

2,10,11-Trioxatricyclo [4,4,4,0^{1,6}]tetradecane: a Stable Orthoester

BY S. H. BANYARD* AND J. D. DUNITZ

Organic Chemistry Laboratory, Swiss Federal Institute of Technology (ETH), 8006 Zürich, Switzerland

(Received 6 September 1975; accepted 22 September 1975)

Abstract. Monoclinic, $P2_1/c$, $a=6.111$, $b=12.060$, $c=14.037$ Å, $\beta=90.363^\circ$, $C_{11}O_3H_{18}$, $M=199.71$, $Z=4$, $D_x=1.282$. The molecules have virtual, non-crystallographic C_3 symmetry with the six-membered rings in the chair conformation. The crystal structure is slightly disordered, a small proportion (0.075) of molecular sites being occupied by molecules of the wrong chirality sense.

Introduction. According to the stereoelectronic rules proposed by Deslongchamps, Atlanti, Fréhel & Malaval (1972), hydrolysis of the tetrahedral intermediate involved in the hydrolysis of esters and amides can proceed with a low activation energy only if the bond to be cleaved is oriented antiperiplanar to lone-pair orbitals on the other two heteroatoms. This situation is impossible in the conformationally rigid title compound so it should be unusually resistant to hydrolysis, as has indeed been confirmed (Deslongchamps, Chênevert, Taillefer, Moreau & Saunders, 1975). Since structural information on orthoesters is sparse, we have determined the crystal structure of the title compound.

Crystals were prepared by slow evaporation of a toluene solution at room temperature. Samples for X-ray analysis were sealed in a thin film of slow-setting araldite.

Intensities from a crystal $0.3 \times 0.3 \times 0.08$ mm were collected on an automated Hilger-Watts Y290 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.71069$ Å, $\mu=0.98$ cm⁻¹). Of the 1617 symmetry-independent reflexions measured, the intensities of 1359 were significantly (3σ) above background. The structure was solved by direct methods and refined by full-matrix least squares with experimental weights $w=\sigma^{-1}(F)$.

After inclusion of H atoms ($R=0.061$), six significant peaks were still found in an (F_o-F_c) synthesis. Three peaks (~ 0.6 e Å⁻³) occurred at positions related to the O positions by 60° rotation about C(1)-C(6), three smaller peaks (~ 0.4 e Å⁻³) at positions similarly related to C(2), C(7) and C(11). This suggested that a small proportion of sites might be occupied by molecules of opposite chirality sense to that required by the perfectly ordered structure. Inversion of configuration of a given molecule involves large displacements only of these six atoms, which were included in subsequent refinements with their scattering power distributed over the two possible sites. For the minor site the occupancy factor p was found to lie between 0.07 and 0.08. Subsequent refinement with $p=0.075$ and with anisotropic extinction correction gave a final R of 0.034 and yielded an (F_o-F_c) synthesis with residual electron density less than 0.1 e Å⁻³. Scattering factors for C and O were taken from *International Tables for X-ray Crystallography* (1962), for H from Stewart, Davidson

* Present address: Department of Biochemistry, University of Sheffield, Sheffield, U. K.

Table 1. Atomic coordinates ($\times 10^4$) and vibrational tensor components ($\times 10^3$) for non-hydrogen atoms of the prime component molecule (e.s.d.'s in parentheses)

