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## Structure of (*trans*-2-Hydroxycyclohexyl)dimethylphosphine Oxide, C<sub>8</sub>H<sub>17</sub>O<sub>2</sub>P

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**Abstract.**  $M_r = 176.20$ , monoclinic,  $P2_1/c$ ,  $a = 8.674$  (2),  $b = 11.532$  (3),  $c = 10.050$  (2) Å,  $\beta = 106.32$  (2)°,  $V = 964.7$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.211$ ,  $D_m = 1.19$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 2.17$  mm<sup>-1</sup>,  $F(000) = 384$ ,  $T = 298$  K,  $R = 0.049$  for 1581 observed reflections. The cyclohexyl ring is in a chair conformation and the 2-hydroxyl and dimethylphosphine groups are both in the equatorial conformation. The bonding around the phosphorus has a slightly distorted tetrahedral configuration. There is an intermolecular hydrogen bond which links the hydroxy group to the phosphine oxide.

**Introduction.** Trialkylphosphines deoxygenate epoxides at high temperatures to produce olefins of inverted configuration and the corresponding trialkylphosphine oxide. For example, (*E*)-2-butene oxide on treatment with tributylphosphine at 423 K produces a 4:1 mixture of (*Z*)- and (*E*)-2-butene (Boskin & Denney, 1959). The mechanism is believed to involve a nucleophilic ring opening of the epoxide by the phosphine with inversion of configuration at carbon, a rotation about the carbon-carbon single bond to place the phosphorus and oxygen in close proximity, and a *syn* elimination of the phosphine oxide. It has been demonstrated recently (Buynak, McKenzie-Graff & Jadhav, 1984) that this reaction is catalyzed by zinc bromide and that when it is performed with phosphines containing an Si-N-P linkage, the silicon can be transferred to the oxygen after the initial ring-opening to produce air- and moisture-sensitive  $\beta$ -trimethylsiloxyiminophosphoranes. These compounds can be hydrolyzed to the more stable  $\beta$ -hydroxyphosphine oxides. Previously, no intermediates have been isolated from the reaction of neutral phosphines (Vedejs & Fuchs, 1973) and epoxides. It is mechanistically important to demonstrate that this

process does occur with inversion of configuration, even in the presence of Lewis acids and with the rather unusual silylamino phosphines. The crystal structure of a  $\beta$ -hydroxyphosphine oxide (I) is reported in this paper. (I) was prepared by the reaction of [bis(trimethylsilyl)amino]dimethylphosphine with cyclohexane oxide and subsequent hydrolysis of the iminophosphorane as shown in the reactions in Fig. 1.

**Experimental.** Chemical formula established by NMR data, single crystals obtained by crystallization from toluene in the form of transparent colorless cubic prisms, unit-cell parameters by least-squares analysis of 15 reflections with  $2\theta$  from 15 to 79°, space group  $P2_1/c$  determined from systematic absences ( $h0l$  absent with  $l$  odd,  $0k0$  absent with  $k$  odd),  $D_m$  by flotation in a mixture of chlorocyclohexane and bromocyclohexane, automatic diffractometer, graphite-monochromatized Cu  $K\alpha$  radiation, crystal  $0.22 \times 0.22 \times 0.22$  mm,  $c$  axis of the crystal approximately along the  $\phi$  axis of the diffractometer,  $\theta/2\theta$  scanning mode, 1615 independent reflections with  $2\theta < 130^\circ$ , range of  $hkl$ :  $-10 \rightarrow 9$ ,  $0 \rightarrow 13$ ,  $0 \rightarrow 11$ , 1585 observed,  $I > 3\sigma(I)$ ; three standard reflections measured after every 50 reflections showed a

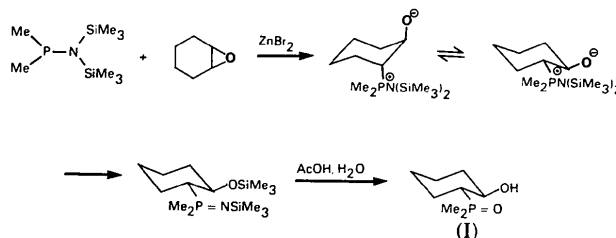


Fig. 1. Proposed reaction scheme for the preparation of (I).

