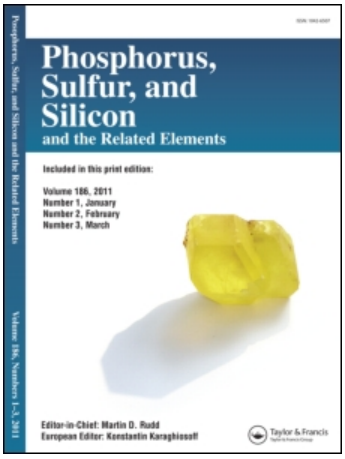

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THE CHEMISTRY AND STRUCTURE OF THEP(O)NC(O) SYSTEM. PART 2. CRYSTAL ANDMOLECULAR STRUCTURE OF N-DIETHOXYPHOSPHORYLFORMAMIDINE

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THE CHEMISTRY AND STRUCTURE OF THE P(O)NC(O) SYSTEM. PART 2. CRYSTAL AND MOLECULAR STRUCTURE OF N-DIETHOXYPHOSPHORYLFORMAMIDINE

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The crystal and molecular structure of N-diethoxyphosphorylformamidine (**2**) has been determined. $P2_1/n$, a = 8.343(1), b = 9.249(1), c = 12.413(1) Å, β = 102.06 (1)°; V = 937(1) Å.^{3} Final R_w = 0.052 for 1705 reflections with $I > 3\sigma(I)$ and 113 parameters. Molecular parameters indicate strong electron-donating effect of the amidine substituent, resulting in high P—N bond order and small difference between the two C—N bond distances. The geometry of the molecule is different from that observed for phosphoric-carboxylicimides: the O=P—N=C—NH_2 system is almost planar with the phosphoryl oxygen in short contact with the sp^2 carbon atom.

Key words: N-phosphorylated formamidine; Crystal and molecular structure; P—N bond distance; O=P—N bond angle; Geometry of the O=P—N—C—X skeleton; electrophilicity/nucleophilicity of the P(O)NC(O) system.

INTRODUCTION

In our current studies on the ambident nucleophilicity of phosphoric-carboxylic imides, $(RO)_2P(O)NHC(O)R'$ (**1**), we investigated the trimethylsilylation reaction of diethyl N-formylphosphoramidate (**1a**) (**1**, R = Et; R' = H).[1] The reaction of **1a** with hexamethyldisilazane involved the initial silylation of the carbonyl oxygen, followed by the nucleophilic displacement of the Me_3SiO group by ammonia, released in the first step of the reaction (Scheme I).

The N-phosphorylated formamidine (**2**), reported previously by Khyat and Al-Isa,[2] is a crystalline compound, and we decided to determine its crystal and molecular structure for the following reasons. Firstly, neither n.m.r. (^1H, ^{13}C, ^{31}P) nor i.r. spectroscopy could unambiguously distinguish between structure (**2**) and its tautomeric form, $(EtO)_2P(O)$—NH—C(NH)H. In the crystal structure analysis, however, the NH hydrogens were located experimentally and refined, thus we were

$$2\ (EtO)_2P(O)\text{—}NH\text{—}C(O)H + (Me_3Si)_2NH \rightarrow 2\ (EtO)_2P(O)\text{—}N{=}C(OSiMe_3)H + NH_3$$

(1a)

$$(EtO)_2P(O)\text{—}N{=}C(OSiMe_3)H + NH_3 \rightarrow (EtO)_2P(O)\text{—}N{=}C(NH_2)H + Me_3SiOH$$

(2)

SCHEME I

able to determine unequivocally the solid state structure of the compound. Secondly, molecular parameters obtained for (**2**) could be compared with those reported for a variety of related structures, hence could provide additional information about the bond order, hybridization, geometry, hydrogen bonding, etc., for the nitrogen-substituted phosphoryl derivatives.

