O(32)–C(32)	114·99 (7)
C(1)–C(2)–C(21)	123·76 (8)	O(31)–C(31)–H(311)	111·7 (10)
C(3)–C(2)–C(21)	114·05 (7)	O(31)–C(31)–H(312)	111·7 (10)
C(2)–C(3)–C(1′)	115·50 (6)	O(31)–C(31)–H(313)	103·6 (10)
C(2)–C(3)–O(31)	110·16 (6)	O(32)–C(32)–H(321)	111·0 (10)
C(2)–C(3)–O(32)	110·65 (6)	O(32)–C(32)–H(322)	111·4 (10)
C(1′)–C(3)–O(31)	109·55 (6)	O(32)–C(32)–H(323)	107·1 (10)
C(3′)–C(1)–C(2)–C(3)	−2·0 (1)	O(32)–C(3)–O(31)–C(31)	−179.4 (1)
C(11)–C(1)–C(2)–C(21)	−0·9 (1)	C(2)–C(3)–O(32)–C(32)	−65·7 (1)
C(2)–C(1)–C(3′)–C(2′)	1·9 (1)	C(1′)–C(3)–O(32)–C(32)	63·7 (1)
C(2)–C(1)–C(3′)–O(31′)	−123·2 (1)	O(31)–C(3)–O(32)–C(32)	178·7 (1)
C(2)–C(1)–C(3′)–O(32′)	128·7 (1)	C(2)–C(1)–C(11)–H(111)	109·6 (16)
C(1)–C(2)–C(3)–C(1′)	1·9 (1)	C(2)–C(1)–C(11)–H(112)	−129·7 (14)
C(1)–C(2)–C(3)–O(31)	−122·9 (1)	C(2)–C(1)–C(11)–H(113)	−9·2 (14)
C(1)–C(2)–C(3)–O(32)	128·7 (1)	C(1)–C(2)–C(21)–H(211)	155·8 (13)
C(2)–C(3)–O(31)–C(31)	64·7 (1)	C(1)–C(2)–C(21)–H(212)	−86·9 (16)
C(1′)–C(3)–O(31)–C(31)	−63·4 (1)	C(1)–C(2)–C(21)–H(213)	34·6 (14)

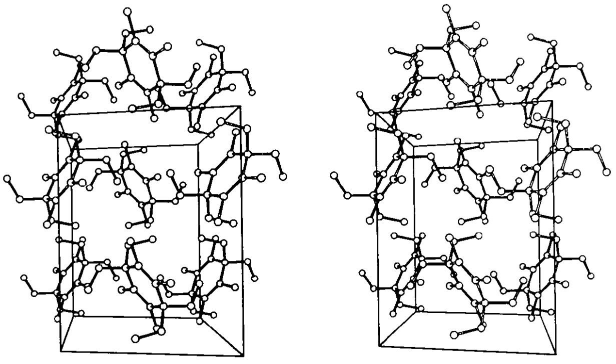


Fig. 2. Stereoscopic view of packing seen down the *a* axis. H atoms have been omitted.

adopt the ordinary *gauche,gauche* conformation (Liebich, Yvon & Margaretha, 1976). Further discussion of these unusual features is deferred to a more general report describing several quinone bisacetals having *anti,anti* dimethyl acetal groups (Ettlinger *et al.*, 1982).

The remaining molecular dimensions are similar to those of related molecules. Table 3 shows that although the 1,4-cyclohexadiene ring can be described as planar, it exhibits the same type of weak centrosymmetric pucker as observed in crystalline diethyl 2,5-dihydroxy-1,4-cyclohexadiene-1,4-dicarboxylate (Mez & Rihs, 1973) and 3,3,6,6-tetramethoxy-1,4-cyclohexadiene (Liebich *et al.*, 1976). Other 1,4-cyclohexadienes also seem to be close to planar (Jandacek & Simonsen, 1969; Bennett, Purdham, Takada & Masamune, 1971; Saebø & Boggs, 1981). Owing to the structural features described above the overall molecular symmetry is close to *mmm*, although the crystallographic symmetry is $\bar{1}$.

In the methoxy groups the O–C–H angles show the same tilt of the methyl group as found in *ab initio* calculations on dimethoxymethane (Van Alsenoy, Schäfer, Scarsdale, Williams & Geise, 1981) and in microwave studies of methanol and dimethyl ether (Harmony, Laurie, Kuczkowski, Schwendeman, Ramsay, Lovas, Lafferty & Maki, 1979). The methyl groups attached to the cyclohexadiene ring are not in the expected staggered conformation (Table 2). The unequal torsion of these groups may be caused by packing forces, as it is likely that the barrier to rotation is lower than that in (*Z*)-2-butene, where it is 3·6 kJ mol^{-1} (Durig, Hudson & Natter, 1979).

The packing of the molecules (Fig. 2) can be described as layers parallel to the (100) plane separated by H–H contacts. Within the layers molecules seem to be linked by O–H interactions across distances of 2·6–2·8 Å, each O having two hydrogen contacts. The angle between the cyclohexadiene ring and the (100) plane is 54°.

Table 3. *Distances* (Å) *of atoms from the least-squares plane*

Plane defined by the six ring atoms. E.s.d.'s are 0·001 Å.

