small. The bond angles (Table 4) of equivalent sites in the two molecules are also similar except for those of the Si—O—Si angle which differ by 18.4°.

The Si—O—Si bond angle of disiloxanes has been observed over an unusually large range. Typically, unstrained disiloxanes adopt a bent configuration with the Si—O—Si angle ranging from 140 to 160° (see for example Wiese, Wannagat, Thewalt & Debaerdemaeker, 1987; Chandra, Lo, Hitchcock & Lappert, 1987; Michalczyk, Fink, Haller, West & Michl, 1986; Karle, Karle & Nielsen, 1986; Fink, Haller, West & Michl, 1984; Curtis, D'Errico, Duffy, Epstein & Bell, 1983; Eaborn, Hitchcock & Lickiss, 1983; Verdegaal, De Kok, Westerink, Van Boom & Romers, 1981; Yanovskii, Struchkov, Kalinin, Ismailov & Myakushev, 1981; Voronkov, Nesterov, Gusev, Alexeev & Lotarev, 1981; Barrow, Ebsworth & Harding, 1979) although, in cases where the organosubstituents are bulky, a linear configuration with Si—O—Si equal to 180° has been observed (Gusev, Los, Vlasenko, Zhun & Sheludyakov, 1984; Gusev, Antipin, Yufit, Struchkov, Sheludyakov, Zhun & Vlasenko, 1983; Glidewell & Liles, 1977, 1981). All of the disiloxanes whose structures have been determined differ in structure by at least one of the substituents on the silicon atoms. There has not been a previous example of X-ray diffraction studies where the difference in structures is remote to the silicon atom. Furthermore, as stated in the *Introduction*, (2) is unstrained. These structures illustrate the large number of conformations the siloxane may assume and the relative ease with which the Si—O—Si bond angle may be distorted.

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8-Cyclohexyl-16*H*-dinaphtho[2,1-*d*:1′,2′-*g*][1,3,2]dioxaphosphocine 8-Oxide

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(*Received* 15 *October* 1990; *accepted* 25 *June* 1991)

Abstract. $C_{27}H_{25}O_3P$, $M_r = 428{\cdot}47$, triclinic, $P\bar{1}$, $a = 9{\cdot}5223\,(12)$, $b = 11{\cdot}1702\,(9)$, $c = 11{\cdot}4109\,(13)$ Å, $\alpha = 75{\cdot}938\,(11)$, $\beta = 76{\cdot}451\,(10)$, $\gamma = 68{\cdot}651\,(12)°$, $V = 1082{\cdot}2\,(2)$ Å^3, $Z = 2$, $D_m = 1{\cdot}32$, $D_x = 1{\cdot}315$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 13{\cdot}2$ cm^{-1}, $F(000) = 452$, $T = 298$ K, final $R = 0{\cdot}055$ for 1937 observed reflections. The dioxaphosphocine ring exhibits a distorted boat conformation with the phosphoryl O

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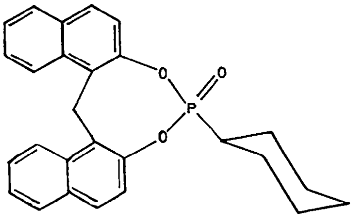
in an axial and the cyclohexane ring in an equatorial orientation; the cyclohexane ring is in a chair conformation. The dihedral angle between the planes of the two naphthalene rings is 74·4 (1)°.

Introduction. Organophosphorus compounds have attracted considerable interest because of their applications as insecticides, bactericides, flame retardants, lubricants, *etc.* (Ismail, 1975). Structures of phosphorus heterocycles with ring sizes larger than six are still rare and there is little data concerning their stereochemistry in the solid state or in solution. Crystal structure analysis of the title compound (I) was undertaken as part of our programme to study the effect of the substituents on the conformation of eight-membered heterocyclic rings.



(I)

