

ions, the difference between  $M\text{-Cl}_{\text{axial}}$  and  $M\text{-Cl}_{\text{eq}}$  is exactly the same, 0.09 Å. Thus, this should be a near ideal lattice for EPR studies on  $\text{Mn}^{2+}$  doped into a diamagnetic lattice.

The PDA ion is nearly planar, with the plane of the ion sitting athwart the crystallographic  $bc$  plane. This presumably allows the  $\text{-NH}_3^+$  groups to hydrogen bond to the Cd-Cl layers in a manner analogous to that in the Mn and Fe salts, the disorder being absent. The C(1)-N and C(1)-C(2) distances are slightly longer than normal, 1.534 (8) and 1.570 (9) Å respectively, probably because of neglect of the H scattering. Those determined for the Mn, Fe and Cu salts are normal (1.47-1.48 Å, 1.49-1.50 Å).

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## 1,4,9,12-Tetraoxadispiro[4.2.4.2]tetradecane

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**Abstract.**  $\text{C}_{10}\text{H}_{16}\text{O}_4$ ,  $M_r = 200.12$ , monoclinic,  $P2_1/c$ ,  $a = 5.767$  (5),  $b = 8.566$  (8),  $c = 10.635$  (10) Å,  $\beta = 109.02$  (2)°,  $Z = 2$ ,  $D_x = 1.34$  g cm $^{-3}$ . The cyclohexane ring has the usual chair conformation, and the ketal rings have an intermediate conformation between twist and envelope. Axial and equatorial C-O lengths (uncorrected for libration) are 1.424 (3) and 1.431 (3) Å, equal within experimental error. The corrected values are both 1.437 Å.

**Introduction.** Our main aim in this study was to find out whether axial and equatorial C-O bonds on a cyclohexane ring differ in length. Crystals (m.p. 79-80°C), obtained by slow cooling of a saturated  $n$ -hexane solution, were kindly provided by Dr K. Müller. They were sealed in capillaries for X-ray analysis.

Intensities from a crystal, 0.3 mm in edge, were collected on an automated Hilger & Watts Y290 diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å,  $\mu = 1.10$  cm $^{-1}$ ); 871 reflexions ( $2\theta < 50^\circ$ ), 833 with  $I \geq 3\sigma(I)$ . The structure (Fig. 1) was solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1970) and refined by full-matrix least squares (XRAY system, Stewart, Kruger, Ammon, Dickinson & Hall, 1972) with experimental weights. At an intermediate stage, all H atoms were located from a difference map (sin  $\theta/\lambda$  limit 0.45 Å $^{-1}$ ) and subsequently included. The final  $R$  was 0.055,

including extinction corrections. Final positional parameters and isotropic thermal parameters (for H) are

Table 1. *Atomic coordinates (e.s.d.'s in parentheses) for non-hydrogen atoms ( $\times 10^4$ ) (asymmetric unit only)*

	$x$	$y$	$z$
O(1)	4450 (3)	3046 (2)	3987 (2)
C(2)	2264 (4)	3931 (3)	3706 (3)
C(3)	731 (5)	3024 (3)	4334 (3)
O(4)	1522 (3)	1468 (2)	4320 (2)
C(5)	4058 (4)	1534 (3)	4453 (2)
C(6)	4588 (4)	287 (3)	3594 (2)
C(14)	5654 (4)	1342 (3)	5889 (2)

Table 2. *Atomic coordinates and isotropic  $U$  values for hydrogen atoms (all  $\times 10^3$ ) (asymmetric unit only)*

	$x$	$y$	$z$	$U$ (Å $^2$ )
H(1)C(2)	152 (10)	401 (7)	271 (5)	101 (18)
H(2)C(2)	269 (11)	503 (7)	404 (6)	128 (21)
H(1)C(3)	104 (11)	338 (7)	536 (6)	147 (22)
H(2)C(3)	-104 (10)	305 (6)	379 (5)	93 (18)
H(1)C(6)	345 (8)	44 (6)	263 (4)	61 (14)
H(2)C(6)	630 (8)	46 (5)	358 (4)	61 (14)
H(1)C(14)	739 (8)	156 (5)	596 (4)	58 (14)
H(2)C(14)	520 (8)	213 (5)	642 (4)	58 (14)

listed in Tables 1 and 2.\* Corresponding interatomic distances and angles, involving C and O atoms, are shown in Fig. 2; C—H distances and H—C—H angles lie in the ranges 0.97–1.09 Å and 106–112° respectively.

