

dihedral angles, $\chi[C(4)]$, $\chi[C(6)]$ and $\tau[C(4)=C(6)]$, similar to that for the amide group (Winkler & Dunitz, 1971); these are $\chi[C(4)] = 2.0$ (5), $\chi[C(6)] = 18.1$ (6), $\tau[C(4)=C(6)] = 15.6$ (5) $^\circ$ respectively. A similar analysis about N(1) and C(4) gives $\chi[N(1)] = 5.6$ (6), $\chi[C(4)] = 2.0$ (6) and $\tau[C(4)-N(1)] = 7.2$ (6) $^\circ$, showing the nonplanar characteristics about the C-N bond. There are significant changes in the bond lengths due to conjugation. The $C_{sp^2}-C_{sp}$ bond length of 1.419 (6) Å differs significantly from the values reported in ethylenetetra-carbonitrile [1.437 (2) Å (Little, Pautler & Coppens, 1971)]. The N(1)-C(4) distance [1.363 (5) Å] is significantly shorter than the corresponding N-C distance in *N,N',N'',N'''*-tetraphenyl-2,2'-bi(imidazolidinylidene) [1.403 (3) Å (Hitchcock, 1979)] but compares with those observed in (1,3-dimethyl-2-imidazolidinylidene)malononitrile and (1,3-dimethyl-2-perhydropyrimidinylidene)malononitrile [1.335 (5)-1.352 (2) Å (Adhikesavalu & Venkatesan, 1982)]. The two six-membered rings are inclined at an angle of 81.3 (6) $^\circ$. The crystal packing is solely through van der Waals interactions.

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Structure of 2-Chloro-5-methyl-6-phenyl-3-(*p*-tolyl)perhydro-1,3,2 λ^5 -oxazaphosphorine 2-Oxide, C₁₇H₁₉ClNO₂P*

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Abstract. $M_r = 335.8$, monoclinic, $P2_1/a$, $Z = 4$, $a = 12.253$ (2), $b = 11.650$ (2), $c = 12.646$ (2) Å, $\beta = 109.05$ (2) $^\circ$, $V = 1706.3$ Å³, D_m (floatation) = 1.25, $D_x = 1.31$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 2.51$ mm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $F(000) = 704.0$, $T = 293$ K, $R = 0.070$ for 942 observed reflections. The 1,3,2-oxazaphosphorine ring adopts a chair conformation. The exocyclic O and Cl connected to P are in equatorial and axial positions respectively. The bond lengths and angles are normal. The packing of the molecules in the unit cell involves van der Waals contacts.

Introduction. As part of a programme of X-ray studies on the structure and conformation of oxazaphosphorine ring systems, which are known to be clinically useful anticancer drugs, the title compound was prepared (Sahasrabudhe & Tilak, 1983). Several

recent studies have shown that the 1,3,2-oxazaphosphorine ring undergoes conformational changes due to steric and electronic influences on P (Bajwa, Bentrude, Pantaleo, Newton & Hargis, 1979; Gorenstein & Rowell, 1979; Gorenstein, Rowell & Findlay, 1980; Maryanoff, Hutchins & Maryanoff, 1979) and to the substituents on ring N (Chandrasekharan & Bentrude, 1980; Bajwa, Chandrasekharan, Hargis, Sopchik, Blatter & Bentrude, 1982).

Experimental. Crystal (orange needle from alcohol solution) approximately 0.15 × 0.25 × 0.38 mm. Lattice parameters from 21 reflections ($12^\circ < 2\theta < 36^\circ$). Nonius CAD-4F-11M single-crystal X-ray diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, scan speed 1 $^\circ$ min⁻¹, $\theta \leq 24^\circ$, h 0 to 10, k 0 to 13, l -14 to 12. 2819 reflections collected, 942 significant ($|F_o| \geq 3\sigma|F_o|$). No correction for absorption. Structure solved by direct methods,

* NCL communication No. 3406.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for non-H atoms, with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3} \pi^2 \sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Cl	2887 (4)	1426 (3)	1563 (3)	3.9 (2)
P	3827 (3)	2909 (3)	1853 (3)	3.3 (2)
O(1)	3514 (7)	3460 (7)	2843 (7)	3.6 (2)
O(2)	5006 (7)	2634 (9)	2102 (8)	3.6 (1)
N(3)	3218 (8)	3725 (9)	782 (8)	3.2 (1)
C(4)	2041 (10)	4148 (11)	644 (11)	2.5 (1)
C(5)	2031 (9)	4782 (11)	1726 (10)	2.6 (2)
C(6)	2375 (10)	3955 (12)	2733 (11)	2.9 (2)
C(7)	4300 (12)	2982 (13)	-3288 (11)	4.6 (3)
C(8)	806 (11)	5250 (13)	1552 (10)	4.2 (3)
C(1')	2505 (11)	4555 (11)	3805 (10)	3.2 (2)
C(2')	1656 (13)	4411 (14)	4278 (12)	2.8 (2)
C(3')	1731 (13)	5036 (14)	5320 (11)	3.2 (3)
C(4')	2669 (12)	5769 (13)	5764 (11)	3.4 (2)
C(5')	3537 (11)	5901 (14)	5263 (12)	3.2 (2)
C(6')	3436 (11)	5308 (15)	4257 (12)	2.9 (2)
C(1'')	3456 (11)	3510 (12)	-259 (11)	3.2 (2)
C(2'')	4599 (10)	3650 (13)	-251 (11)	3.3 (3)
C(3'')	4847 (11)	3450 (13)	-1252 (11)	3.6 (2)
C(4'')	3963 (12)	3202 (13)	-2246 (11)	3.4 (2)
C(5'')	2839 (12)	3095 (13)	-2242 (10)	3.5 (2)
C(6'')	2591 (11)	3254 (13)	-1220 (10)	3.6 (2)