The U_{ij} values (in Å²) correspond to the temperature factor expression $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+\dots+2U_{12}hka^*b^*\dots)]$. In the final calculations C(2), C(7), C(11), O(5), O(10), O(14) were assigned an occupancy factor p of 0.925; for the others $p=1$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	3024 (3)	5580 (2)	7938 (1)	32 (1)	53 (1)	42 (1)	-1 (1)	2 (1)	1 (1)
C(2)	3858 (4)	5106 (3)	6995 (3)	44 (2)	72 (2)	56 (2)	3 (1)	13 (1)	-4 (1)
C(3)	2799 (5)	5631 (2)	6133 (2)	88 (2)	91 (2)	43 (1)	2 (2)	19 (1)	0 (1)
C(4)	379 (4)	5634 (2)	6224 (1)	78 (2)	70 (1)	37 (1)	2 (1)	-9 (1)	5 (1)
C(6)	519 (3)	5614 (2)	7917 (1)	38 (1)	38 (1)	37 (1)	1 (1)	0 (1)	0 (1)
C(7)	3898 (4)	6770 (2)	8083 (2)	41 (1)	70 (2)	64 (1)	-15 (1)	-2 (1)	3 (1)
C(8)	2801 (4)	7381 (2)	8882 (2)	84 (2)	54 (1)	71 (1)	-26 (1)	-5 (1)	-10 (1)
C(9)	368 (4)	7324 (2)	8766 (2)	74 (2)	44 (1)	53 (1)	1 (1)	10 (1)	-8 (1)
C(11)	3772 (4)	4840 (2)	8772 (2)	37 (1)	72 (2)	56 (1)	9 (1)	-6 (1)	6 (1)
C(12)	2607 (4)	3739 (2)	8809 (2)	70 (2)	59 (1)	60 (1)	17 (1)	0 (1)	14 (1)
C(13)	184 (4)	3914 (2)	8764 (2)	58 (1)	42 (1)	55 (1)	-2 (1)	4 (1)	7 (1)
O(5)	-318 (2)	6140 (1)	7098 (1)	47 (1)	49 (1)	39 (1)	4 (1)	-7 (1)	5 (1)
O(10)	-367 (2)	6195 (1)	8693 (1)	43 (1)	40 (1)	44 (1)	0 (1)	9 (1)	-3 (1)
O(14)	-420 (2)	4555 (1)	7940 (1)	42 (1)	40 (1)	44 (1)	-6 (1)	-2 (1)	1 (1)

& Simpson (1965).^{*} Final positional and vibrational parameters are given in Tables 1–3, bond distances and angles in Fig. 1 and torsion angles in Table 4.

^{*} A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. 31406 (3 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Atomic coordinates ($\times 10^3$) and isotropic B values ($B=8\pi^2U$) for hydrogen atoms (*e.s.d.*'s in parentheses)

Unit occupancy factors were assumed.

	x	y	z	$B(\text{\AA}^2)$
H(2,1)	545 (3)	521 (1)	696 (1)	5.8 (5)
H(2,2)	357 (3)	430 (2)	695 (1)	6.8 (6)
H(3,1)	331 (3)	643 (2)	606 (1)	7.9 (6)
H(3,2)	314 (3)	530 (2)	561 (1)	7.6 (5)
H(4,1)	-40 (2)	604 (1)	574 (1)	3.9 (4)
H(4,2)	-21 (3)	492 (2)	621 (1)	7.2 (5)
H(7,1)	538 (3)	671 (2)	819 (1)	5.6 (5)
H(7,2)	363 (3)	719 (1)	747 (1)	6.4 (5)
H(8,2)	330 (3)	704 (2)	949 (1)	6.2 (5)
H(8,1)	329 (3)	810 (1)	892 (1)	4.9 (6)
H(9,1)	-38 (3)	763 (1)	930 (1)	4.8 (4)
H(9,2)	-9 (3)	774 (2)	820 (1)	5.5 (5)
H(11,1)	534 (3)	471 (1)	871 (1)	5.8 (5)
H(11,2)	355 (3)	525 (1)	939 (1)	5.3 (3)
H(12,1)	304 (3)	325 (2)	829 (1)	7.5 (5)
H(12,2)	292 (3)	333 (1)	938 (1)	6.3 (5)
H(13,1)	-61 (3)	328 (2)	870 (1)	5.4 (5)
H(13,2)	-33 (3)	430 (1)	931 (1)	5.0 (5)

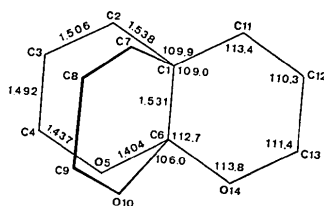


Fig. 1. Bond distances and bond angles averaged over C_3 symmetry. Mean deviations from averaged values are about 0.002 Å and 0.2° with maximum deviations of 0.007 Å [C(3)–C(4)] and 0.7° [C(3)–C(4)–O(5)]. All bond lengths should be increased by 0.009–0.010 Å to take account of thermal motion corrections.

