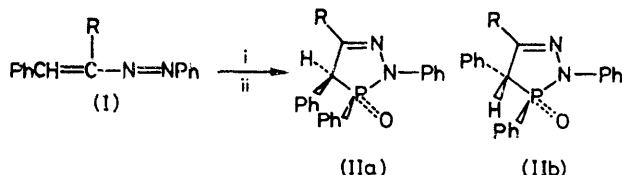


## Crystal and Molecular Structure of *trans*-3,4-Dihydro-2,3,4-triphenyl-5-phenylmethyl-2*H*-1,2,3-diazaphosphole 3-Oxide

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The crystal and molecular structure of the first reported example of a new five-membered cyclic diazaphospholene oxide was solved by *X*-ray crystallographic techniques. This compound crystallizes in space group  $P\bar{1}$  with unit-cell dimensions  $a = 5.815(2)$ ,  $b = 9.688(4)$ ,  $c = 20.207(9)$  Å,  $\alpha = 95.47(6)$ ,  $\beta = 95.04(4)$ ,  $\gamma = 89.32(4)^\circ$ , with  $Z = 2$ . The five-membered ring is an irregular and almost planar pentagon. The geometry about the phosphorus atom is that of a distorted tetrahedron with angles ranging from  $91$  to  $118^\circ$ . The formation of a trigonal bipyramidal phosphorane intermediate by addition of nucleophiles at the face opposite to the P–N bond involves relatively small additional bond-angle deformations: this factor may explain the reactivity of this new heterocyclic system toward nucleophiles.

DIAZAPHOSPHOLENE oxides (II) represent the first cases of a new heterocyclic system which is easily synthesized<sup>1</sup> from the reaction of the azoalkene (I) with dichloro(phenyl)phosphine and successive hydrolysis of the cycloadduct formed.



SCHEME R = PhCH<sub>2</sub>; (IIa) m.p. 163–165 °C, (IIb) m.p. 171–173 °C; reagents: i, PhPCl<sub>2</sub>; ii, H<sub>2</sub>O

Two diastereoisomers (IIa) and (IIb) are formed in this reaction, and their respective configurations have been tentatively deduced<sup>1</sup> from their <sup>1</sup>H n.m.r. spectra.

We now describe the crystal and molecular structure of the title compound (IIa). We were particularly interested in the unequivocal assignment of molecular configuration. Nucleophilic displacement reactions at the phosphoryl centre of (II) gave stereoselective results<sup>2,3</sup> which were explained in terms of formation of five-co-ordinated phosphorus intermediates; consequently, knowledge of the molecular structure of this heterocyclic system was highly desirable.

Moreover, we hoped to correlate the reactivity and selectivity of this system with some features of its molecular structure.

### EXPERIMENTAL

The synthesis of the diazaphospholes (II) and the isolation of the pure crystalline diastereoisomer (IIa) were carried out as described previously.<sup>1</sup> Suitable crystals, m.p. 163–165 °C, for *X*-ray crystallographic analysis were obtained by recrystallization from hexane–methylene chloride.

The isomer (IIb) has not been obtained as suitable crystals. Crystals of (IIa) present a needle-shaped morphology along the *a* axis. Precise unit-cell dimensions were determined by a least-squares fit of 23 independent 2θ values. The crystal used was 0.5 × 0.2 × 0.2 mm.

**Crystal Data.**—C<sub>27</sub>H<sub>23</sub>N<sub>2</sub>OP,  $M = 422.45$ , Triclinic,  $a = 5.815(4)$ ,  $b = 9.688(2)$ ,  $c = 20.207(9)$  Å,  $\alpha = 95.47(6)$ ,  $\beta = 95.04(4)$ ,  $\gamma = 89.32(4)^\circ$ ,  $U = 1\ 128.9$  Å<sup>3</sup>,  $D_m = 1.26$  g cm<sup>-3</sup>,

$Z = 2$ ,  $D_c = 1.25$  g cm<sup>-3</sup>. Mo- $K_\alpha$  radiation,  $\lambda = 0.710\ 7$  Å;  $\mu(\text{Mo-}K_\alpha) = 1.48$  cm<sup>-1</sup>. Space group  $P\bar{1}$ .

