

MOLECULAR AND CRYSTAL STRUCTURE OF 2-AMINO-2-OXO-1,3,2-DIOXAPHOSPHORINANE

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To study the spatial structure and stereochemical effects in phosphorus-containing heterocycles, we have carried out an X-ray structural investigation of the title compound (I).

Experimental. The synthesis of I is described in [1]. Crystals I, $C_3H_8NO_3P$, (mp 68–69°C) are orthorhombic. At –150°C, $a = 12.321(7)$, $b = 9.840(4)$, $c = 9.01(1)$ Å, $d_{calc} = 1.67$ g/cm³, $Z = 8$, and space group $Pbca$. The unit cell parameters and intensities of 1057 independent reflections with $F^2 \geq 3\sigma$ were measured on an ENRAF-NONIUS CAD-4 automatic 4-circle diffractometer with K geometry (λMoK_α , graphite monochromator, $\omega/(5/3\theta)$ scan mode, $\theta \leq 30^\circ$). The structure was solved by direct methods using the MULTAN program and refined in an isotropic and then in an anisotropic approximation. All hydrogen atoms were revealed from difference synthesis and refined isotropically in the final stage. The final $R = 0.039$ and $R_w = 0.051$ for 1044 reflections with $F^2 \geq 2\sigma$. All calculations were performed on a PDP 11/23 computer using the SDP program package.

The atomic coordinates are listed in Table 1, the molecular geometry and bond lengths are shown in Fig. 1. The bond and torsion angles are given in Table 2.

Discussion of results. Structural investigations of some 2-amino-substituted 2-oxo-1,3,2-dioxaphosphorinanes have been reported in literature: 5-methyl-5-chloromethyl-2-piperidino-2-oxo-1,3,2-dioxaphosphorinane (II) [2], 5,5-dimethyl-2-phenylamino-2-oxo-1,3,2-dioxaphosphorinane (III) [3], 5,5-dimethyl-2-formylamino-2-oxo-1,3,2-dioxaphosphorinane (IV) [4], *cis*-2-*tert*-butylamino-4-methyl-1,3,2-dioxaphosphorinane-2-oxide (V) [5], and *N,N'*-dibenzyl-*N*-(4-methyl-2-oxo-1,3,2 λ^5 -dioxaphosphorinan-2-yl) thiourea (VI) [6]. In molecules II, V, and VI, the P–N bonds are equatorial and P=O are axial, while in III and IV the P–N bonds have an axial orientation. In I the heterocycle has an armchair conformation as in II–VI. The P–N bond occupies an axial position and P=O an equatorial one. The P=O² bond length (1.468(1) Å) is close to that found in IV (1.461(6) Å). In I the endocyclic P–O bond lengths are slightly different (P–O¹ 1.582(2) and P–O³ 1.574(2) Å) and close to those found in III (1.58(2) Å) and IV (1.570(4) Å). The axial P–N bond length (1.616(2) Å) is larger than the equatorial one (1.591(8) Å) in V but smaller than that in VI (1.684(4) Å) and than the axial bond lengths in III and IV (1.65(1) and 1.702(5) Å, respectively).

Some papers report structural studies of bicyclic molecules containing the 1,3,2-dioxaphosphorinane fragment

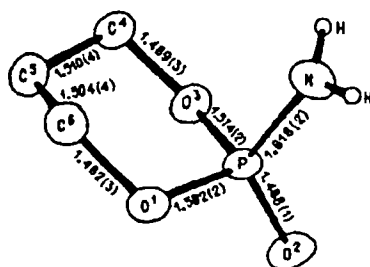


Fig. 1. The geometry and bond lengths (d , Å) of I. The H atoms are not shown.

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TABLE 1. Atomic Coordinates of Structure I, Equivalent Isotropic Thermal Parameters of Nonhydrogen Atoms $B_{\text{iso}}^{\text{eq}} = 4/3 \sum \sum (a_i a_j) B(i, j)$ (\AA^2) and Isotropic Thermal Parameters of Hydrogen Atoms (B , \AA^2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
P	0.67020(5)	0.21872(6)	0.63748(8)	1.77(1)
O ¹	0.5510(2)	0.2702(2)	0.6041(2)	2.14(4)
O ²	0.7416(2)	0.3371(2)	0.6550(3)	2.90(4)
O ³	0.6621(2)	0.1363(2)	0.7868(2)	2.07(4)
N	0.7009(2)	0.105(2)	0.5150(3)	2.39(5)
C ⁴	0.5723(2)	0.0392(3)	0.8033(4)	2.25(5)
C ⁵	0.4650(2)	0.1066(3)	0.7695(4)	2.48(6)
C ⁶	0.4632(2)	0.1711(3)	0.6182(4)	2.40(5)
H ^{1N}	0.726(2)	0.035(3)	0.548(3)	2.6(7)
H ^{2N}	0.714(2)	0.125(3)	0.439(4)	2.8(7)
H ^{4.1}	0.589(2)	0.041(3)	0.742(3)	2.5(6)
H ^{4.2}	0.579(2)	0.05(3)	0.905(3)	2.2(6)
H ^{5.1}	0.450(2)	0.170(3)	0.836(3)	3.7(8)
H ^{5.2}	0.403(2)	0.042(3)	0.778(3)	2.9(7)
H ^{6.1}	0.405(2)	0.216(3)	0.597(3)	3.4(7)
H ^{6.2}	0.465(2)	0.106(3)	0.543(4)	2.2(6)

