plane [average: 0·007 (4) Å]. The N atoms deviate slightly from this plane [N(2) is 0·165 (4) Å above the plane, N(4) is 0·066(4) Å below the plane], in order to avoid the strain caused by the short contact between N(2) and N(4) [2·873 (7) Å]: this distance is shorter than the sum of the van der Waals radii of nitrogen, 3·0 Å. The N(1)—C(23)—C(12) and N(3)—C(24)—C(13) bond angles are 128·3 (4) and 127·9 (4)°, respectively, which shows that both of the diazo groups extend outwards at the foot of the C(23), C(24) atoms. Closer examination of the diazo groups also shows that the C(23)—N(1)—N(2) and C(24)—N(3)—N(4) bonds are bent outwards slightly at atoms N(1) and N(3). The strain arising from the close location of the diazo groups seems to be reduced by the deformations of these bond angles.

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Structure of 6-*tert*-Butyl-3-cyclohexyl-2-(2,5-dimethylphenoxy)-3,4-dihydro-2*H*-1,3,2-benzoxazaphosphorine 2-Oxide

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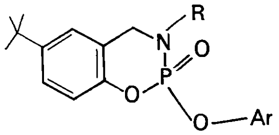
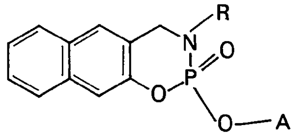
Abstract. $C_{25}H_{34}NO_3P$, $M_r = 427·5$, monoclinic, $P2_1/n$, $a = 13·623\ (3)$, $b = 11·427\ (2)$, $c = 15·177\ (3)$ Å, $\beta = 91·08\ (2)°$, $V = 2362·2$ Å^3, $Z = 4$, $D_x = 1·20$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 1·3$ cm^{-1}, $F(000) = 920$, $T = 297$ K, $R = 0·04$ for 3378 observed reflections. The oxazaphosphorine ring adopts a sofa conformation. The phosphoryl O atom, O(2), occupies an equatorial position and the O atom, O(3), an axial position, which is in agreement with the anomeric effect. On comparing the geometry of five phosphorus compounds, bond angles around the P atom show no systematic variations, and the only trend in the torsion angles is a change about the O—Ar bond, from synclinal towards coplanar. The molecular packing involves only van der Waals contacts.

Introduction. This type of phosphorus heterocycle has been found to possess significant antitumour activity (Friedman, Papanastassiou & Levi, 1963) and for this reason its X-ray structure is of great interest. The crystal and molecular structures of three derivatives of 1,3,2-benzoxazaphosphorine 2-oxide have been reported by Subramanian, Selladurai & Ponnuswamy (1989), Selladurai, Subramanian & Nagaraju (1989) and Selladurai & Subramanian (1990). We now report the X-ray crystallographic results for a fourth derivative (1*e*).



(1*a*) Ar = 2-chlorophenyl, *R* = cyclohexyl
(1*b*) Ar = 3,5-dimethylphenyl, *R* = cyclohexyl
(1*d*) Ar = 4-methylphenyl, *R* = cyclohexyl
(1*e*) Ar = 2,5-dimethylphenyl, *R* = cyclohexyl



(1*c*) Ar = 3,5-dimethylphenyl, *R* = 4-methylphenyl

Experimental. Transparent, colourless crystals were grown from ethanol solution. Crystal dimensions 0·40 × 0·53 × 0·66 mm. Unit-cell parameters and their e.s.d.'s derived from a least-squares treatment of 25 medium-angle reflections ($25 < 2\theta < 35°$).