The intensity data were collected by a Philips PW 1100 diffractometer out to 2θ 40°, by use of Mo- $K_\alpha$  radiation, with a scan speed 0.06° s<sup>-1</sup>, scan width 0.8°, take-off angle 1.8°, window 0.6 mm, and a counting background for 10 s on either side of the peak.

No appreciable changes in intensity were observed during data collection. Of 3 714 independent reflections, 2 257 having  $I > 3\sigma(I)$  were considered observed and used in the analysis. No correction for absorption effects was made. After correction for Lorentz and polarization factors, the structure amplitudes were put on an absolute scale first by Wilson's method and then by correlation between calculated and observed structure factor values.

**Structure Determination and Refinement.**—The structure was solved by direct methods with the MULTAN program:<sup>4</sup> the first *E* map indicated positions for all the non-hydrogen atoms, except those of the phenyl ring linked to the phosphorus atom, which were subsequently identified from a difference map.

The SHELX system of programs<sup>5</sup> was used for the least-squares refinement. The weighting scheme was  $w = 0.54/[\sigma^2(F_o) + 0.003F_o^2]$ .

The hydrogen atoms were geometrically positioned (assuming C–H 1.08 Å) and constrained to refine riding on their attached carbon atoms. The final agreement factor was 0.048 for 2 257 reflections, with anisotropic temperature factors assigned to all non-hydrogen atoms.

Positional parameters with their estimated standard deviations are listed in Table 1, and the most significant distances and angles in Tables 2 and 3; drawings were made with PLUTO.<sup>6</sup> In the four phenyl rings the mean bond length is 1.377 Å with a mean standard deviation of 0.009 Å and a maximum shift of 0.02 Å. Final observed and calculated structure factors and atom thermal parameters are listed in Supplementary Publication No. SUP 22362 (21 pp.).†

### DISCUSSION

The molecule is illustrated in Figure 1, and the packing is shown in Figure 2. The *X*-ray analysis shows that the crystalline diastereoisomer (IIa) has the *P*-phenyl group *trans* to the C(5)-phenyl group. This result confirms

† See Notice to Authors No. 7 in *J.C.S. Perkin I*, 1978, Index issue.

TABLE 1

Heavy-atom co-ordinates ( $\times 10^4$ ), with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
P	5 767(2)	11 505(1)	2 941(1)
N(2)	5 332(5)	9 799(3)	2 739(2)
N(3)	3 734(6)	9 475(3)	2 170(2)
C(4)	2 641(6)	10 557(4)	2 009(2)
C(5)	3 142(6)	11 919(4)	2 435(2)
C(6)	5 342(7)	11 870(4)	3 809(2)
C(7)	6 737(11)	12 820(6)	4 183(3)
C(8)	6 347(18)	13 163(8)	4 859(4)
C(9)	4 678(17)	12 577(12)	5 131(3)
C(10)	3 295(13)	11 603(12)	4 759(4)
C(11)	3 618(10)	11 249(8)	4 098(3)
C(12)	6 645(6)	8 671(4)	2 974(2)
C(13)	5 838(8)	7 327(4)	2 847(2)
C(14)	7 124(9)	6 247(5)	3 091(2)
C(15)	9 179(9)	6 491(5)	3 473(2)
C(16)	9 951(8)	7 824(6)	3 604(3)
C(17)	8 706(8)	8 920(5)	3 357(3)
C(18)	727(8)	10 541(5)	1 460(2)
C(19)	656(7)	9 273(4)	946(2)
C(20)	2 289(8)	9 071(5)	500(2)
C(21)	2 143(9)	8 011(6)	2(2)
C(22)	277(11)	7 139(5)	-61(3)
C(23)	-1 379(9)	7 280(5)	369(3)
C(24)	-1 234(8)	8 364(5)	887(2)
C(25)	3 225(6)	13 194(4)	2 054(2)
C(26)	1 519(6)	14 189(4)	2 122(2)
C(27)	1 535(8)	15 352(4)	1 770(2)
C(28)	3 244(8)	15 540(5)	1 360(2)
C(29)	4 968(8)	14 541(5)	1 290(2)
C(30)	4 959(7)	13 373(4)	1 636(2)
O(31)	7 981(4)	12 079(3)	2 790(1)