**Discussion.** The axial C(5)—O(4) bond [1.424 (3) Å] is slightly shorter than the equatorial C(5)—O(1) [1.431 (3) Å]. Apart from the dubious statistical significance of the difference, there are two other reasons for believing the bond lengths to be virtually equal. One is based on the observation that differences in geminal C—O bond distances correlate with differences in CCO

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32460 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

angles (Bürgi, Dunitz & Shefter, 1973); the difference between the angle sums C(6)C(5)O(4) + C(14)-C(5)O(4) [219.8°] and C(6)C(5)O(1) + C(14)-C(5)O(1) [219.9°] is essentially zero. The second reason is that on applying approximate corrections for librational motion (Cruickshank, 1956) the two C—O lengths become equal at 1.437 Å.

The cyclohexane ring adopts the normal chair conformation with a mean bond angle of 111.4° [standard value 111.5° (Dunitz, 1968)], and the ketal ring is intermediate between a twist and an envelope conformation. In terms of the phase-angle description proposed by Altona, Geise & Romers (1968),  $\Delta = 29.5^\circ$ . In this description,  $\Delta = 0^\circ$  would correspond to the form with a twofold rotation axis passing through C(5) and the mid-point of C(2)—C(3); other twist forms occur at  $\Delta = 36, 72^\circ, \dots$ , and envelope forms at  $\Delta = 18,$

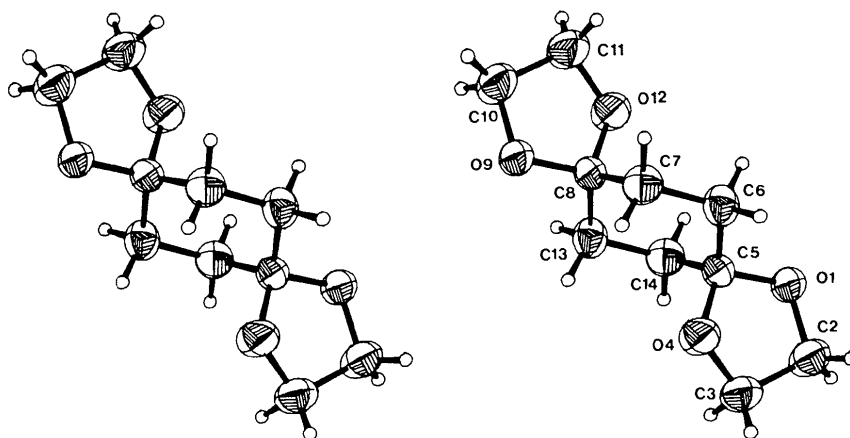


Fig. 1. Stereoscopic view of the molecule drawn by ORTEP (Johnson, 1965). The thermal vibration ellipsoids are at the 50% probability level.