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Table 1. *Positional parameters and equivalent isotropic thermal parameters of non-*H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
P(1)	0·2952 (0)	0·2246 (0)	0·1349 (0)	3·8 (0)
O(2)	0·2373 (1)	0·1182 (1)	0·1307 (1)	4·8 (0)
O(3)	0·3139 (1)	0·2872 (1)	0·0433 (1)	4·3 (0)
O(4)	0·4070 (1)	0·2004 (1)	0·1612 (1)	4·4 (0)
N(5)	0·2562 (1)	0·3248 (1)	0·2010 (1)	3·9 (0)
C(6)	0·2424 (1)	0·3494 (2)	−0·0054 (1)	3·8 (0)
C(7)	0·2783 (1)	0·4431 (2)	−0·0530 (1)	4·1 (0)
C(8)	0·2094 (2)	0·5042 (2)	−0·1033 (2)	5·3 (1)
C(9)	0·1124 (2)	0·4727 (2)	−0·1065 (2)	5·6 (1)
C(10)	0·0780 (2)	0·3778 (2)	−0·0596 (1)	4·8 (1)
C(11)	0·1456 (1)	0·3165 (2)	−0·0077 (1)	4·3 (0)
C(12)	0·4650 (1)	0·2849 (2)	0·2052 (1)	3·7 (0)
C(13)	0·5608 (1)	0·2547 (2)	0·2232 (1)	4·2 (0)
C(14)	0·6207 (1)	0·3310 (2)	0·2696 (1)	4·3 (0)
C(15)	0·5870 (1)	0·4386 (2)	0·2986 (1)	3·8 (0)
C(16)	0·4895 (1)	0·4659 (2)	0·2786 (1)	3·7 (0)
C(17)	0·4269 (1)	0·3914 (2)	0·2318 (1)	3·5 (0)
C(18)	0·3217 (1)	0·4271 (2)	0·2110 (1)	3·9 (0)
C(19)	0·1812 (1)	0·3024 (2)	0·2676 (1)	3·8 (0)
C(20)	0·2251 (2)	0·2876 (2)	0·3592 (1)	5·4 (1)
C(21)	0·1461 (3)	0·2654 (3)	0·4266 (2)	7·8 (1)
C(22)	0·0696 (3)	0·3610 (3)	0·4248 (2)	9·4 (1)
C(23)	0·0252 (2)	0·3764 (3)	0·3331 (3)	8·5 (1)
C(24)	0·1033 (2)	0·3968 (2)	0·2649 (2)	5·5 (1)
C(25)	0·6516 (1)	0·5246 (2)	0·3514 (1)	4·5 (0)
C(26)	0·6562 (2)	0·6399 (2)	0·3021 (2)	6·6 (1)
C(27)	0·7569 (2)	0·4789 (3)	0·3648 (2)	6·6 (1)
C(28)	0·6091 (2)	0·5410 (3)	0·4424 (2)	6·6 (1)
C(29)	0·3846 (2)	0·4742 (2)	−0·0517 (2)	5·4 (1)
C(30)	−0·0267 (2)	0·3400 (3)	−0·0675 (2)	7·1 (1)

Intensity data were collected at room temperature by $\omega/2\theta$ scan technique up to $2\theta \simeq 50°$ with h $-15\rightarrow15$, k $0\rightarrow13$, l $0\rightarrow18$. Two standard reflections monitored every 100 measurements, variation less than 2%; 4326 independent reflections measured of which 3378 intensities observed $[I > 3\sigma(I)]$. Structure solved by direct methods using *SHELXS*86 (Sheldrick, 1986). The H atoms were located on a difference density map. Positional parameters of all atoms and anisotropic thermal parameters of non-H atoms refined by full-matrix least squares on F. Final $R = 0{\cdot}04$ and $wR = 0{\cdot}047$ for 3378 observed reflections. $w = 1/[\sigma^2|F_o| + m|F_o|^2]$, $m = 0{\cdot}000318$. Max. Δ/σ 0·01, max. and min. heights in final $\Delta\rho$ map $+0{\cdot}02$ and $-0{\cdot}03$ e Å^{-3}. Atomic scattering factors used were from the *SHELX*76 program. Computer programs: *SHELX*76 (Sheldrick, 1976) used for refinement and *PARST* (Nardelli, 1983) for geometrical calculations.