with the oxo and amino group at the phosphorus atom. These are three bicyclo[4.3]nonane systems with the dimethylamino group (VII) [7], diethylamino group (VIII) [8], and benzylamino group at the phosphorus atom (IX) [9] as well as the bicyclo[4.4]decane system with the dimethylamino group at the phosphorus atom (X) [10]. In VII-IX, the amino groups are equatorial while in X they are axial. In the monograph [11] it is shown that the amino group exhibits the inverse anomeric effect, i.e., it occupies preferentially the equatorial position. In this case, the lone electron pair of the nitrogen atom interacts with the antibonding orbitals of the P–O bonds of the cycle. This interaction shows itself in a lengthening of the P–O bonds of the cycle and a shortening of the exocyclic P–N bond.

TABLE 2. Bond Angles ω (deg) and Torsion Angles τ (deg)

Angle	ω	Angle	ω
O ¹ PO ²	108.80(9)	PO ³ C ⁴	118.0(1)
O ¹ PO ³	105.58(8)	PNH ^{1N}	116(2)
O ¹ PN	108.0(1)	PNH ^{2N}	121(1)
O ² PO ³	110.80(9)	H ^{1N} PH ^{2N}	119(3)
O ² PN	118.8(1)	O ³ C ⁴ C ⁵	110.7(2)
O ³ PN	104.0(1)	C ⁴ C ⁵ C ⁶	112.4(2)
PO ¹ C ⁶	117.2(1)	O ¹ C ⁶ C ⁵	110.4(2)
Angle	τ	Angle	τ
O ³ PO ¹ C ⁶	–46.8	C ⁴ O ³ PO ²	–165.7
PO ¹ C ⁶ C ⁵	54.8	NPO ³ C ⁴	68.2
O ¹ C ⁶ C ⁵ C ⁴	–57.1	O ¹ PNH ^{1N}	–131.1
C ⁶ C ⁵ C ⁴ O ³	55.5	O ¹ PNH ^{2N}	74.7
C ⁵ C ⁴ O ³ P	–51.9	O ² PNH ^{1N}	104.5
C ⁴ O ³ PO ¹	45.4	O ² PNH ^{2N}	–49.7
O ² PO ¹ C ⁶	–165.7	O ³ PNH ^{1N}	–19.2
NPO ¹ C ⁶	64.0	O ³ PNH ^{2N}	–173.4

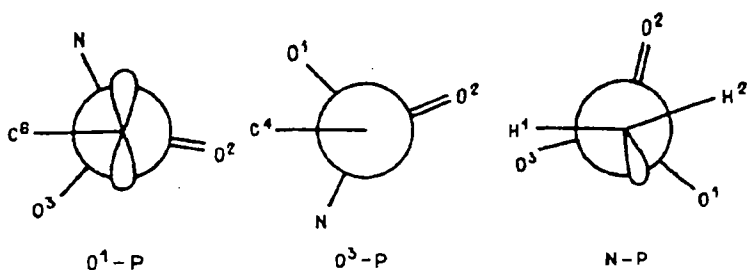


Fig. 2. The Newman projections along the O-P and N-P bonds in molecule I.

The sum of the bond angles at the nitrogen atom in I is $356(7)^\circ$. The error is too large to allow us to judge the coordination of the nitrogen atom (planar-trigonal or flattened pyramidal). Figure 2 shows the Newman projections along the endocyclic O-P bonds and the N-P bond. With the axial orientation of the P-N bond, the conformation is favorable for the interaction of lone electron pairs of endocyclic O atoms with the antibonding orbital of the P-N bond (anomeric effect). Thus in 1,3,2-dioxaphosphorinanes the axial P-N bonds, as a rule, are longer than the equatorial ones. Along the N-P bond, a conformation is realized which is favorable for the interaction of the lone electron pair of the nitrogen atom with σ^* -orbitals of the P-O¹ and P=O² bonds and unfavorable for the interaction with the P-O³ bond. Conceivably, the somewhat larger P-O¹ bond length as compared to the P-O³ bond is due to this interaction. The O¹PN bond angles larger than O³PN and O²PN larger than O²PO¹ and O²PO³ confirm the participation of the nitrogen lone pair in the interaction.

The arguments above lead to the conclusion that in 2-oxo-1,3,2-dioxaphosphorinanes the amino group at the phosphorus atom may occupy either an equatorial or an axial position. The dialkylamino group, as a rule, exhibits the inverse anomeric effect, i.e., preferentially occupies an equatorial position. The amino or monosubstituted amino group preferentially occupies an axial position.

In a crystal, molecules I form a three-dimensional framework via the N-H...O hydrogen bonds of type N-H^{1N}...O^{2'} ($3/2-x; y-1/2; z$; a zigzag chain along the y axis), N...O^{2'} 3.008(2) Å, N-H^{1N} 0.81(3) Å, H...O^{2'} 2.21(3) Å, the N-H...O angle $167(2)^\circ$; N-H^{2N}...O^{2''} ($x; 1/2-y; z-1/2$; a zigzag chain along the z axis), N...O^{2''} 3.332(2) Å, N-H^{2N} 0.73(4) Å, H^{2N}...O^{2''} 2.61(3) Å, the N-H...O angle $171(2)^\circ$.

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