random variation of less than 2% in intensity; Lorentz-polarization corrections, absorption corrections using *SHELX76* (Sheldrick, 1976), max. and min. transmission factors 0.723 and 0.643 respectively, no extinction correction, direct methods, refinement by full-matrix anisotropic least squares, H positions located in a difference Fourier synthesis, isotropic temperature factors for H atoms,  $w = 1/[\sigma(F)]^2$ ,  $\sigma(F)$  from counting statistics,  $\sum w(|F_o| - |F_c|)^2$  minimized;  $R = 0.049$ ,  $wR = 0.050$  for 1581 observed reflections, four low-order strong reflections (020, 100, 012 and  $\bar{1}04$ ) excluded from refinement due to extinction,  $(\Delta/\sigma)_{\max} = 0.14$ , max. and min. heights in final  $\Delta F$  map 0.27 and  $-0.25 \text{ e } \text{Å}^{-3}$ ; *SHELX76* system of programs (Sheldrick, 1976), atomic scattering factors for P, O, C and H from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The final parameters are given in Table 1.\* The identification of the atoms and the conformation of the molecule are shown in Fig. 2. The cyclohexyl ring is in a chair conformation as shown by the torsion angles in Table 2.\* The Cremer & Pople (1975) puckering parameters for the cyclohexyl ring are:  $q_2 = 0.038$  (3),  $q_3 = 0.561$  (3),  $Q = 0.562$  (3) Å, and  $\theta = 3.9$  (3)°. For ideal chair conformation, these parameters are:  $q_2 = 0$ ,  $q_3 = \pm Q$ , and  $\theta = 0$ °. Both the hydroxyl and dimethylphosphine oxide groups are in the equatorial conformation. The torsion angles about the C(1)–P and C(2)–O(2) bonds are also shown in Table 2.\*

The bond lengths and bond angles with their standard deviations are shown in Fig. 3. The P–C and P–O bond lengths and the bond angles around the phosphorus atom have values similar to those observed in other phosphine oxides (Cotton, Darensbourg, Friedrich, Ilsley & Troup, 1981; Ruban & Zabel, 1976). The bonding around the phosphorus has a slightly distorted tetrahedral configuration with tetrahedral angles ranging from 104.2 (1) to 112.7 (1)°. The P–O bond length is 1.501 (1) Å. The lengths of the P–C bonds which link the phosphorus atom to the two methyl carbon atoms are 1.795 (2) and 1.793 (2) Å; however, the P–C bond [1.827 (2) Å] which links the phosphorus atom to the cyclohexyl ring is significantly longer. This longer distance is apparently due to the nonbonded interaction between the dimethylphosphine oxide and hydroxy groups, both being in equatorial conformation. The nonbonded intermolecular distance between P and O(2) is 3.049 (2) Å. All the C–H bond lengths and

\* Lists of structure factors, anisotropic thermal parameters and torsion angles (Table 2) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42075 (12 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 for non-hydrogen ( $\times 10^4$ ,  $\times 10^5$  for P) and for hydrogen atoms ( $\times 10^3$ ), with equivalent isotropic thermal parameters for non-hydrogen ( $\times 10^4$ ) and isotropic for hydrogen atoms ( $\times 10^3$ )

E.s.d.'s are given in parentheses.  $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ .

	x	y	z	$U_{\text{eq}}/U^*(\text{Å}^2)$
C(1)	4637 (2)	2254 (2)	6295 (2)	335 (4)
C(2)	3743 (2)	1120 (2)	5824 (2)	342 (4)
C(3)	2020 (3)	1179 (2)	5901 (3)	452 (5)
C(4)	1115 (3)	2180 (2)	5047 (3)	528 (6)
C(5)	1964 (3)	3314 (2)	5549 (3)	567 (6)
C(6)	3704 (3)	3297 (2)	5504 (3)	460 (5)
P	66476 (6)	21862 (4)	60556 (5)	322 (1)
O(P)	6614 (2)	1788 (1)	4627 (1)	419 (3)
C(7)	7509 (3)	3606 (2)	6418 (3)	556 (6)
C(8)	7891 (3)	1291 (2)	7391 (2)	480 (5)
O(2)	4598 (2)	213 (1)	6654 (2)	423 (3)
H(1)	477 (3)	240 (2)	722 (2)	36 (5)
H(2)	373 (3)	97 (2)	485 (2)	33 (5)
H(3)1	200 (3)	125 (2)	682 (3)	59 (7)
H(3)2	156 (3)	46 (2)	553 (3)	53 (6)
H(4)1	4 (4)	219 (2)	515 (3)	76 (9)
H(4)2	103 (4)	208 (2)	402 (3)	72 (9)
H(5)1	138 (3)	396 (3)	499 (3)	65 (8)
H(5)2	197 (3)	343 (2)	650 (3)	64 (8)
H(6)1	368 (3)	330 (2)	460 (3)	49 (6)
H(6)2	426 (3)	402 (3)	592 (3)	71 (8)
H(7)1	741 (3)	389 (3)	744 (3)	82 (3)
H(7)2	694 (4)	405 (3)	569 (4)	82 (3)
H(7)3	855 (4)	359 (3)	630 (3)	82 (3)
H(8)1	790 (4)	169 (3)	823 (3)	82 (3)
H(8)2	901 (4)	139 (3)	732 (3)	82 (3)
H(8)3	754 (4)	46 (3)	739 (3)	82 (3)
H(O2)	420 (4)	-36 (2)	631 (3)	82 (3)

\* The standard deviations of  $U_{\text{eq}}$ 's were calculated in accordance with the expressions derived by Schomaker & Marsh (1983).