Table 3. Atomic coordinates ($\times 10^3$) and isotropic B values ($B=8\pi^2U$) for non-hydrogen atoms of the secondary component molecules (*e.s.d.*'s in parentheses)

Occupancy factor $p=0.075$.

	x	y	z	$B(\text{\AA}^2)$
C(2')	404 (7)	583 (4)	694 (3)	6.7 (1.0)
C(7')	403 (5)	626 (3)	872 (3)	6.2 (0.7)
C(11')	387 (5)	432 (3)	818 (2)	5.1 (0.6)
O(5')	-40 (3)	504 (1)	715 (1)	4.0 (0.4)
O(10')	-26 (3)	667 (2)	785 (1)	4.8 (0.4)
O(14')	-39 (3)	507 (2)	868 (1)	4.1 (0.4)

Table 4. Torsion angles

The values given have been averaged over the three rings.

C(1)–C(2)–C(3)–C(4)	-50.9°
C(2)–C(3)–C(4)–O(5)	-54.6
C(3)–C(4)–O(5)–C(6)	59.8
C(1)–C(6)–O(5)–C(4)	58.2
O(10)–C(6)–O(5)–C(4)	-178.0
O(14)–C(6)–O(5)–C(4)	-65.5
C(7)–C(1)–C(2)–C(3)	-71.2
C(11)–C(1)–C(2)–C(3)	167.6
C(6)–C(1)–C(2)–C(3)	48.1
O(5)–C(6)–C(1)–C(2)	50.9
O(5)–C(1)–C(6)–C(7)	-69.1
O(5)–C(1)–C(6)–C(11)	170.8

Discussion. The conformation of the title molecule (Fig. 2) is, as expected, very similar to that of the parent hydrocarbon, [4,4,4]propellane, which has virtual D_3 symmetry with all three six-membered rings in the chair form (Ermer, Gardil & Dunitz, 1971). Introduction of the three O atoms lowers the molecular symmetry to C_3 . No molecular symmetry is imposed by the space group but the molecules as observed in the crystal do have virtual C_3 symmetry. Differences between symmetry-equivalent parameters are less than 0.007 Å for bond lengths, less than 0.7° for bond angles and less than 0.8° for torsion angles. The bond lengths and angles shown in Fig. 1 have accordingly been averaged over C_3 symmetry, and similarly for the torsion angles listed in Table 4. The values shown are uncorrected for the effects of disorder and rigid-body libration. Corrections estimated from the observed

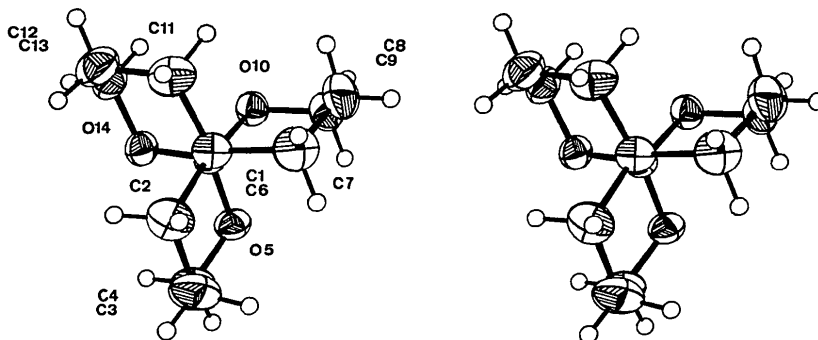


Fig. 2. Stereoscopic view of the molecule, looking along a direction close to the approximate C_3 axis. Thermal ellipsoids (for non-hydrogen atoms) are drawn at the 50% probability level.