TABLE 2

Relevant bond lengths ( $\text{\AA}$ ) with standard deviations in parentheses

P-N(2)	1.680(3)	N(3)-C(4)	1.274(5)
P-C(5)	1.824(3)	C(4)-C(5)	1.521(5)
P-C(6)	1.793(4)	C(4)-C(18)	1.500(5)
P-O	1.476(3)	C(5)-C(25)	1.520(5)
N(2)-N(3)	1.426(4)	C(18)-C(19)	1.529(6)
N(2)-C(12)	1.421(5)		

the tentative configurational assignments made<sup>1</sup> on the basis of the relative positions of the <sup>1</sup>H n.m.r. signals in

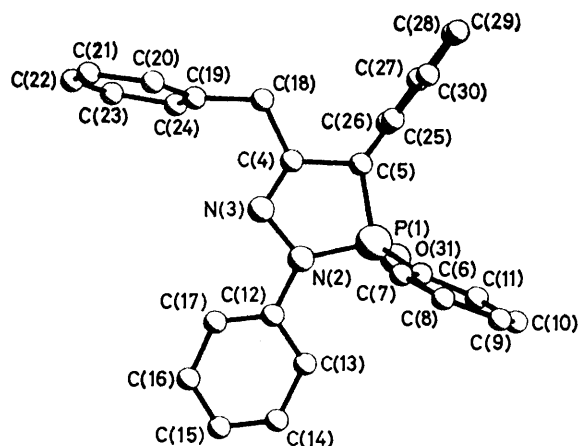


FIGURE 1 The molecule viewed normally to the plane formed by N(2), N(3), C(4), showing the atom numbering system used in the crystallographic analysis

the isomers (II) and, by analogy, confirms the configurational assignments of other reported<sup>1</sup> parent compounds.

Tables 3 and 4 indicate that the unsaturated five-membered ring is an irregular and almost planar pentagon

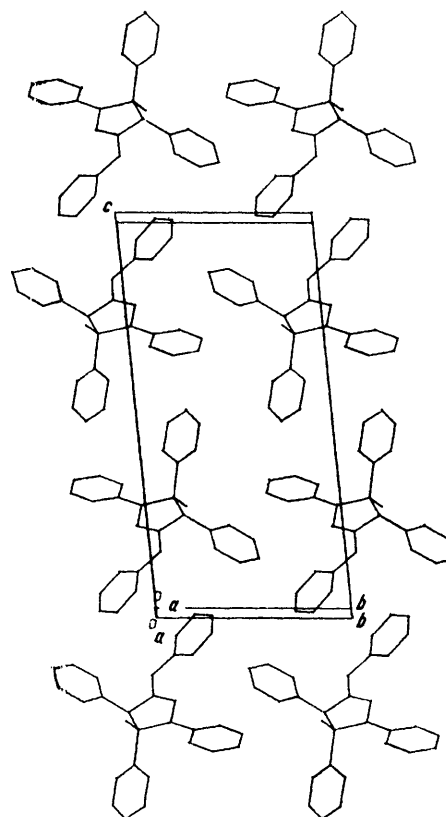


FIGURE 2 A perspective view of the molecular packing

which contains angles ranging from N(2)-P-C(5) 91° to N(3)-C(4)-C(5) 118°.

TABLE 3

Relevant bond angles (°) with standard deviations in parentheses

N(2)-P-C(5)	91.0(2)	N(2)-N(3)-C(4)	110.6(3)
N(2)-P-C(6)	107.6(2)	N(3)-C(4)-C(5)	118.5(3)
N(2)-P-O	117.2(2)	N(3)-C(4)-C(18)	123.5(4)
C(5)-P-C(6)	109.7(2)	C(5)-C(4)-C(18)	117.8(3)
C(5)-P-O	118.7(2)	P-C(5)-C(4)	102.1(2)
C(6)-P-O	110.8(2)	P-C(5)-C(25)	116.5(3)
P-N(2)-N(3)	114.4(2)	C(4)-C(5)-C(25)	115.6(3)
P-N(2)-C(12)	128.2(3)	C(4)-C(18)-C(19)	115.7(3)
N(3)-N(2)-C(12)	116.1(3)		

TABLE 4

Details of plane N(2), N(3), C(4), and C(5)

Equation of plane:  $0.7059x + 0.2014y - 0.6791z = -1.1193$

Deviations ( $\text{\AA}$ ) of atoms from plane: P 0.3578, N(2) 0.0040, N(3) -0.0078, C(4) 0.0077, C(5) -0.0039

The *N*-phenyl group is nearly coplanar with the diazaphosphole ring (interplanar angle 17°; see also Table 5) requiring the nitrogen atom to be *sp*<sup>2</sup> hybridized; in accord with this the sum of the bond angles around nitrogen is close to 360° while in reported related phospholes<sup>7,8</sup> the phenyl substituent on the *sp*<sup>2</sup> hybridized nitrogen is almost orthogonal to the phosphole ring.