Discussion. Table 1* lists the final atomic coordinates and equivalent isotropic temperature factors of non-H atoms. The molecule with atom-numbering scheme is shown in Fig. 1. The P(1)—O(2) bond length of 1·45 (3) Å agrees with those in the related 1,3,2-benzoxazaphosphorine structures given in the scheme (Selladurai, Subramanian & Nagaraju, 1989; Subramanian, Selladurai & Ponnuswamy, 1989). The dihedral angle between the least-squares planes P(1)—N(5)—C(18) and P(1)—O(4)—C(17)—C(18) is 45° and between C(17)—C(12)—C(12)—O(4) and P(1)—O(4)—C(17)—C(12) is 2·8°. The cyclohexyl ring adopts a chair conformation with the N atom, N(5), occupying an equatorial position. The least-squares plane of the 2,5-dimethylphenyl ring is inclined at an angle of 66·6° to that of phosphorine ring. The phenyl and *tert*-butyl groups are *trans* to each other and they occupy equatorial positions on the phosphorine ring. The dihedral angle between the two phenyl rings is 62·1°. Table 2 presents selected data for the compounds (1*a*)–(1*e*). In all the oxazaphosphorine ring adopts a sofa conformation, with the phosphoryl O atom O(2) in an equatorial position and the atom O(3) in an axial position. This is in agreement with the 'anomeric effect' which can be explained as a 'back donation' from the oxygen lone-pair electrons into an antibonding σ level (Jeffrey, Pople & Radom, 1972). This effect has been noted previously in a cyclic phosphate by van Nuffel, Lenstra & Geise (1980), who determined the structure of the methyl ester.

The anomeric effect causes an increase of electron density around the P atom. This results in a flattening of the six-membered ring around the P atom as can be seen from the torsion angles shown in Table 2. Bond angles around the P atom show no systematic variations over the whole set of five compounds, and the only trend in torsion angles (Table 2) is from synclinal towards coplanar about O(3)—C(6) as the aromatic ring becomes more strongly electron withdrawing. Fig. 2 shows the packing of molecules, which is stabilized by van der Waals contacts.

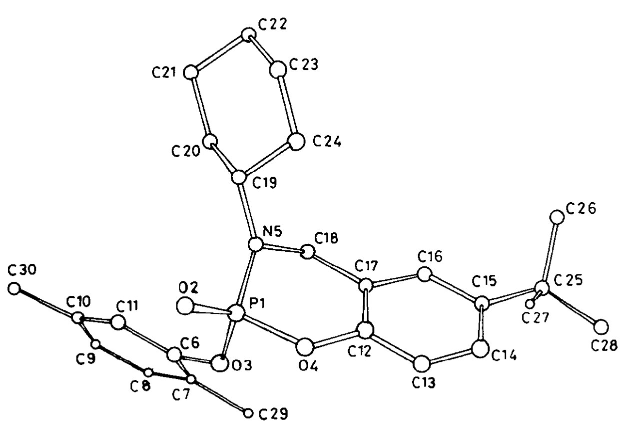

Fig. 1. View of the molecule with the atom-numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, complete bond lengths and angles, least-squares-planes calculations and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53545 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *for phosphorus compounds* (1*a*)–(1*e*)

