

pair may be at least partly responsible for the variations in the N—N bond lengths.

Apart from the N—N bond, the bond distances and angles in RDX are similar to those found in pure RDX (Choi & Prince, 1972). The sulfolane molecule is structurally similar to that in other complexes (Swank & Willet, 1974), except that the bond distances and angles are more uniform in the RDX–sulfolane complex.

Because of the decrease in the density of the RDX–sulfolane lattice ( $1.64 \text{ g cm}^{-3}$ ) compared to pure RDX ( $1.8 \text{ g cm}^{-3}$ ), fewer short intermolecular contacts exist. The shortest intermolecular distances are given in Fig. 3. These tend to be O...N and O...C attractions between RDX molecules, and O...N attractions between RDX and sulfolane. RDX packs as interlocked molecules related by the inversion operation. The axial  $\text{NO}_2$  of one molecule nests in the 'basket' of a neighbor in a manner similar to that in pure RDX. However, according to Fig. 3 the sulfolane molecule may also play a role in the stereochemistry of N(1). O(8) is positioned to repel the lone pair on N(1) and could be responsible for this lone pair preferring to localize in an equatorial rather than axial region of space.

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## Structure of 1,4:3,6-Dianhydro-D-sorbitol,\* $\text{C}_6\text{H}_{10}\text{O}_4$ , at 100 K

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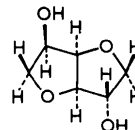
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**Abstract.**  $M_r = 146.14$ , orthorhombic,  $P2_12_12_1$ ,  $a = 5.313$  (2),  $b = 7.006$  (3),  $c = 17.174$  (5) Å,  $V = 639.3$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.52 \text{ Mg m}^{-3}$ ,  $D_m$  not measured,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.138 \text{ mm}^{-1}$ ,  $F(000) = 312$ ,  $T \approx 100 \text{ K}$ . Final  $R = 0.026$  for 1263 observed data. Evidence is obtained for the existence of a bifurcated hydrogen bond consisting of an intermolecular ( $\text{O}\cdots\text{O} = 2.771$  Å) and an intramolecular ( $\text{O}\cdots\text{O} = 2.826$  Å) hydrogen bond.

**Introduction.** In the course of an investigation of the complexation behaviour of 1,4:3,6-dianhydrohexitols with lanthanoid compounds, information was needed

about the conformation of 1,4:3,6-dianhydro-D-sorbitol (DIAN):



The compound has both an *endo*- and an *exo*-OH function. With the use of IR spectroscopy it has been shown that in dilute  $\text{CCl}_4$  solution ( $< 0.005 \text{ M}$ ) a strong intramolecular hydrogen bond exists between the *endo*-OH and the neighbouring ether O atom (Brimacombe, Foster, Stacey & Whiffen, 1958). The two fused five-membered rings of DIAN may adopt several envelope and half-chair conformations. A

\* IUPAC name: 1,4:3,6-dianhydro-D-glucitol.

derivative of DIAN, 2-*O*-(*p*-bromophenylsulphonyl)-1,4:3,6-dianhydro-D-sorbitol 5-nitrate (hereafter called BrDIAN), exhibits a conformation in which the five-membered rings are significantly non-planar. Each ring may be described in terms of planes through four atoms – the two atoms which are common to the two five-membered rings, and the two atoms bonded to these; the fifth atoms are displaced from these planes by about 0.5 Å (Camerman, Camerman & Trotter, 1965). However, interpretation of the <sup>1</sup>H NMR vicinal coupling constants in DIAN (Hopton & Thomas, 1969) does not result in definite conclusions about the actual conformation of the ring system. To facilitate the interpretation of <sup>1</sup>H NMR data DIAN was studied by X-ray analysis.

**Experimental.** Title compound prepared according to Shen (1963) and recrystallized from acetone at 298 K. The very deliquescent crystals were enclosed in thin-walled glass capillaries. A crystal (approximate dimensions 0.25 × 0.3 × 0.4 mm) was mounted on an Enraf-Nonius CAD-4 diffractometer. Unit-cell dimensions obtained by a least-squares fit of setting angles of 25 reflections. An independent set *hkl* (*h*: 0 to 7; *k*: 0 to 10; *l*: 0 to 25) was measured [ $\omega/2\theta$  scan mode,  $\omega$ -scan angle (0.95 + 0.35 tg  $\theta$ )°] with graphite-monochromated Mo *K*α radiation at *T* = 100 K to  $\theta = 32^\circ$ ; three standard reflections measured every 50 reflections, variation within 6%. This gave 1302 independent data of which 1263 reflections with  $I > \sigma(I)$  were used in subsequent calculations. No correction for absorption applied. Structure solved by direct methods (MULTAN, Germain, Main & Woolfson, 1970). H atoms located from a difference map. Full-matrix least-squares refinement on *F* (XRAY72, Stewart, Kruger, Ammon, Dickinson & Hall, 1972) of *x*, *y*, *z* of all atoms, anisotropic temperature factors for heavy atoms and isotropic *U*'s for H atoms, with equal weights given to all reflections, converged at *R* = 0.026 for 1263 observed reflections. In final cycles shifts in parameters all < 0.05  $\sigma$ ; in final difference synthesis the largest features were peaks halfway along C–C bonds, with heights about 0.3 e Å<sup>-3</sup>.