RESULTS AND DISCUSSION

The perspective view of (**2**), together with atomic nomenclature, is given in Figure 1, while Figure 2 represents the unit cell for the compound. The location of the NH hydrogens (hence the detailed molecular structure of (**2**)) is evident; it is also clear that the molecules are arranged into the infinite chains *via* intermolecular P=O . . . H—N hydrogen bonds, with the O . . . N distance of 2.775 Å. Selected molecular parameters are listed in Table I together with the available data for such related structures as phosphoric-carboxylic imides (**1**), N-phosphorylated urea (**3**), N-phosphorylated dimethylsulfoximides (**4**), and simple phosphoramidates (**5**). While the distance of the phosphoryl bond, P=O, remains remarkably constant for all structures (**1**)–(**5**) (1.461(6) Å), the length of the P—N bond is sensitive to the nature of the N-substituent. The structures discussed can be divided into three groups, that is those with a long (1.670, 1.646 Å, (**1**), (**3**)), medium (1.630, 1.631 Å; (**2**), (**5**)), and short (1.618 Å; (**4**)) P—N bonds. When the nitrogen atom is substituted by the electron-withdrawing group (carbonyl, compounds (**1**) and (**3**)),

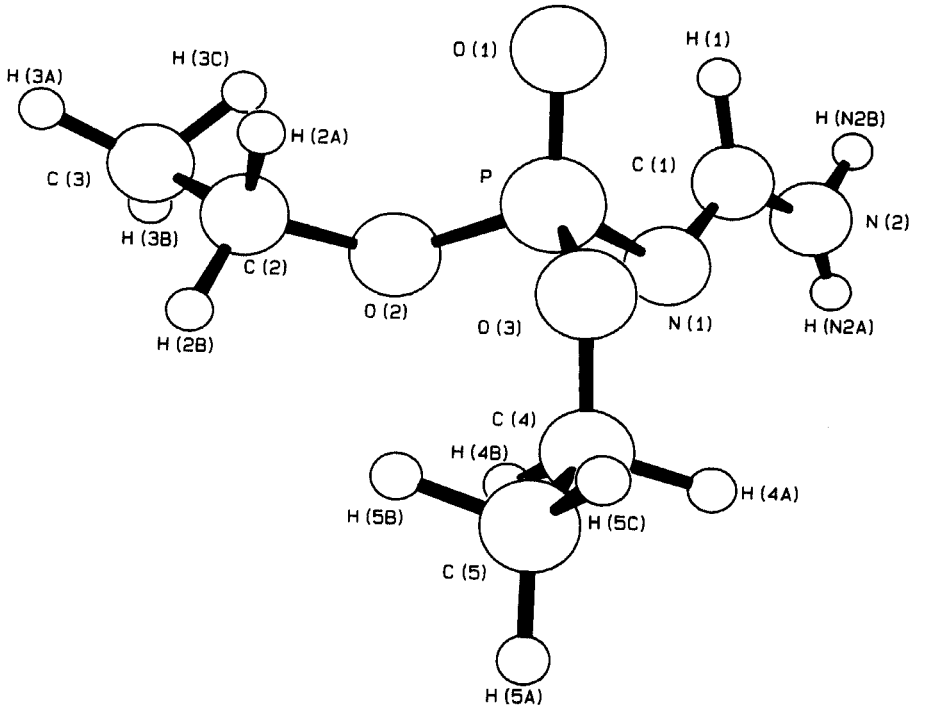


FIGURE 1 A perspective view of **2** with atomic numbering.