The phenyl groups have normal geometry. Probably,

the most interesting features of the structure of the diazaphosphole (IIa) are described by the geometry

TABLE 5

Relevant torsion angles (°)

N(2)-P-C(6)-C(7)	143	N(3)-N(2)-C(12)-C(13)	-24
N(2)-P-C(6)-C(11)	-39	N(3)-N(2)-C(12)-C(17)	158
C(5)-P-C(6)-C(7)	-120	P-C(5)-C(25)-C(26)	-128
C(5)-P-C(6)-C(11)	58	P-C(5)-C(25)-C(30)	53
P-N(2)-C(12)-C(13)	169	C(4)-C(5)-C(25)-C(26)	112
P-N(2)-C(12)-C(17)	-8	C(4)-C(5)-C(25)-C(30)	-67

about the phosphorus atom: a distorted tetrahedron with three angles smaller and three larger than 109.5°. The endocyclic N(2)-P-C(5) angle (91°) shows the largest deviation from the tetrahedral value around the phosphorus atom (see Table 6). The angles formed by the

TABLE 6

Deviations (°) from a regular tetrahedron (109.5°) in the P-O-N(2)-C(5)-C(6) group. Bond-angle deformations (°) in the transformation of the P-O-N(2)-C(5)-C(6) group into diazaphosphorane (III)

Bond angle	Deviation	Deformation	
N(2)-P-C(5)	-18.5	-1.0	-45.8
N(2)-P-C(6)	-1.9	-17.6	
N(2)-P-O	7.7	-27.2	
C(5)-P-C(6)	0.2	10.3	20.8
C(5)-P-O	9.2	1.3	
C(6)-P-O	1.3	9.2	

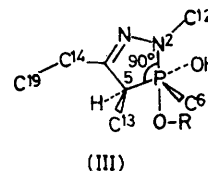
phosphoryl oxygen, the phosphorus, and the ring ligands are significantly larger than the tetrahedral value (by 7 and 9°). The angle N(2)-P-C(6) is smaller by 2° than the tetrahedral value, whereas C(5)-P-C(6) and C(6)-P-O are close to the tetrahedral value.

These deviations suggest that there is now evidence for the hypothesis that in our system also nucleophilic displacement at the phosphoryl centre occurs *via* trigonal bipyramidal five-co-ordinated phosphorus intermediates.

The transformation of the diazaphosphole (II) into the trigonal bipyramidal diazaphosphorane (III) by addition, at the face opposite the P-N bond, of the nucleophile R-OH might be relatively easy as it involves relatively small additional angle deformations.

Three of the angles should therefore tend to reach a value of 90° (apical-equatorial angle). Compared to a

regular tetrahedron, this would correspond to an overall bond-angle contraction of  $ca. 3(-19) = 57^\circ$ , but from the actual distorted tetrahedron this contraction amounts



to only  $(-1) + (-27.2) + (-17.6) = 45.8^\circ$ , a net saving of 11.2° in the overall angle contraction. Moreover, the remaining three angles should expand to a value of 120° (diequatorial angle). If the tetrahedron were regular, this would amount to an overall angle expansion of about  $3(11) = 33^\circ$ , but from the actual distorted tetrahedron, it is  $+10.3 + 1.3 + 9.2 = 20.8^\circ$ , or a net economy of 12.2 in the overall angle expansion.

Since the nucleophilic apical attack at the face opposite the other phosphorus ligands would require a greater additional bond-angle deformation, the favoured attack of the nucleophile is at the face opposite to the P-N bond with formation of (III). This preference in our heterocyclic system is in agreement with the stereoselective and stereospecific results obtained<sup>2,3</sup> previously.

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