Hydrogen Bonding in Phosphoramides: Structures of Dimethyl N-Phenylphosphoramidate and Dimethyl N-(p-Nitrophenyl)phosphoramidate

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Abstract

$C_8H_{12}NO_3P$ (I), $M_r = 201 \cdot 2$, monoclinic, $P2_1/n$, $a = 16 \cdot 929$ (8), $b = 7 \cdot 706$ (4), $c = 15 \cdot 883$ (8) Å, $\beta = 90 \cdot 24$ (2)°, $V = 2072$ Å^3, $Z = 8$, $D_m = 1 \cdot 28$, $D_c = 1 \cdot 29$ Mg m^{-3}, μ(Mo $K\alpha$) = $0 \cdot 20$ mm^{-1}. $C_8H_{11}N_2O_5P$ (II), $M_r = 246 \cdot 2$, orthorhombic, $Pbcn$, $a = 24 \cdot 74$ (1), $b = 7 \cdot 421$ (4), $c = 12 \cdot 327$ (6) Å, $V = 2263 \cdot 4$ Å^3, $Z = 8$, $D_m = 1 \cdot 42$, $D_c = 1 \cdot 44$ Mg m^{-3}, μ(Mo $K\alpha$) = $0 \cdot 20$ mm^{-1}. Compound (I) has two independent centro-symmetrically related hydrogen-bonded dimers in the cell. Compound (II) crystallizes as a monomer stabilized by a network of hydrogen bonding extending along **b**. $R = 0 \cdot 064$ for 2148 observed reflections [compound (I)] and $0 \cdot 075$ for 719 observed reflections [compound (II)].

Introduction

The crystal structures of a series of ring-substituted dimethyl N-phenylphosphoramidates $(CH_3O)_2P(O)$-NHC_6H_4X have been determined as part of a study on structure–reactivity relationships in the chemistry of phosphoryl derivatives (Davidowitz & Modro, 1980). We wish to seek a correlation between the molecular parameters (particularly bond distances and angles within the amide function, hydrogen bonding, *etc.*) and the observed spectroscopic and solvolytic properties of this system. The solution properties of these compounds indicate that the self-association involving intermolecular hydrogen bonding persists even in non-polar solvents and at high dilution (Foulds, Modro & Rijkmans, 1981). In the case of the first compound in this series ($X = p$-OCH_3) a dimeric, hydrogen-bonded structure has been demonstrated in the solid state (du Plessis, Modro & Nassimbeni, 1980). We now report the structures of a further two compounds in this series, $X = H$ (I) and $X = p$-NO_2 (II). The phosphoramidates should therefore contain substituents (p-OCH_3, H, p-NO_2) covering a wide range of

polar effects, transmitted effectively through the aromatic ring. We expected that the analysis of the molecular structures of these compounds would provide information on the bonding in the phosphoramidate function and on the response of this function to polar effects.

Experimental

The preparation of both compounds will be discussed elsewhere (Modro & Rijkmans, 1981). Preliminary cell dimensions and space-group symmetry were determined photographically. Accurate lattice constants were obtained from a least-squares analysis of the settings of 25 reflections measured on a Philips PW1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0 \cdot 7107$ Å). During the diffractometer data collection three reference reflections were periodically monitored to check crystal stability. In the case of compound (II) one of these standard reflections showed a somewhat high % standard deviation (4·7%), indicative of some crystal decay. No corrections were made to take into account the possibility of crystal decay. Also in the case of (II) the proximity of reflections, due to the

Table 1. *Experimental and refinement parameters for the crystal-structure analyses of* (I) *and* (II)