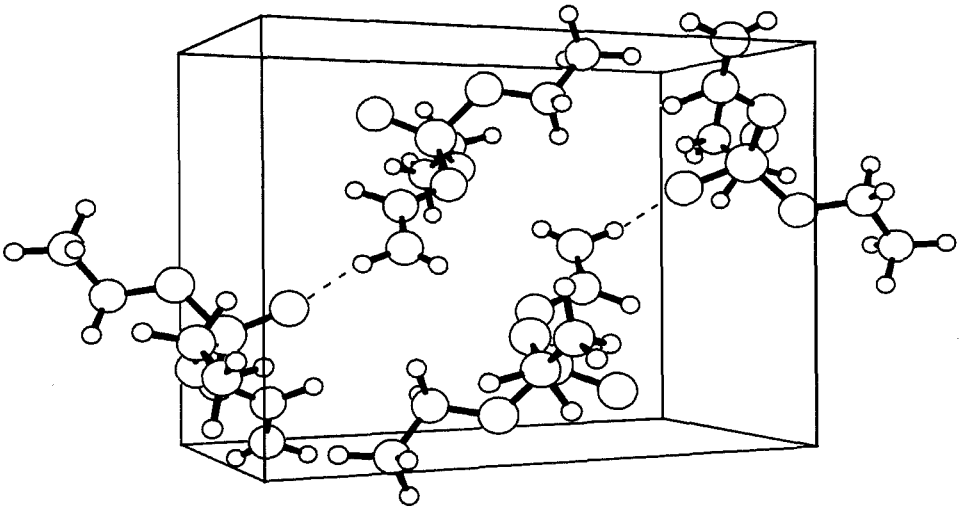


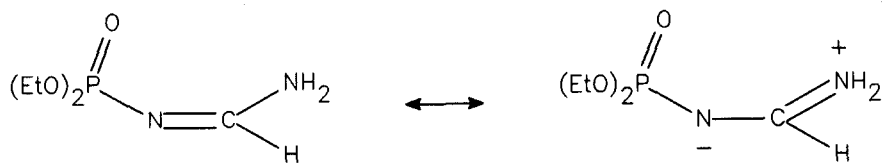
FIGURE 2 Packing diagram for **2**; hydrogen bonding is indicated by dotted lines.

no N→P back donation is expected, and the P—N bond order is not far from unity. For the compounds in which an electron-rich group is attached to the nitrogen (*R* in (**5**), amidine function in (**2**)), the back donation results in a serious shortening of the P—N bond. The exceptionally short distance found in (**4**) was interpreted[5] in terms of the heteroallenic system, reported for other sulfur-containing organophosphorus compounds.[7]

As expected, both C—N bonds in (**2**) are considerably shorter than those in (**3**). Although they differ from each other, the difference is not large, implying significant contribution of the resonance form (**2a**) to the bonding description of the molecule (Scheme II).

The C—N bonds in (**3**) are much longer, indicating little resonance with the carbonyl group because of the presence of two electronegative substituents (phosphoryl and phenyl) at each of the N atoms. Taking the difference in the P—N distances into account (1.402 *vs* 1.359 Å), it follows that the diethoxyphosphoryl substituent has a stronger effect on a nitrogen atom than does the phenyl group.

It is known[8] that multiple-bond orbitals repel other orbitals more stongly than do single bond orbitals, the value of a X—P—Y angle reflects therefore the P—X



2 **2a**

SCHEME II

TABLE I

Selected molecular parameters for (2) and related systems

Intramolecular bond distances (Å)					
Compound	Ref.	P=O	P-N	N=C (N=S)	C-N
$(EtO)_2P(O)NC(H)NH_2$ (2)	a	1.463(2)	1.631(2)	1.296(3)	1.326(4)
$(EtO)_2P(O)NHC(O)Me$ (1a)	1	1.449(2)	1.682(3)		1.381(4)
$(EtO)_2P(O)NHC(O)Ph$ (1b)	1	1.468(2)	1.662(2)		1.378(3)
$(MeO)_2P(O)NHC(O)Ph$ (1c)	3	1.461(4)	1.667(5)		1.393(7)
$(PhO)_2P(O)NHC(O)NMePh$ (3)	4	1.462(4)	1.646(5)	1.406(8)	1.358(7)
$(RO)_2P(O)NS(O)Me_2$ [b] (4)	5	1.463(7)	1.618(8)	(1.526(8))	
(RO)(R'O)P(O)NHR" [b] (5)	6	1.464	1.630		1.424
Intramolecular bond angles (°)					
Compound	O=P-N	P-N-C	P-N=S	N=C-N	N-C=O (N=S-O)
(2)	118.4(1)	118.0(2)		123.2(3)	
(1a)	109.2(1)	127.6(3)			121.6(4)
(1b)	108.6(1)	126.3(2)			121.3(3)
(1c)	107.5(2)	124.7(4)			120.0(5)
(3)	109.5(2)	125.6(4)		114.1(5)	122.9(5)
(4)[b]	116.4(5)		126.1(5)		118.8(5)
(5)[b]	112.0	127.0			
Torsion angles (°)					
Compound	O=P-N-C	P-N-C-N	P-N-C=O	O=P-N-S	P-N-S-O
(2)	-11.3(3)	-177.7(2)			
(1a)	172.6(7)		-4.06(1.25)		
(1b)	177.0(2)		0.64(0.39)		
(1c)	c		c		
(3)	-179.4(5)	170.1(4)	-10.9(9)		
(4)[b]				33.8	57.0
(5)[b]	4.7				