Experimental. Colourless needle-shaped crystals from 1-butanol; D_m by flotation (KI solution); preliminary cell parameters from photographic methods, crystal size $0·3 \times 0·2 \times 0·4$ mm, accurate cell parameters from least-squares refinement of 25 reflections ($45 < 2\theta < 55°$). Intensity data collected using an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation; $\omega/2\theta$ scan technique; intensities of two standard reflections monitored during the course of data collection showed no significant variation. Intensities of 3198 independent reflections with $0 < 2\theta < 140°$ were measured, 1937 reflections were observed [$I > 3\sigma(I)$]; range of hkl $0 \leq h \leq 11$, $-13 \leq k \leq 13$ and $-13 \leq l \leq 13$; Lp corrections, but no absorption correction. Structure solved by direct methods using *SHELXS*86 (Sheldrick, 1986), refinement on F by full-matrix least-squares method using *SHELX*76 (Sheldrick, 1976). Positional parameters and anisotropic displacement parameters refined for all non-H atoms; the H-atom positions, which were found from difference Fourier maps, and their isotropic displacement parameters, which were set equal to those of the related C atoms, were included in the final cycles of refinement, but not refined. Final $R = 0·055$, $wR = 0·054$, $w = 0·9061/[\sigma^2(F_o) + 0·0021F_o^2]$, $S = 1·55$, $(\Delta/\sigma)_{\max} = 0·007$, the final difference map was featureless with maximum (near phosphorus) and minimum peak heights of 0·40 and $-0·35$ e Å^{-3}; no correction for secondary extinction; atomic scattering factors for all atoms as in *SHELX*76 (Sheldrick, 1976); geometrical calculations using *PARST* (Nardelli, 1983).

Discussion. Table 1* lists the final atomic coordinates and equivalent isotropic displacement parameters of the non-H atoms. A perspective view of the molecule with the atomic numbering scheme is shown in Fig. 1. The bond lengths, angles and selected torsion angles for the non-H atoms are given in Table 2.

The P=O(1) bond length [1·459 (3) Å], the endocyclic bond distances P—O(2) [1·586 (2) Å] and P—O(3) [1·601 (3) Å], the average C_{ar}—O length [1·404 (3) Å], and the endocyclic bond angle O(2)—P—O(3) [104·3 (2)°] are in agreement with values observed in related structures (Grand & Robert, 1978; Poll & Wunderlich, 1980; Goddard, Payne, Cook & Luss, 1988; Sivakumar, Subramanian, Natarajan, Krishnaiah & Ramamurthy, 1989). The mean values of the bond lengths and angles for the naphthalene groups are 1·393 (4) Å and 120°, respectively. The P—C(22) bond length [1·778 (4) Å] is normal and comparable (within an experimental e.s.d. of 3σ) to the corresponding value for the structure of (2,6-diphenyl-1,3-dioxa-6-aza-2-phospha-2-cyclooctyl)trihydroborane [1·794 (6) Å] (Dubourg, Declercq, Contreras, Murillo & Klaebe, 1985). The $C(sp^3)$—$C(sp^3)$ bond lengths in the cyclohexane ring range from 1·511 (6) to 1·534 (5) Å and the individual bond angles vary from 110·5 (4) to 111·8 (4)°. The average bond length [1·522 (6) Å] is less than that (1·540 Å) reported by Allcock (1967).

The best plane of the eight-membered ring passes through the atoms O(2), C(1), C(12) and C(21) with the O(2)—C(1) and C(12)—C(21) bonds crossing the plane in opposite directions while the other atoms in the ring pucker to the same side of the plane with varying magnitudes [O(2) = −0·017 (2), C(1) = 0·033 (3), C(12) = −0·043 (4), C(21) = 0·064 (4), P = 1·211 (1), O(3) = 1·075 (3), C(10) = 0·456 (3) and C(11) = 0·943 (3) Å], explaining the distorted boat conformation of the dioxaphosphocine ring. In contrast, a boat–chair form has been observed in the structure of 2,10-dichloro-6-cyclohexyl-12*H*-dibenzo-[*d*,*g*][1,3,2]dioxaphosphocine 6-oxide (Mani Naidu, 1990), where chlorobenzene groups are fused to the heterocyclic ring in place of the naphthyl groups. Thus, the conformation of the eight-membered ring

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles involving H atoms, least-squares planes and intermolecular contact distances, and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54379 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent isotropic thermal parameters for non-*H *atoms*

$B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$.