Table 2. Bond distances (\AA) and angles ($^\circ$) involving non-H atoms, with e.s.d.'s in parentheses

P—Cl	2.041 (6)	P—O(1)	1.562 (9)
P—O(2)	1.41 (1)	P—N(3)	1.62 (1)
N(3)—C(4)	1.48 (2)	C(4)—C(5)	1.56 (2)
C(5)—C(6)	1.54 (2)	O(1)—C(6)	1.47 (2)
N(3)—C(1'')	1.46 (2)	C(1'')—C(2'')	1.41 (2)
C(2'')—C(3'')	1.41 (2)	C(3'')—C(4'')	1.40 (2)
C(4'')—C(5'')	1.38 (2)	C(5'')—C(6'')	1.43 (2)
C(6'')—C(1'')	1.36 (2)	C(4'')—C(7)	1.52 (2)
C(6'')—C(1')	1.40 (2)	C(1')—C(2')	1.37 (2)
C(2')—C(3')	1.48 (2)	C(3')—C(4')	1.39 (2)
C(4')—C(5')	1.41 (2)	C(5')—C(6')	1.42 (2)
C(1')—C(6)	1.49 (2)	C(5)—C(8)	1.54 (2)
O(1)—P—Cl	102.8 (4)	O(2)—P—Cl	108.9 (5)
O(1)—P—N(3)	105.1 (5)	O(2)—P—N(3)	118.5 (6)
O(1)—P—O(2)	114.5 (6)	N(3)—P—Cl	105.5 (4)
P—O(1)—C(6)	123.9 (8)	P—N(3)—C(4)	117.3 (8)
C(4)—N(3)—C(1'')	115.1 (9)	P—N(3)—C(1'')	118.6 (9)
N(3)—C(4)—C(5)	110 (1)	C(4)—C(5)—C(6)	110 (1)
C(4)—C(5)—C(8)	109 (1)	C(6)—C(5)—C(8)	109 (1)
C(5)—C(6)—O(1)	108 (1)	C(5)—C(6)—C(1')	112 (1)
O(1)—C(6)—C(1')	106 (1)	C(1')—C(2')—C(3')	119 (1)
C(6)—C(1')—C(6')	120 (1)	C(6)—C(1')—C(2')	118 (1)
C(2')—C(1')—C(6')	122 (1)	C(2')—C(3')—C(4')	117 (1)
C(3')—C(4')—C(5')	122 (1)	C(4')—C(5')—C(6')	119 (1)
C(5')—C(6')—C(1')	119 (1)	N(3)—C(1'')—C(2'')	118 (1)
N(3)—C(1'')—C(6'')	121 (1)	C(2'')—C(1'')—C(6'')	121 (1)
C(1'')—C(2'')—C(3'')	118 (1)	C(2'')—C(3'')—C(4'')	121 (1)
C(3'')—C(4'')—C(5'')	120 (1)	C(3'')—C(4'')—C(7)	117 (1)
C(5'')—C(4'')—C(7)	123 (1)	C(4'')—C(5'')—C(6'')	120 (1)
C(5'')—C(6'')—C(1'')	120 (1)		

Table 3. Some important torsion angles ($^\circ$), with e.s.d.'s in parentheses

O(2)—P—O(1)—C(6)	171.5 (9)	C(4)—N(3)—C(1'')—C(6'')	-26 (1)
O(2)—P—N(3)—C(4)	-170.6 (9)	N(3)—C(4)—C(5)—C(6)	-62 (1)
O(1)—P—N(3)—C(4)	-41.1 (9)	N(3)—C(4)—C(5)—C(8)	178.2 (9)
P—O(1)—C(6)—C(5)	-49.7 (9)	C(4)—C(5)—C(6)—O(1)	56.3 (9)
P—N(3)—C(4)—C(5)	55.1 (9)	C(8)—C(5)—C(6)—O(1)	176.4 (9)
C(4)—N(3)—C(1'')—C(2'')	150.1 (9)		

MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix refinement of scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from a difference map) converged to $R = 0.070$ and $R_w = 0.063$; $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = (4.5 + 1.0|F_i| + 0.025|F_o|^2)^{-1}$. $(\Delta/\sigma)_{\max} = 0.01$. Final $\Delta\rho$ map featureless. No correction for secondary extinction. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). LALS (Gantzel, Sparks & Trueblood, 1961) for refinement.