**Discussion.** Positional and isotropic thermal parameters are given in Table 1.\* Bond distances, bond angles and selected torsion angles are given in Table 2. An ORTEP plot (Johnson, 1965) of the molecule is given in Fig. 1. The geometry of the ring system in DIAN differs significantly from that in BrDIAN (Camerman *et al.*, 1965).

\* Lists of structure factors, anisotropic thermal parameters and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39036 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) with e.s.d.'s and  $U_{eq}$  values ( $\text{\AA}^2 \times 10^4$ );  $U_{iso}$  ( $\text{\AA}^2 \times 10^3$ ) for H atoms

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}^*/U_{iso}$
C(1)	1834 (2)	-2645 (2)	3101 (1)	133
C(2)	3312 (2)	-3045 (2)	3845 (1)	116
C(3)	3133 (2)	-1119 (2)	4257 (1)	102
C(4)	504 (2)	-428 (2)	4053 (1)	91
C(5)	893 (2)	1698 (2)	3906 (1)	104
C(6)	3441 (1)	1693 (2)	3515 (1)	122
O(1)	4849 (2)	218 (1)	3906 (1)	124
O(2)	-192 (2)	-1395 (1)	3337 (1)	122
O(3)	1168 (2)	2657 (1)	4636 (1)	134
O(4)	5782 (2)	-3727 (1)	3719 (1)	154
H(11)	291 (3)	-198 (2)	272 (1)	11
H(12)	113 (4)	-381 (3)	288 (1)	20
H(21)	236 (3)	-402 (2)	414 (1)	13
H(31)	342 (3)	-116 (2)	482 (1)	11
H(41)	-77 (3)	-68 (2)	443 (1)	15
H(51)	-42 (3)	224 (2)	359 (1)	10
H(61)	330 (3)	139 (2)	296 (1)	15
H(62)	433 (3)	287 (2)	357 (1)	18
H(O3)	-10 (4)	264 (4)	487 (1)	39
H(O4)	665 (4)	-283 (3)	355 (1)	21

E.s.d. in  $U_{eq}/U_{iso}$  is 4 in last significant digit.

\*  $U_{eq} = \frac{1}{3} \text{trace } \bar{U}$ .

Table 2. Molecular geometry

Maximum e.s.d.'s for C–O and C–C bonds are 0.002 Å, for O–H and C–H bonds 0.02 Å and for angles 0.1°.

Bond distances (Å)			
C(1)–C(2)	1.526	C(1)–H(11)	0.98
C(1)–O(2)	1.445	C(1)–H(12)	0.98
C(2)–C(3)	1.526	C(2)–H(21)	0.99
C(2)–O(4)	1.413	C(3)–H(31)	0.97
C(3)–C(4)	1.519	C(4)–H(41)	0.95
C(3)–O(1)	1.440	C(5)–H(51)	0.96
C(4)–C(5)	1.525	C(6)–H(61)	0.98
C(4)–O(2)	1.452	C(6)–H(62)	0.96
C(5)–C(6)	1.511	O(3)–H(O3)	0.78
C(5)–O(3)	1.429	O(4)–H(O4)	0.83
C(6)–O(1)	1.441		
Bond angles*(°)			
C(2)–C(1)–O(2)	105.1	C(3)–C(4)–C(5)	103.0
C(1)–C(2)–C(3)	101.2	O(2)–C(4)–C(5)	110.5
C(1)–C(2)–O(4)	114.3	C(4)–C(5)–C(6)	101.1
C(3)–C(2)–O(4)	115.3	C(4)–C(5)–O(3)	109.2
C(2)–C(3)–O(1)	110.0	C(6)–C(5)–O(3)	107.4
C(2)–C(3)–C(4)	103.4	C(5)–C(6)–O(1)	105.0
O(1)–C(3)–C(4)	106.1	C(6)–O(1)–C(3)	109.4
C(3)–C(4)–O(2)	106.3	C(1)–O(2)–C(4)	109.3
Torsion angles(°)			
O(2)–C(1)–C(2)–C(3)	-36.5	C(4)–C(5)–C(6)–O(1)	-37.0
C(1)–C(2)–C(3)–C(4)	36.2	C(3)–C(4)–C(5)–C(6)	36.9
C(2)–C(3)–C(4)–O(2)	-23.8	O(1)–C(3)–C(4)–C(5)	-24.3
C(3)–C(4)–O(2)–C(1)	0.7	C(6)–O(1)–C(3)–C(4)	1.0
C(4)–O(2)–C(1)–C(2)	22.8	C(5)–C(6)–O(1)–C(3)	23.0
O(1)–C(3)–C(4)–O(2)	92.0	O(4)–C(2)–C(3)–O(1)	47.1
C(2)–C(3)–C(4)–C(5)	-140.1	O(2)–C(4)–C(5)–O(3)	170.6