	(1*a*)					
	I	II	(1*b*)	(1*c*)	(1*d*)	(1*e*)
P(1)—O(2)	1·446 (3)	1·452 (3)	1·456 (2)	1·453 (3)	1·451 (3)	1·450 (1)
P(1)—O(3)	1·608 (3)	1·601 (4)	1·585 (3)	1·583 (2)	1·590 (3)	1·588 (1)
P(1)—O(4)	1·580 (3)	1·587 (3)	1·592 (2)	1·567 (2)	1·589 (2)	1·591 (1)
P(1)—N(5)	1·617 (4)	1·624 (3)	1·631 (3)	1·635 (3)	1·625 (3)	1·619 (1)
N(5)—C(18)	1·484 (5)	1·447 (6)	1·471 (4)	1·483 (4)	1·485 (5)	1·477 (2)
C(12)—O(4)	1·400 (5)	1·404 (5)	1·396 (4)	1·397 (3)	1·406 (3)	1·408 (2)
C(6)—O(3)	1·394 (6)	1·383 (5)	1·395 (4)	1·408 (3)	1·409 (4)	1·405 (2)
C(18)—N(5)—P(1)	118·3 (3)	122·7 (3)	113·3 (2)	116·5 (2)	113·2 (2)	114·7 (1)
N(5)—P(1)—O(4)	104·6 (2)	104·0 (2)	109·0 (1)	103·8 (1)	107·6 (1)	107·0 (1)
P(1)—O(4)—C(12)	122·1 (2)	118·4 (3)	120·2 (2)	124·4 (2)	122·5 (2)	121·7 (1)
N(5)—P(1)—O(3)	104·0 (3)	104·4 (2)	105·3 (1)	109·1 (1)	105·9 (1)	106·5 (1)
O(4)—P(1)—O(2)	110·8 (2)	112·2 (2)	111·8 (1)	114·0 (2)	112·1 (1)	112·5 (1)
O(3)—P(1)—O(2)	114·2 (2)	113·0 (2)	117·7 (1)	114·2 (1)	115·8 (1)	115·8 (1)
P(1)—O(3)—C(6)	119·7 (3)	123·7 (3)	123·1 (2)	121·8 (2)	122·7 (2)	124·6 (1)
N(5)—P(1)—O(3)—C(6)	177·6 (4)	170·4 (3)	−56·1 (3)	−89·7 (3)	−63·5 (3)	−57·4 (2)
O(4)—P(1)—O(3)—C(6)	62·6 (3)	74·7 (4)	−167·7 (2)	162·3 (2)	−174·5 (3)	−167·6 (1)
O(2)—P(1)—O(3)—C(6)	−47·5 (4)	−36·5 (4)	73·9 (3)	40·9 (3)	66·1 (3)	73·0 (2)
P(1)—O(3)—C(6)—C(7)	−82·1 (6)	−63·8 (6)	150·6 (3)	−78·8 (3)	131·3 (3)	147·5 (2)

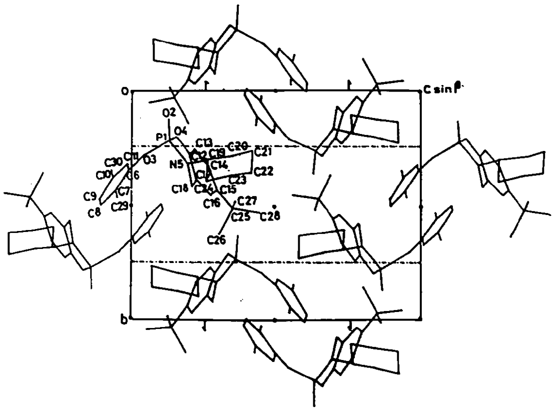

Fig. 2. The packing of the molecule viewed down the *a* axis.

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12-Imino-12*H*-benzimidazo[2,1-*b*][1,3]benzothiazine

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Abstract. $C_{14}H_9N_3S$, $M_r = 251{\cdot}3$, monoclinic, $P2_1/c$, $a = 7{\cdot}698$ (1), $b = 18{\cdot}436$ (4), $c = 8{\cdot}360$ (2) Å, $\beta = 107{\cdot}09$ (1)°, $V = 1134{\cdot}1$ (8) Å^3, $Z = 4$, $D_x = 1{\cdot}472$ Mg m^{-3}, $\mu = 0{\cdot}25$ mm^{-1}, λ(Mo $K\bar{\alpha}$) = 0·7107 Å, $F(000) = 520$, $T = 293$ (1) K, $R = 0{\cdot}035$ for 1491 independent observed reflections. The molecule

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