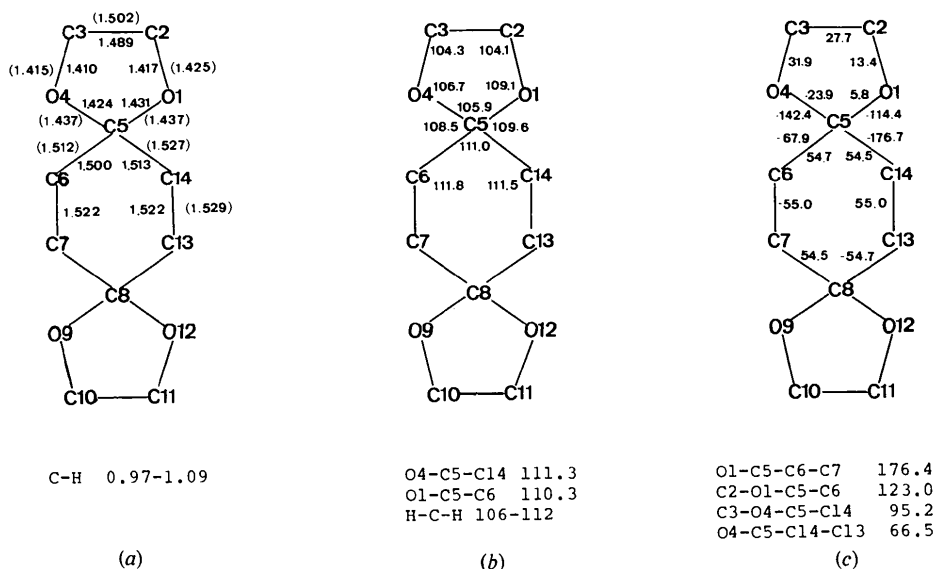


Fig. 2. (a) Bond lengths (Å) (values corrected for molecular libration are in brackets), (b) bond angles (°) and (c) torsion angles (°). E.s.d.'s are about 0.003 Å for bond lengths and 0.2° for bond angles not involving H atoms.

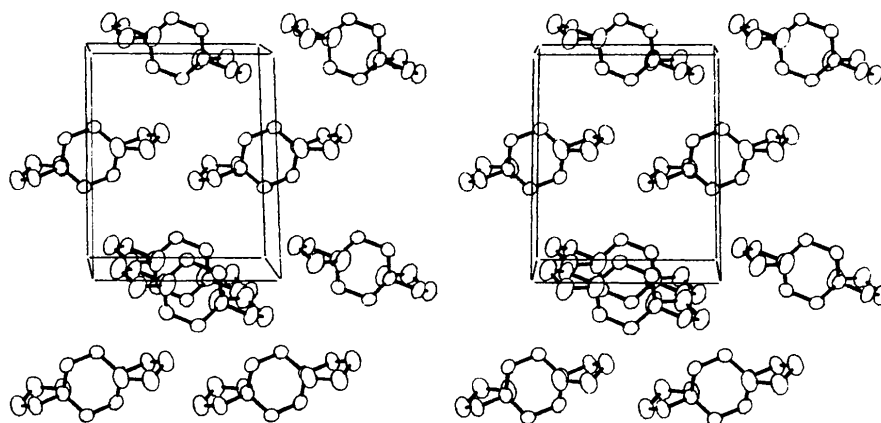


Fig. 3. Stereoscopic view of the crystal structure drawn by *ORTEP* (Johnson, 1965). The axial directions are *b*→, *c*↓, and *a* into the plane of the paper.

54, 90°,.... The observed conformation is thus somewhat nearer to a twist [twofold axis through O(1)] than to an envelope.

Analysis of the vibrational ellipsoids in terms of rigid-body motion (Cruickshank, 1956) leads to only modest agreement between observed and calculated  $U_{ij}$  values ( $\langle \Delta U_{ij}^2 \rangle^{1/2} = 45 \times 10^{-4} \text{ \AA}^2$ ). The eigenvalues of the **T** tensor are 0.0454, 0.0436 and 0.0283  $\text{\AA}^2$ , the largest component being roughly normal to the mean plane of the ketal ring (simulation of an internal puckering motion?), the next largest parallel to the long axis of the molecule. This is also the direction of the main librational axis, with a mean-square amplitude of 61.5 deg<sup>2</sup> (other eigenvalues: 11.2 and 4.9 deg<sup>2</sup>). Libration corrections amount to 0.005–0.014 Å for bond lengths (Fig. 2) but they are negligible for bond angles.

The molecular packing is illustrated in Fig. 3. There are no unusually short intermolecular contacts.

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