	x	y	z	B_{eq}(Å^2)
P	−0·1780 (1)	0·3212 (1)	0·2897 (1)	3·6 (0)
O(1)	−0·0176 (3)	0·2526 (3)	0·3009 (2)	5·0 (1)
O(2)	−0·2821 (2)	0·3845 (2)	0·4040 (2)	3·5 (1)
O(3)	−0·2614 (3)	0·2278 (2)	0·2704 (2)	4·1 (1)
C(1)	−0·2533 (3)	0·3457 (3)	0·5240 (3)	3·1 (1)
C(2)	−0·2460 (4)	0·4444 (4)	0·5758 (4)	4·0 (1)
C(3)	−0·2233 (4)	0·4170 (4)	0·6933 (4)	4·1 (2)
C(4)	−0·2085 (3)	−0·2924 (4)	0·7643 (3)	3·4 (1)
C(5)	−0·1845 (4)	0·2622 (4)	0·8873 (4)	4·3 (2)
C(6)	−0·1686 (4)	0·1421 (5)	0·9550 (4)	5·1 (2)
C(7)	−0·1707 (4)	0·0428 (4)	0·9022 (4)	4·8 (2)
C(8)	−0·1941 (4)	0·0670 (4)	0·7845 (4)	3·9 (1)
C(9)	−0·2150 (3)	0·1918 (4)	0·7107 (3)	3·2 (1)
C(10)	−0·2410 (3)	0·2211 (3)	0·5872 (3)	2·9 (1)
C(11)	−0·2509 (3)	0·1214 (3)	0·5240 (3)	3·3 (1)
C(12)	−0·3951 (4)	0·1633 (3)	0·4665 (3)	3·2 (1)
C(13)	−0·5353 (4)	0·1510 (3)	0·5408 (4)	3·7 (1)
C(14)	−0·5486 (4)	0·1045 (4)	0·6667 (4)	4·3 (2)
C(15)	−0·6834 (5)	0·0899 (4)	0·7352 (4)	5·4 (2)
C(16)	−0·8128 (4)	0·1261 (5)	0·6773 (6)	6·0 (2)
C(17)	−0·8054 (4)	0·1727 (4)	0·5579 (5)	5·4 (2)
C(18)	−0·6665 (4)	0·1857 (4)	0·4829 (4)	4·2 (2)
C(19)	−0·6546 (4)	0·2278 (4)	0·3562 (5)	4·9 (2)
C(20)	−0·5228 (5)	0·2411 (4)	0·2884 (4)	4·6 (2)
C(21)	−0·3952 (4)	0·2103 (4)	0·3470 (4)	3·7 (1)
C(22)	−0·2141 (4)	0·4558 (4)	0·1671 (3)	3·6 (1)
C(23)	−0·3813 (4)	0·5187 (4)	0·1475 (4)	4·6 (2)
C(24)	−0·3975 (4)	0·6245 (4)	0·0354 (4)	4·9 (2)
C(25)	−0·3334 (5)	0·7279 (4)	0·0426 (4)	5·2 (2)
C(26)	−0·1676 (4)	0·6669 (4)	0·0627 (4)	5·4 (2)
C(27)	−0·1489 (4)	0·5592 (4)	0·1744 (4)	4·6 (2)

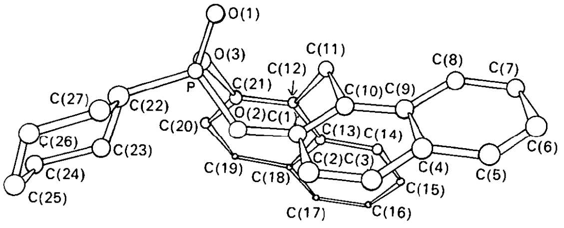

Fig. 1. A perspective view of the molecule and the numbering scheme.

seems to depend on the bulkiness of the groups attached to the heterocyclic ring. The cyclohexane ring shows a perfect chair conformation as seen from the endocyclic torsion angles in Table 2. The phosphoryl O(1) atom is axial and the cyclohexane ring is equatorial to the heterocyclic ring. The dihedral angle between the naphthalene groups in this structure is 74·4 (1)°. The crystal structure is stabilized by van der Waals contacts.

The authors acknowledge Drs C. D. Reddy and R. S. N. Reddy, Department of Chemistry, College of Engineering, S. V. University, Tirupati, for providing the compound, and Professor S. Natarajan, Head of Department of Physics, Anna University, Madras, for use of the computer facilities.

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

P—O(2)	1·586 (2)	P—O(3)	1·601 (3)
O(2)—C(1)	1·393 (4)	O(3)—C(21)	1·415 (5)
C(1)—C(10)	1·380 (4)	C(12)—C(21)	1·337 (5)
C(10)—C(11)	1·506 (6)	C(11)—C(12)	1·530 (5)
P—O(1)	1·459 (3)	C(12)—C(13)	1·438 (5)
C(2)—C(3)	1·351 (7)	C(3)—C(4)	1·406 (6)
C(1)—C(2)	1·401 (7)	P—C(22)	1·778 (4)
C(4)—C(5)	1·414 (6)	C(4)—C(9)	1·430 (7)
C(5)—C(6)	1·350 (6)	C(6)—C(7)	1·393 (8)
C(7)—C(8)	1·359 (7)	C(8)—C(9)	1·414 (6)
C(9)—C(10)	1·427 (5)	C(13)—C(14)	1·396 (6)
C(13)—C(18)	1·434 (6)	C(14)—C(15)	1·380 (6)
C(15)—C(16)	1·417 (7)	C(16)—C(17)	1·330 (8)
C(17)—C(18)	1·432 (6)	C(18)—C(19)	1·399 (7)
C(19)—C(20)	1·349 (6)	C(20)—C(21)	1·416 (7)
C(22)—C(23)	1·534 (5)	C(22)—C(27)	1·523 (7)
C(23)—C(24)	1·511 (6)	C(24)—C(25)	1·515 (8)
C(25)—C(26)	1·523 (6)	C(26)—C(27)	1·520 (6)