	Compound (I)	Compound (II)
Data collection		
Crystal dimensions (mm)	$0 \cdot 32 \times 0 \cdot 68 \times 0 \cdot 98$	$0 \cdot 4 \times 0 \cdot 1 \times 0 \cdot 1$
Scan mode	ω–2θ	ω–2θ
Scan width (°θ)	1·5	0·4
Scan speed (°θ s^{-1})	0·05	0·005
Range scanned (2θ) (°)	6–40	6–40
Stability of standard reflections (%)	1·0	2·63
Number of reflections collected	2803	1263
Number of observed reflections	2148 with	719 with
	I(rel) > $2\sigma I$(rel)	I(rel) > $2\sigma I$(rel)
Final refinement		
Number of variables	259	157
$R = \Sigma \|\|F_o\| - \|F_c\|\| / \Sigma \|F_o\|$	0·064	0·075
$R_w = \Sigma w^{1/2} \|\|F_o\| - \|F_c\|\| / \Sigma w^{1/2}\|F_o\|$	0·074	0·059
Weighting scheme w	$(\sigma^2 F + 0 \cdot 002 F^2)^{-1}$	$(\sigma^2 F)^{-1}$
U (aromatic H) (Å^2)	0·10 (1), 0·08 (1)	0·12 (2)
U (methyl H) (Å^2)	0·20 (2), 0·17 (2)	0·28 (3)
U (amine H) (Å^2)	0·07 (2), 0·10 (2)	0·16 (4)

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relatively large a parameter, precluded the measurement of backgrounds for individual reflections. A background vs θ curve was used to estimate the background for all the reflections. Details of the data collection are listed in Table 1. The data were corrected for the Lorentz–polarization factor, but not for absorption.

Solution and refinement of the structures

Both structures were solved by the automatic centrosymmetric direct-methods routine of *SHELX* (Sheldrick, 1978). The E map yielded the positions of most of the heavy atoms. Subsequent least-squares refinements yielded the positions of the remaining heavy

atoms and most of the H atoms including the amide H atoms. The final refinements were carried out with the heavy atoms treated anisotropically, with the methyl H atoms refined as rigid groups and the aromatic H atoms in calculated positions (C—H = 1·08 Å). The amide H atoms were constrained at 1·00 ± 0·01 Å from their N atoms. The isotropic temperature factors of the H atoms were treated as three single parameters. Details of the final refinements are listed in Table 1. Final atomic parameters are listed in Table 2.*

Table 2. *Fractional atomic coordinates* $(\times 10^4)$ *with e.s.d.'s in parentheses and isotropic temperature factors* $(\text{Å}^2 \times 10^3)$ *equivalent to the refined anisotropic values for the non-H atoms*

$$U_{eq} = \tfrac{1}{3} \text{ (trace of the orthogonalized } U_{ij} \text{ matrix).}$$

	Molecule A				Molecule B				Compound (II)			
	x	y	z	U_{eq}	x	y	z	U_{eq}	x	y	z	U_{eq}
P	−234 (1)	3965 (2)	1340 (1)	55	5835 (1)	2079 (2)	481 (1)	65	3099 (1)	1889 (4)	2043 (2)	77
O(1)	−601 (2)	3397 (5)	555 (2)	69	4986 (2)	2204 (5)	364 (3)	79	2533 (2)	2069 (7)	2366 (5)	91
O(2)	101 (2)	2468 (5)	1909 (2)	71	6152 (3)	2478 (7)	1412 (3)	116	3533 (2)	2857 (8)	2756 (6)	94
O(3)	−797 (2)	4889 (4)	1977 (2)	68	6311 (2)	3410 (6)	−20 (3)	101	3263 (3)	2827 (10)	960 (7)	105
O(4)	–	–	–	–	–	–	–	–	5617 (3)	−2687 (15)	727 (7)	135
O(5)	–	–	–	–	–	–	–	–	5246 (3)	−5270 (13)	1141 (6)	114
N(1)	462 (2)	5357 (5)	1147 (2)	60	6150 (2)	137 (5)	340 (3)	67	3258 (2)	−257 (9)	1972 (7)	68
N(2)	–	–	–	–	–	–	–	–	5230 (5)	−3596 (16)	1008 (8)	98
C(1)	1010 (3)	6183 (6)	1702 (3)	53	6917 (3)	−571 (6)	421 (3)	51	3758 (4)	−1050 (15)	1719 (7)	57
C(2)	966 (3)	6043 (7)	2571 (3)	66	6995 (3)	−2369 (6)	362 (3)	61	4209 (4)	−21 (15)	1468 (7)	74
C(3)	1514 (4)	6881 (8)	3066 (4)	78	7737 (4)	−3116 (7)	427 (4)	79	4700 (5)	−869 (19)	1229 (7)	79
C(4)	2111 (4)	7878 (8)	2700 (4)	84	8400 (4)	−2127 (8)	558 (4)	81	4710 (4)	−2711 (21)	1251 (7)	69
C(5)	2149 (3)	8017 (8)	1838 (4)	77	8314 (3)	−330 (7)	616 (3)	71	4273 (5)	−3788 (15)	1506 (7)	77
C(6)	1603 (3)	7173 (7)	1342 (3)	65	7581 (3)	438 (6)	548 (3)	60	3791 (4)	−2918 (16)	1730 (7)	66
C(7)	634 (4)	1178 (9)	1555 (5)	100	5957 (5)	3890 (9)	1874 (5)	110	3586 (5)	2404 (22)	3888 (9)	142
C(8)	−1493 (4)	4010 (10)	2297 (4)	99	6076 (5)	3778 (11)	−898 (5)	116	3016 (5)	2530 (22)	−26 (10)	146