Discussion. The atomic parameters with their e.s.d.'s and equivalent isotropic thermal parameters for non-H atoms are given in Table 1.* Bond lengths and angles are given in Table 2. Table 3 gives some important torsion angles. Fig. 1 gives a perspective view of the molecule along with the numbering of the atoms. The bond lengths and bond angles are normal. The bond length P—O(2) of 1.41 (1) \AA agrees with those found in other cyclophosphamide, isophosphamide and tropophosphamide compounds (Mikolajczyk, Omelanczuk, Abdulkharov, Müller, Wiczorek & Wojciechowska, 1982). The six-membered oxazaphosphorine ring has a chair conformation in which the exocyclic O and Cl atoms connected to P are in equatorial and axial positions respectively. The possibility that this ring undergoes conformational changes due to steric and electronic demands of these substituents with respect to the substituent on the ring N (Chandrasekharan & Bentrude, 1980) does exist in the present study because, firstly, the substituent at N(3) is rotated away by 131.8° and, secondly, the distance O(2)—C(1'') is 3.14 (2) \AA . The methyl substituent at C(5) is *trans* with respect to the equatorial O at P. However, this substitution does not affect the overall conformation of the 1,3,2-oxazaphosphorine ring considerably. The present study

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39180 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

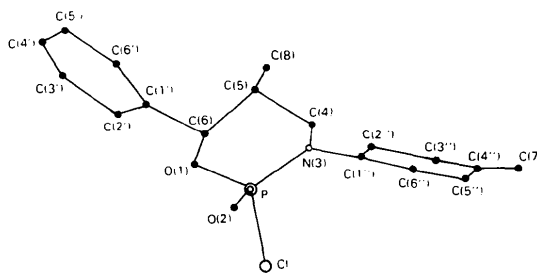


Fig. 1. A perspective view of the molecule down the a axis.

favours the chair-twist equilibrium hypothesis (Chandrasekharan & Bentrude, 1980). The angle between the two rings at N(3) and C(6) is 28°. The packing of the molecules in the unit cell essentially involves van der Waals contacts.

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Structure of Bis(trifluoroacetato)(phenyl)iodine(III), C₁₀H₆F₆IO₄

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Abstract. $M_r = 430.04$, triclinic, $P\bar{1}$, $a = 9.824$ (2), $b = 9.111$ (1), $c = 7.688$ (2) Å, $\alpha = 88.75$ (2), $\beta = 99.80$ (2), $\gamma = 90.91$ (1)°, $V = 677.93$ Å³, $Z = 2$, $D_x = 2.106$, $D_m = 2.076$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.48$ mm⁻¹, $F(000) = 408$, $T = 298$ K. Final $R = 0.052$ for 1362 independent non-zero reflections. The molecule shows the characteristic T-shaped coordination geometry of three covalent bonds around the I atom, complemented by two inter- and one intramolecular I...O contacts, which may be considered as secondary bonds. The latter cause the formation of dimers between symmetry-equivalent molecules which, repeated along the b axis, form columns interconnected by O...H—C hydrogen bridging bonds.

Introduction. In the past decade considerable attention was given to compounds containing iodine(III) and a number of crystallographic and solid-state chemical studies appeared in the literature (e.g. Gougoutas & Lessinger, 1974; Etter, 1976; Alcock & Countryman, 1977). The main characteristic of almost all these compounds is the slightly distorted T-shaped coordination geometry around the I^{III} atom which forms three covalent bonds to other atoms. In addition, weak inter- and intramolecular coordination contacts

between the I atom and its next-nearest neighbours are observed, which may be considered as secondary bonds.

The crystal-structure analysis of the title compound (FAIB) was carried out in order to investigate the features of the iodine coordination in the presence of the trifluoro groups. The compound is of special interest because of its strong oxidative character, which renders it especially effective not only in conventional oxidations but also in the conversion of amides to amines and the cleavage of several kinds of ethers, oxiranes and cyclopropanes (Spyroudis & Varvoglis, 1975, 1979, 1981; Radhakrishna, Parham, Riggs & Loudon, 1979; Shabarov, Pisanova & Saginova, 1981).

Experimental. Transparent, colourless crystals, $0.35 \times 0.18 \times 0.12$ mm, m.p. 388–390 K; D_m measured by flotation in 1,3-dibromobutane/1,2-dibromoethane, computer-controlled Philips PW 1100 four-circle single-crystal diffractometer, three-dimensional data, graphite-monochromated Mo $K\alpha$, ω -scan mode; cell parameters and standard deviations by least-squares analysis of measured θ angles of the 41 strongest reflections; intensity statistics indicated $P\bar{1}$; three standard reflections exhibiting the same percentage linear decrease in intensity; 1663 measured reflections, $\theta = 3$ –22°, index