C(1)	0·007	C(11)	0·000
C(2)	−0·007	C(21)	−0·052
C(3)	0·007		

References

Bennett, M. J., Purdham, J. T., Takada, S. & Masamune, S. (1971). *J. Am. Chem. Soc.* **93**, 4063–4065.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Destro, R., Gramaccioli, C. M. & Simonetta, M. (1968). *Acta Cryst.* B**24**, 1369–1386.

Durig, J. R., Hudson, S. D. & Natter, W. J. (1979). *J. Chem. Phys.* **70**, 5747–5750.

Ettlinger, M. G., Jaroszewski, J. W., Nørskov-Lauritsen, L. & Watson, K. J. (1982). In preparation.

Harmony, M. D., Laurie, V. W., Kuczkowski, R. L., Schwendeman, R. H., Ramsay, D. A., Lovas, F. J., Lafferty, W. J. & Maki, A. G. (1979). *J. Phys. Chem. Ref. Data*, **8**, 619–721.

Hope, H. (1979). Personal communication. Department of Chemistry, Univ. of California, Davis, California, USA.

Jandacek, R. J. & Simonsen, S. H. (1969). *J. Am. Chem. Soc.* **91**, 6663–6665.

Jaroszewski, J. W. (1979). Thesis, Univ. of Copenhagen.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Liebich, B. W., Yvon, K. & Margaretha, P. (1976). *Acta Cryst.* B**32**, 269–271.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. & Woolfson, M. M. (1978). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structues from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Messmer, G. G. & Palenik, G. J. (1971). *Acta Cryst.* B**27**, 314–321.

Mez, H.-C. & Rihs, G. (1973). *Helv. Chim. Acta*, **56**, 2766–2772.

Norrestam, R., Bock, K. & Thøgersen, H. (1981). *Acta Cryst.* B**37**, 1689–1693.

Saebø, S. & Boggs, J. E. (1981). *J. Mol. Struct.* **73**, 137–144.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Szarek, W. A. & Horton, D. (1979). Editors, *Anomeric Effect. Origin and Consequences. Am. Chem. Soc. Symp. Ser.* No. 87. Washington DC, USA.

Tvaroška, I. & Bleha, T. (1979). *Can. J. Chem.* **57**, 424–435.

Ueda, H., Sakabe, N., Tanaka, J. & Furusaki, A. (1968). *Bull. Chem. Soc. Jpn*, **41**, 2866–2871.

Van Alsenoy, C., Schäfer, L., Scarsdale, J. N., Williams, J. O. & Geise, H. J. (1981). *J. Mol. Struct.* **86**, 111–117.

XRAY system (1976). Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Zheng, C.-D., Qin, J.-Z., Gu, Y.-X. & Zheng, Q.-T. (1981). *Wu Li Hsueh Pao*, **30**, 242–248.

Acta Cryst. (1982). B**38**, 3110–3111

t-3-Ethyl-*r*-2,*c*-4,*c*-5-triphenyl-1,3-oxazolidine

By T. Skarżyński

Department of Crystallography, Institute of Chemistry, University of Łódź, Nowotki 18, *Łódź, Poland*

(*Received* 15 *April* 1982; *accepted* 16 *June* 1982)

Abstract. $C_{23}H_{23}NO$, orthorhombic, *Pcab*, $a = 7{\cdot}641\,(2)$, $b = 17{\cdot}324\,(2)$, $c = 29{\cdot}042\,(6)$ Å, $Z = 8$, $D_x = 1{\cdot}14$ Mg m^{-3}, m.p. 324–325 K, $R = 0{\cdot}044$ for 1781 reflexions with $I > 2{\cdot}5\sigma(I)$. The central oxazolidine ring is in the half-chair conformation.

Introduction. The title compound was synthesized by G. Mlostoń (1981) and was recrystallized from ethanol. The unit-cell parameters and intensities were measured at room temperature on a CAD-4 diffractometer using Cu $K\alpha$ radiation. 3018 independent reflexions with θ values below 75° were measured; of these, 1781 were considered as observed by the criterion $I > 2{\cdot}5\sigma(I)$. No absorption corrections were applied.

The *E* map showed the positions of only six non-hydrogen atoms. The remaining non-hydrogen atoms were located by application of the partial-structure procedure using *SHELX* 76 (Sheldrick, 1976). The refinement was carried out by the full-matrix least-squares method. Most of the H-atom positions were located on a difference Fourier map and the rest were calculated from the geometry of the molecule. Isotropic temperature factors were used for the H atoms and anisotropic values for non-H atoms. A weighting scheme of the form $w = 1/[\sigma^2(F) + pF^2]$ was employed with the *p* equal to 0·002. The final *R* index was 0·044 and R_w was 0·052.

The atom parameters are listed in Table 1, the bond lengths and angles are given in Table 2, and Fig. 1 shows the numbering of the atoms.*

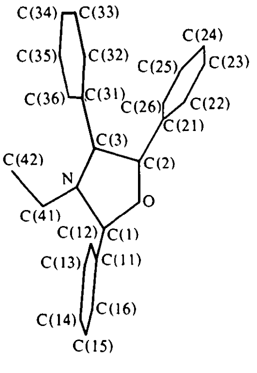


Fig. 1. The atom-numbering scheme.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38018 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/82/123110-02$01.00