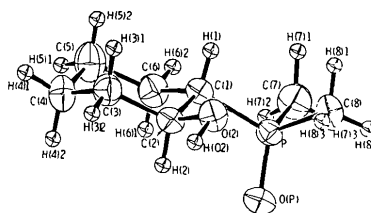


Fig. 2. ORTEP drawing (Johnson, 1965) of a molecule of (I).

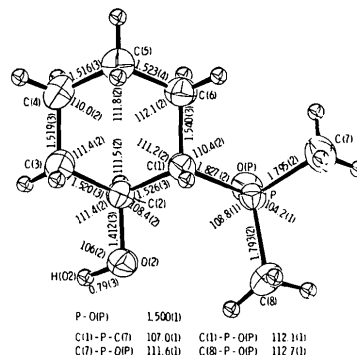


Fig. 3. Bond lengths (Å) and bond angles (°) of (I) with e.s.d.'s in parentheses.

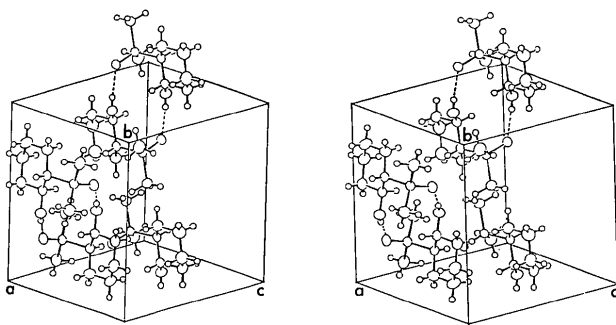


Fig. 4. Stereoscopic drawing of molecular packing of (I) in the unit cell. Dashed lines represent the intermolecular hydrogen bonds.

C—C—H and H—C—H bond angles are within reasonable ranges of magnitudes. The O—H bond length of the hydroxy group is 0.79 (3) Å, and there is an intermolecular hydrogen bond which links the hydroxy group to the phosphine oxide, as shown in the molecular packing diagram in Fig. 4. The hydrogen-bond distance  $O(2)\cdots O(P)(1-x, -y, 1-z)$  is 2.707 (2) Å, and the angle  $O(2)—H(O2)\cdots O(P)$  is 174 (3)°. There are no other intermolecular contacts shorter than van der Waals interactions. The closest

contacts involving non-hydrogen atoms are 3.485 (2) and 3.387 (3) Å for  $C(1)\cdots O(P)$  and  $C(2)\cdots O(P)$  respectively.

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## Structure of 1-Azacarbazole, $C_{11}H_8N_2$

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**Abstract.**  $M_r = 168.20$ , monoclinic,  $P2_1/n$ ,  $a = 11.318$  (2),  $b = 5.547$  (1),  $c = 13.516$  (6) Å,  $\beta = 95.71$  (2)°,  $V = 844.3$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.32$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54187$  Å,  $\mu = 5.5$  cm<sup>-1</sup>,  $F(000) = 352$ , room temperature, final  $R = 0.055$  for 1160 observed reflections. The molecules form hydrogen-bonded dimers [ $N\cdots N' = 2.946$  (2) Å] in centrosymmetrically related pairs. The ring system deviates significantly from planarity, maximum atomic deviations  $-0.039$  (2) and  $+0.046$  (2) Å.

**Introduction.** Waluk, Grabowska, Pakuła & Sepiół (1984) and Waluk & Pakuła (1984) suggested that 1-azacarbazole dimers undergo tautomerization in excited states *via* co-operative two-proton transfer between the monomeric units. For photochemical study it is important to know the geometry of the azacarbazole molecules and this study was therefore undertaken in order to establish in particular whether the

azacarbazole molecules exist as planar or distorted dimers.

**Experimental.** Crystal dimensions 0.2 × 0.2 × 0.3 mm; accurate cell dimensions by least squares from setting angles of 20 reflections; Siemens AED diffractometer, monochromated Cu  $K\alpha$  radiation; 1871 reflections with  $3 \leq \theta \leq 70^\circ$  measured;  $\omega$ - $2\theta$  scans; reference reflection 212 measured periodically during data collection exhibited no significant decrease in intensity; intensities corrected for Lorentz and polarization factors but not for absorption or extinction.

Structure solved by direct methods with *SHELX76* (Sheldrick, 1976). All non-H atoms located in best  $E$  map. Subsequent refinement based on 1160 observed reflections above threshold [ $I_o \geq 2\sigma(I_o)$ ]; index range  $h \pm 13$ ,  $k 0/6$ ,  $l 0/16$ . All H atoms, except for H(9) which was located in a difference Fourier map, introduced in calculated positions [ $d(\text{C—H}) = 1.08$  Å].