Table 3. *Bond lengths* (Å) *for* (I) *and* (II) *and selected bond lengths* (Å) *for the p*-OCH$_3$ *analogue with e.s.d.'s in parentheses*

	Compound (I)			p-OCH₃ analogue*	
	Molecule A	Molecule B	Compound (II)	Molecule A	Molecule B
P—O(1)	1·458 (3)	1·452 (4)	1·462 (5)	1·462 (2)	1·466 (2)
P—O(2)	1·570 (4)	1·601 (5)	1·563 (6)	1·557 (2)	1·567 (2)
P—O(3)	1·564 (3)	1·530 (5)	1·559 (7)	1·595 (2)	1·582 (2)
P—N(1)	1·624 (4)	1·605 (4)	1·643 (7)	1·626 (2)	1·630 (2)
N(1)—C(1)	1·427 (6)	1·414 (6)	1·405 (9)	1·419 (4)	1·413 (4)
C(1)—C(2)	1·387 (7)	1·395 (7)	1·387 (11)	1·391 (4)	1·387 (4)
C(2)—C(3)	1·375 (7)	1·385 (7)	1·400 (11)	1·381 (4)	1·361 (4)
C(3)—C(4)	1·398 (9)	1·372 (8)	1·367 (12)	1·385 (4)	1·386 (4)
C(4)—C(5)	1·375 (8)	1·395 (8)	1·381 (12)	1·369 (4)	1·388 (4)
C(5)—C(6)	1·375 (7)	1·379 (7)	1·384 (11)	1·380 (4)	1·386 (4)
C(6)—C(1)	1·386 (7)	1·381 (6)	1·389 (10)	1·392 (4)	1·386 (4)
O(2)—C(7)	1·457 (7)	1·354 (7)	1·441 (10)	1·457 (4)	1·448 (4)
O(3)—C(8)	1·453 (7)	1·476 (8)	1·378 (11)	1·438 (4)	1·450 (4)
N(2)—C(4)	–	–	1·475 (12)	–	–
N(2)—O(4)	–	–	1·221 (11)	–	–
N(2)—O(5)	–	–	1·254 (11)	–	–

* du Plessis, Modro & Nassimbeni (1980).