[a] This work

[b] Average value

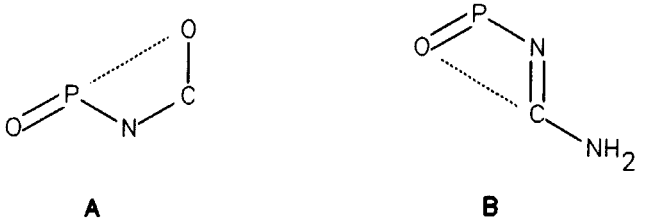
[c] No values of the torsion angles given, but for the plane determined by the O=P-N(H)-C=O backbone, the root mean square deviation was found to be only 0.041.

and/or P—Y bond order. Since the phosphoryl bond order in the series included in Table I is approximately constant (*vide supra*), it can be concluded from the values of the O=P—N bond angles that the P—N bond order decreases in a sequence: (**4**), (**2**) > (**5**) > (**3**), (**1**), in agreement with the observed P—N bond distances. As far as the P—N—C bond angle is concerned, this angle in (**2**) is significantly smaller than that for all N—H containing compounds (**1**), (**3**), (**5**) (118.0° *vs ca* 126°). This difference can be explained as follows. In (**1**), (**3**), (**5**) two big substituents at nitrogen locate as far from each other as possible, bringing the hydrogen atom more close to the lone pair of electrons. In (**2**), short N=C bond implies considerable electron density on nitrogen (see the resonance structure **2a**), hence the electronic repulsion, resulting in the smaller P—N=C angle, just below the value expected for a sp^2 hybridization.

The values of the N—C—N bond angles can be compared for structures (**2**) and (**3**). Large difference between those values reflects the difference in the bonding situation in those two systems. In (**3**) both C—N bonds are essentially "single" (long), hence causing less repulsion (smaller angle), as compared with the electron-rich "single"/"double" (short) bonding system in (**2**). This is confirmed by the average value of the O=C—N angle for (**3**) = 122.9°, reflecting (like in compounds (**1**)) the "single"/"double" interactions.

Analysis of the torsion angles obtained for structures (**1**)–(**4**) offers an insight into the intramolecular interactions operating in those systems. In derivatives (**1**) and (**3**) the O=P—N—C moiety attains an almost ideal antiperiplanar orientation, with the carbonyl oxygen located not far from that plane, with the geometry shown in Figure 3 (structure **A**).

Such a geometry allows for the donor-acceptor, non-bonded interactions between carbonyl oxygen and phosphorus atoms; in (**1c**) this distance (Figure 3, dotted line) is indeed only 2.97 Å, considerably less than the sum of the respective van der Waals radii (3.30 Å). In (**4**) spatial arrangement of the O=P—N=S=O backbone of the molecule is such that *both*, the (S)O . . . P, and the (P)O . . . S non-bonded distances approach the values of the corresponding van der Waals radii. In structure (**2**) the situation is qualitatively different. The O=P—N=C—NH_2 system is again almost planar (the respective two torsion angles are −11.3 and 177.7°), but the arrangement is quite different from that characteristic of mixed imides, as shown in Figure 3, structure **B**. In the molecule of (**2**) it is the phosphoryl oxygen that is in short contact with the sp^2 carbon atom of the amidine group; the O(1) . . . C(1) distance is 2.948 Å, while the sum of the van der Walls radii is 3.30 Å. The change of the geometry of the molecule to the type **B** (Figure 3) reflects the change in the relative nucleophilicity/electrophilicity of the respective centres in the OPNCX



A **B**

FIGURE 3 Geometry of the O=P—N—C—X backbone of systems **1–3**.

TABLE II

Fractional coordinates ($\times 10^4$) and equivalent thermal factors ($\times 10^3 Å^2$) for compound **2**