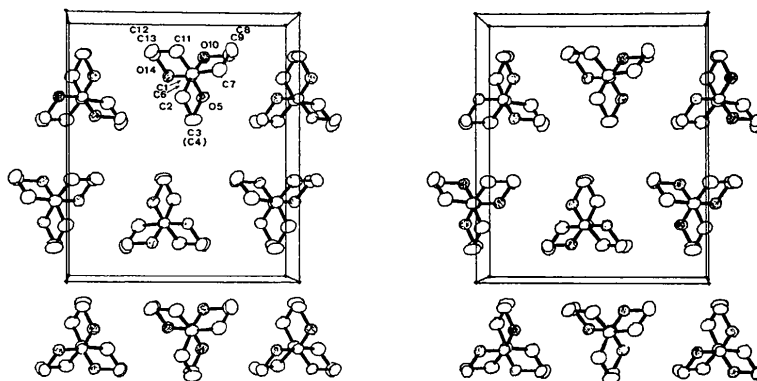


Fig. 3. Stereoscopic view of crystal packing. The origin is at the bottom left corner of the cell, with $+b$ pointing to the right and $+c$ upwards. The a axis is directed towards the reader. The standard molecule (coordinates in Table 1) is lettered.

thermal ellipsoids (Schomaker & Trueblood, 1968) correspond to lengthenings of all bonds by 0.009–0.010 Å.

The mean value of the three C(6)–O lengths [1.404 → 1.413 Å (corr.)] agrees well with the mean C–O length of 1.412 Å in the orthoester moiety of 3,4,6-tri-*O*-acetyl-1,2-*O*-[1-(*exo*-ethoxy)ethylidene]- α -D-glucopyranose (Heitmann, Richards & Schroeder, 1974), the only other orthoester for which we have accurate structural data. The mean length of the three outer C–O bonds is markedly longer (1.437 → 1.446 Å). If we assume that both kinds of bond are subject to roughly similar experimental errors, these results would seem to support the suggestion that, as the number of O atoms attached to the same C atom increases, the C–O distance tends to become shorter. Other effects depending on substituents and conformation (Jeffrey, Pople & Radom, 1972; Lehn, Wipff & Bürgi, 1974) are also undoubtedly present.

The central C(1)–C(6) bond (1.531 → 1.540 Å) is slightly shorter than the corresponding bond (1.556 Å) in the parent hydrocarbon (Ermer, Gerdil & Dunitz, 1971). The roughly parallel C(3)–C(4) bond is also shorter (1.492 → 1.502 Å) than expected; however, this length would be most affected by inadequacies in the correction for thermal motion and disorder.

The crystal packing is illustrated in Fig. 3. The layers perpendicular to c consist of molecules of the same chirality but of alternating polarity in the b direction – molecules related by the 2_1 axis. Successive layers consist of molecules of alternating chirality. No unusually close intermolecular contacts occur. There are eight intermolecular C...O distances less than 3.9 Å [shortest 3.54 Å between O(5) and C(13)], all involving atoms within a common layer, and only one such C...C contact [3.76 Å between C(4) atoms of different layers]. Changing the chirality of a single molecule leads

to changes in the intralayer contacts, but changing the chirality of an entire layer leaves all distances less than 3.9 Å unaltered, since the position of C(4) is unchanged. We have not been able to establish the exact nature of the disorder, which may be different from one crystal specimen to another. It should be noted that the diffraction patterns of most crystal specimens are of low quality (reflexions split or drawn out into arcs, abnormally large intensity fall-off with increase in scattering angle).

We are grateful to Professor Deslongchamps for a sample of the compound. This work was supported by the Swiss National Fund for the Advancement of Scientific Research.

References

- DESLONGCHAMPS, P., ATLANTI, P., FRÉHEL, D. & MALAVAL, A. (1972). *Canad. J. Chem.* **50**, 3405–3408.
- DESLONGCHAMPS, P., CHÉNEVERT, R., TAILLEFER, R. J., MOREAU, C. & SAUNDERS, J. K. (1975). *Canad. J. Chem.* **53**, 1601–1615.
- ERMER, O., GERDIL, R. & DUNITZ, J. D. (1971). *Helv. Chim. Acta*, **54**, 2476–2487.
- HEITMANN, J. A., RICHARDS, G. F. & SCHROEDER, L. R. (1974). *Acta Cryst.* **B30**, 2322–2328.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–216. Birmingham: Kynoch Press.
- JEFFREY, G. A., POPLÉ, J. A. & RADOM, L. (1972). *Carbohydr. Res.* **25**, 107–116.
- LEHN, J. M., WIPFF, G. & BÜRGI, H. B. (1974). *Helv. Chim. Acta*, **57**, 493–496.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.