Table 4. *Bond angles* (°) *with e.s.d.'s in parentheses*

	Compound (I)		Compound
	Molecule A	Molecule B	(II)
O(1)—P—O(2)	115·0 (2)	115·7 (2)	117·6 (4)
O(1)—P—O(3)	115·5 (2)	114·4 (2)	116·2 (3)
O(1)—P—N(1)	110·1 (2)	111·9 (2)	109·4 (4)
N(1)—P—O(2)	109·5 (2)	101·4 (3)	108·1 (4)
O(2)—P—O(3)	100·5 (2)	100·2 (3)	95·6 (4)
N(1)—P—O(3)	105·4 (2)	112·1 (3)	109·0 (4)
P—N(1)—C(1)	130·4 (3)	130·8 (3)	129·0 (6)
C(6)—C(1)—C(2)	119·7 (5)	119·5 (5)	120·3 (9)
C(1)—C(2)—C(3)	119·6 (5)	119·6 (5)	119·9 (10)
C(2)—C(3)—C(4)	120·5 (5)	121·4 (5)	117·5 (10)
C(3)—C(4)—C(5)	119·6 (5)	118·4 (5)	124·7 (10)
C(4)—C(5)—C(6)	120·0 (6)	121·0 (5)	116·8 (10)
C(5)—C(6)—C(1)	120·7 (5)	120·1 (5)	121·0 (9)
P—O(2)—C(7)	120·1 (4)	125·0 (5)	120·0 (7)
P—O(3)—C(8)	120·8 (4)	118·7 (4)	124·6 (8)
C(6)—C(1)—N(1)	117·4 (4)	122·9 (4)	117·9 (10)
C(2)—C(1)—N(1)	122·9 (4)	117·7 (4)	121·8 (10)
N(2)—C(4)—C(3)	–	–	117·2 (13)
N(2)—C(4)—C(5)	–	–	118·1 (12)
O(4)—N(2)—O(5)	–	–	124·0 (12)
C(4)—N(2)—O(4)	–	–	119·7 (11)
C(4)—N(2)—O(5)	–	–	116·2 (12)

Principal bond lengths and angles are shown in Tables 3 and 4 respectively.

Results and discussion

The molecular structure of compound (I) with atomic nomenclature is shown in Fig. 1 (both independent molecules A and B are shown). The unlabelled molecules are related to the labelled molecules through a centre of symmetry. The atomic nomenclature of structure (II) is shown in Fig. 2. In compound (I) there are two independent hydrogen-bonded dimers in the unit cell, whereas compound (II) exists as a monomer. The conformations of the two independent molecules of (I) are similar. Both compounds crystallize in the syncoplanar orientation of the phosphoryl and N—H groups.
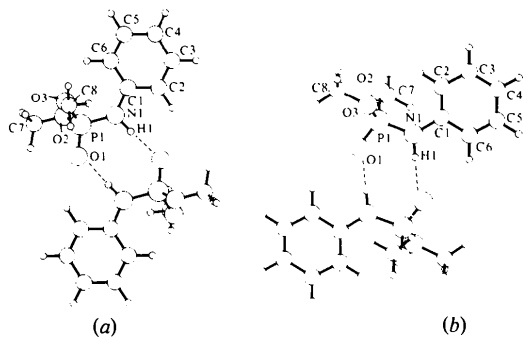

Fig. 1. Perspective view of the molecular structure of (I) with atomic nomenclature. (a) Molecule A, (b) molecule B.
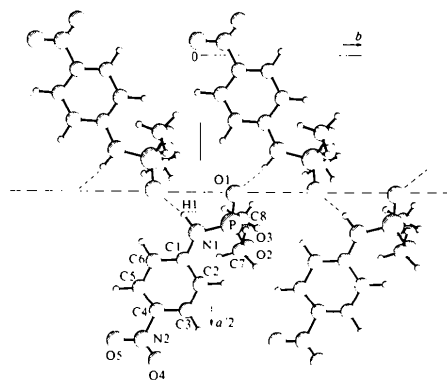

Fig. 2. Perspective view of the molecular structure and hydrogen bonding of (II) with atomic nomenclature.

The bond lengths in both these compounds are within the range of typical values observed for the phosphoramidate system (Kennard, 1962). In particular the P=O bond appears to be insensitive to changes in substituent at the *para* position of the phenyl ring. The values found for the title compounds are similar to the values observed in the *p*-OCH$_3$ analogue (du Plessis *et al.*, 1980) and to the value of 1·459 (4) Å found in *O*-(4-*tert*-butyl-2-chlorophenyl) *O*-methyl *N*-methylphosphoramidate in which no hydrogen bonding occurs (Baughman, Eckey & Jacobson, 1978). On substitution there is a lengthening of the P—N bond and a shortening of the N—C(aromatic) bond. The effect of substitution on the bonding of the phosphoramidate function will be compared with the analogous effects in carboxylic amide systems and the discussion of the results will be presented elsewhere (du Plessis, Modro & Nassimbeni, 1981).