	x/a	y/b	z/c	U_{eq}
P	2168(1)	7880(1)	4577(1)	55(1)
O(1)	1297(3)	8516(3)	3540(2)	85(1)
N(1)	3509(3)	6612(3)	4530(2)	52(1)
C(1)	3553(4)	6054(3)	3578(2)	53(1)
N(2)	4554(4)	4986(3)	3446(2)	63(1)
O(2)	1015(3)	7124(3)	5252(2)	83(1)
C(2)	-455(7)	7816(6)	5440(5)	139(2)
C(3)	-1798(7)	7061(6)	5201(6)	200(3)
O(3)	3075(3)	9115(2)	5340(2)	83(1)
C(4)	4011(6)	8863(5)	6407(3)	130(2)
C(5)	3982(8)	10043(6)	7120(4)	150(2)
H(1)	2734(4)	6480(3)	2858(2)	200(7)*
H(N2A)	5272(65)	4548(57)	3929(38)	200(7)*
H(N2B)	4500(67)	4609(51)	2661(37)	200(7)*
H(2A)	-640(7)	8790(6)	4950(5)	200(7)*
H(2B)	-252(7)	8096(6)	6303(5)	200(7)*
H(3A)	-3020(7)	7485(6)	5140(6)	200(7)*
H(3B)	-1797(7)	5915(6)	5366(6)	200(7)*
H(3C)	-1410(7)	7245(6)	4435(6)	200(7)*
H(4A)	3525(6)	7925(5)	6747(3)	200(7)*
H(4B)	5265(6)	8659(5)	6349(3)	200(7)*
H(5A)	4648(8)	9981(6)	7964(4)	200(7)*
H(5B)	2681(8)	10017(6)	7099(4)	200(7)*
H(5C)	4288(8)	11039(6)	6756(4)	200(7)*

* = isotropic temperature factor, $U_{eq} = 1/3 \Sigma_i \Sigma_j U_{ij} a^*_i a^*_j (\mathbf{a}_i . \mathbf{a}_j)$

system. According to the structure **A** (Figure 3), phosphorus atom represents the most electrophilic, and the carbonyl oxygen the most nucleophilic centre of the molecule. These conclusions are fully supported by the results of the neutral solvolysis of mixed phosphoric-carboxylic imides,[9] and of the trimethylsilylation[1] of these compounds. Strong electron donation from the amidine group to the phosphoryl centre in (**2**) (resonance structure (**2b**)) is also demonstrated by the virtual planarity of the NH_2 group (the deviation of the nitrogen atom from the plane defined by C(1) and two H atoms was found to be only 0.003(3) Å). The N-phosphorylated amidine represents therefore a derivative with a powerfully electron-donating substituent at the phosphoryl centre.

EXPERIMENTAL

Substrate (**2**) was prepared as described elsewhere.[1] It crystallized as colorless, approximately cubic crystals, decaying slowly when exposed to the atmosphere; mp = 68–69°C (from benzene).

Crystal data. $C_5H_{13}N_2O_3P$, M = 180.1. Monoclinic, a = 8.343(1); b = 9.249(1); c = 12.413(1) Å; β = 102.06(1)°; V = 937(1) Å^3 (by least squares refinement on the diffractometer angles for 25 centred reflections with $40 \leq \theta \leq 48°$, λ = 1.5418 Å); space group $P2_1/n$ (no 14); Z = 4, D_x = 1.28 g cm^{-3}. Crystal dimensions: 0.24 × 0.28 × 0.38 mm; $\mu(CuK_\alpha)$ = 22.6 cm^{-1}.

Data collection and processing. CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.50 + 0.14 tanθ, variable but maximum ω scan speed 5.49 deg min^{-1}, graphite monochromated Cu-Kα radiation; 2228 reflections measured ($5 \leq \theta \leq 76°$, h: 0, +10; k: 0, +11; l: −15, +15) 1893 unique reflections [merging R = 0.020 after absorption correction[10] (max., min., ave., correction factors 0.999, 0.940, 0.982)], giving 1705 with $I > 3\sigma(I)$. Decay 4.3%, not corrected.

Structure analysis and refinement. Direct methods (SHELX86)[11] followed by standard difference Fourier and refinement methods using SHELX76.[12] Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and all hydrogen atoms included with a common isotropic thermal parameter that refined to U_{iso} = 0.200(7) Å^2. The hydrogen atoms of the NH_2 moiety were located experimentally, and were also refined without any restriction in these positions. All other hydrogen atoms were placed in expected positions and constrained to ride upon their associated heavy atoms during refinement. Convergence was reached at R = 0.061, Rw = 0.052 using $\sigma^{-2}(F_o)$ weights, and refining 113 parameters. Largest shift/esd in final cycle 0.27, max. residual electron density 0.42 eÅ^{-3}. Atomic scattering factors were taken from SHELX.[11,12] Fractional atomic coordinates are given in Table II. Tables with bond lengths, bond angles and anisotropic thermal parameters have been submitted to the Cambridge Crystallographic Data Centre, Universiyt Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW, U.K.

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