\* See deposition footnote.

Table 3. Geometry of the bifurcated hydrogen bond

O–H...O	O...O (Å)	H...O (Å)	O–H...O (°)
O(4)–H(O4)...O(1)	2.826 (2)	2.42 (2)	111 (2)
O(4)–H(O4)...O(2)	2.771 (2)	1.99 (2)	156 (2)

Symmetry code: (i) *x* + 1, *y*, *z*.

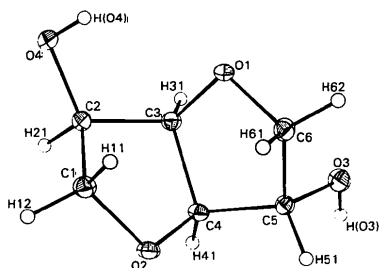


Fig. 1. Atom numbering and thermal ellipsoids (50% probability level) of the non-H atoms. The H atoms were given an arbitrary 0.07 Å radius.

DIAN consists of two planes [defined by C(1)O(2)C(4)C(3) and by C(4)C(3)O(1)C(6) respectively] nearly perpendicular ( $87.0^\circ$ ) to each other. The maximum deviation from the mean planes is 0.004 Å [O(2)] and 0.006 Å [O(1)] respectively; atom O(4) is in the *endo* and atom O(3) in the *exo* position (see Table 2). Atoms C(2) and C(5) are displaced from the planes concerned by 0.58 and 0.59 Å respectively, while in BrDIAN C(1) and C(6) are displaced from the planes through the remaining four atoms. Therefore, in interpreting  $^1\text{H}$  NMR data one must keep in mind that the conformation of the ring system is rather flexible and dependent on the steric demands and electronic properties of the substituents.

The packing of the molecules is illustrated in Fig. 2. There are two O...O contacts shorter than 2.85 Å, which can be interpreted as belonging to a bifurcated hydrogen bond between O(4) and O(1) in the same molecule and between O(4) and O(2) in a symmetry-related molecule (see Table 3). This observation supports the conclusion drawn from IR spectral studies (Brimacombe *et al.*, 1958) that, in dilute solution, there

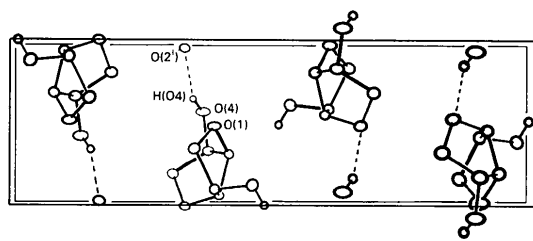


Fig. 2. Unit-cell content viewed down *b*. The intermolecular hydrogen bond is indicated by a broken line. For the sake of clarity the intramolecular hydrogen bond [H(O4)...O(1)] is not indicated.

exists an intramolecular hydrogen bond. In the crystal this intramolecular interaction is much weaker than the intermolecular one. It may be noted that the configuration of the O(2)–C(4)–C(5)–O(3) part of the molecule does not allow an intramolecular hydrogen bond.

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### Structure of (8*aRS*,9*RS*,10*aSR*)-10-Ethoxycarbonyl-1,2,3,4,5,6,7,8,8*a*,10*a*-decahydro-10*H*-9-thia-10-azaphenanthrene 9-Oxide, C<sub>15</sub>H<sub>23</sub>NO<sub>3</sub>S

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**Abstract.**  $M_r = 297.42$ , monoclinic,  $P2_1/c$ ,  $a = 290$  (1) Å,  $Z = 4$ ,  $D_x = 1.30$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu(\text{Cu } K\alpha) = 1.84$  mm<sup>-1</sup>,  $R = 0.064$  for 1518 observed reflections. The relative configuration at S in the title compound has been determined: the S–O bond is *trans* to the two C–H bonds on the heterocyclic ring.

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