Hydrogen bonding

Hydrogen-bonding data are given in Table 5 and perspective views of the hydrogen-bonding schemes in Figs. 2 and 3.

Table 5. *Hydrogen-bonding data with e.s.d.'s in parentheses*

	Compound (I)		
	Molecule A	Molecule B	Compound (II)
N—H (constrained) (Å)	1·00 (5)	1·00 (5)	1·00 (5)
H(1)···O(1) (Å)	1·89 (5)[i]	1·87 (5)[ii]	1·85 (5)[iii]
N(1)···O(1) (Å)	2·88 (1)[i]	2·86 (1)[ii]	2·83 (5)[iii]
N(1)—H(1)—O(1) (°)	171·1 (9)	174·6 (9)	164·4 (9)

Roman-numeral superscripts refer to the following equivalent positions relative to the molecule at x,y,z: (i) $-x$, $1 - y$, $-z$; (ii) $1 - x$, $-y$, $-z$; (iii) $0·5 - x$, $-0·5 + y, z$.

Fig. 3. The molecular packing of (I) showing the hydrogen bonding.

The intermolecular $P=O\cdots N$ distance in (II) indicates a hydrogen bond stronger than that in (I) or in the p-OCH_3 derivative. In all three phosphoramidates the hydrogen bonding is weaker than that in 5,5-dimethyl-2-phenylamino-1,3,2-dioxaphosphorinane 2-oxide [2·802 (10) Å] (Cameron, Gałdecki & Karolak-Wojciechowska, 1976) and stronger than that in diammonium hydrogen phosphate [2·892 (2) Å] (Khan, Roux & James, 1972). The hydrogen-bond angle [$O(1)\cdots H(1)$—$N(1)$] is closer to linearity in the dimerized species than in the polymeric aggregate.

It appears that the nature of the substituent has an influence on the type of hydrogen-bonding scheme. Compound (I) is dimeric with two equivalent hydrogen bonds in the dimer while compound (II) is monomeric, stabilized by a network of hydrogen bonds extending along **b**. The p-OCH_3 derivative is also dimeric but has two independent hydrogen bonds in the dimer (du Plessis et al., 1980). In (II) the presence of the strongly electron-withdrawing p-NO_2 group results in increased acidity of H(1), hence the $N(1)\cdots O(1)$ hydrogen-bond distance is somewhat shorter. This suggests that the hydrogen bonding in this compound is stronger than in (I). The hydrogen-bond angle in (II), 164·4 (9)°, deviates markedly from linearity, whereas the angle in the dimer [compound (I)] is fairly linear. In terms of geometrical considerations it appears, therefore, that the dimer is more favourable for hydrogen-bond stabilization because hydrogen bonds which are close to linearity are achieved.

Benzene-ring geometry

It has been shown that substitution of an H atom with a functional group distorts the C-atom skeleton of the benzene ring (Domenicano, Vaciago & Coulson, 1975a,b; Domenicano, Mazzeo & Vaciago, 1976). These distortions concern the half of the ring nearest the substituent; in particular the *ipso* angle (α) is sensitive to the polar effects of the substituent (Domeni-

cano & Murray-Rust, 1979). In (II) the *ipso* angle, α_{NO_2} [*i.e.* C(3)—C(4)—C(5)] is greater than the average value of 122·1(1)° obtained for derivatives of nitrobenzene (Domenicano et al., 1975a). The large values of α_{NO_2} are found in molecules in which the nitro group is located *para* to a strong π-electron acceptor (Di Rienzo, Domenicano & Riva di Sanseverino, 1980). The observed value of $\alpha_{NO_2} = 124\cdot7$ (10)° in (II) is amongst the largest yet reported and indicates that the NH—$P(O)(OR_2)$ group is strongly π-electron withdrawing.

The *ipso* angle of the amide group (α_{-NH-}) in (I) is close to the 'standard' value of 119·1 (2)° determined for derivatives of aniline (Domenicano & Vaciago, 1979). In (II) this value is slightly larger which is possibly due to the small influence (usually <2°) of the p-NO_2 group.

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