P—O(2)—C(1)	126·0 (2)	P—O(3)—C(21)	123·7 (2)
O(2)—C(1)—C(10)	121·7 (3)	O(3)—C(21)—C(12)	120·3 (4)
C(1)—C(10)—C(11)	119·8 (3)	C(11)—C(12)—C(21)	121·9 (4)
C(10)—C(11)—C(12)	114·7 (3)	O(2)—P—O(3)	104·3 (1)
O(3)—P—C(22)	105·1 (2)	O(2)—P—C(22)	102·2 (2)
O(1)—P—C(22)	115·8 (2)	O(2)—C(1)—C(2)	114·7 (3)
O(1)—P—O(3)	112·5 (2)	O(1)—P—O(2)	115·7 (1)
C(2)—C(1)—C(10)	123·5 (3)	C(1)—C(2)—C(3)	119·0 (4)
C(2)—C(3)—C(4)	121·4 (4)	C(3)—C(4)—C(9)	119·4 (3)
C(3)—C(4)—C(5)	122·1 (4)	C(5)—C(4)—C(9)	118·5 (3)
C(4)—C(5)—C(6)	122·0 (4)	C(5)—C(6)—C(7)	119·7 (4)
C(6)—C(7)—C(8)	120·5 (4)	C(7)—C(8)—C(9)	121·9 (4)
C(4)—C(9)—C(8)	117·3 (3)	C(8)—C(9)—C(10)	123·5 (4)
C(4)—C(9)—C(10)	119·2 (3)	C(1)—C(10)—C(9)	117·5 (3)
C(9)—C(10)—C(11)	122·7 (3)	P—C(22)—C(27)	112·3 (3)
C(11)—C(12)—C(13)	120·2 (3)	C(13)—C(12)—C(21)	118·0 (4)
C(12)—C(13)—C(18)	118·7 (4)	C(12)—C(13)—C(14)	122·8 (4)
C(14)—C(13)—C(18)	118·5 (4)	C(13)—C(14)—C(15)	121·6 (4)
C(14)—C(15)—C(16)	119·4 (5)	C(15)—C(16)—C(17)	120·8 (4)
C(16)—C(17)—C(18)	121·5 (5)	C(13)—C(18)—C(17)	118·1 (4)
C(17)—C(18)—C(19)	122·2 (4)	C(13)—C(18)—C(19)	119·6 (4)
C(18)—C(19)—C(20)	120·8 (5)	C(19)—C(20)—C(21)	119·1 (4)
C(12)—C(21)—C(20)	123·7 (4)	O(3)—C(21)—C(20)	116·0 (4)
P—C(22)—C(23)	115·5 (3)	C(23)—C(22)—C(27)	110·5 (4)
C(22)—C(23)—C(24)	111·3 (3)	C(23)—C(24)—C(25)	111·6 (4)
C(24)—C(25)—C(26)	110·9 (4)	C(25)—C(26)—C(27)	111·8 (4)
C(22)—C(27)—C(26)	111·5 (3)		

O(2)—P—O(3)—C(21)	−1·8 (3)	C(11)—C(12)—C(21)—O(3)	−2·7 (6)
O(3)—P—O(2)—C(1)	100·4 (3)	C(23)—C(22)—C(27)—C(26)	−54·8 (5)
P—O(2)—C(1)—C(10)	−60·0 (4)	C(27)—C(22)—C(23)—C(24)	55·7 (5)
P—O(3)—C(21)—C(12)	−59·9 (5)	C(22)—C(23)—C(24)—C(25)	−56·5 (5)
O(2)—C(1)—C(10)—C(11)	3·1 (5)	C(23)—C(24)—C(25)—C(26)	55·6 (5)
C(1)—C(10)—C(11)—C(12)	−55·0 (4)	C(24)—C(25)—C(26)—C(27)	−54·7 (5)
C(10)—C(11)—C(12)—C(21)	99·0 (4)	C(25)—C(26)—C(27)—C(22)	54·9 (5)

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