

Crystal Structure of the Phosphinyl-stabilised Ylide $\text{Me}_3\text{NNP}(=\text{O})\text{Ph}_2 \cdot \text{H}_2\text{O}^*$

*Kenneth W. Muir,** David G. Morris, and Vickie Innes*

Chemistry Department, Glasgow University, Glasgow G12 8QQ, Great Britain

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Crystals of trimethylammonio-*P,P*-diphenylphosphinamidate hydrate, $\text{Me}_3\text{NNP}(=\text{O})\text{Ph}_2 \cdot \text{H}_2\text{O}$, are held together by hydrogen bonds which link two $\text{Me}_3\text{NNP}(=\text{O})\text{Ph}_2$ and two water molecules to form a centrosymmetric O_4H_4 ring belonging to graph set $\text{R}^2_4(8)$. Each P=O oxygen atom can thereby act as acceptor to two hydrogen bonds, rather than to only one, as in the two-fold symmetric $\text{P}=\text{O} \cdots \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{P}$ motif commonly found in phosphine oxide hemihydrates. The unusual P–N bond in $\text{Me}_3\text{NNP}(=\text{O})\text{Ph}_2$ is short enough [1.614(3) Å] to indicate some multiple character.

Keywords: X-ray structure, ylide, hydrogen bonding.

INTRODUCTION

Earlier work^{1–4} on nitrogen ylides, $\text{R}_3\text{N}-\text{N}-\text{X}$ where R = alkyl, has shown that the dipolar $\text{R}_3\text{N}(+)-\text{N}(-)$ group is highly effective in releasing electrons to the stabilising group X. Thus, the basicity of a suitably located hydrogen bond acceptor site in X is substantially increased when X is attached to $\text{R}_3\text{N}(+)-\text{N}(-)$. As an illustration, the basicity of the cyano N atom has been shown² to increase along the series: $\text{Me}-\text{C}\equiv\text{N} < \text{Me}_2\text{N}-\text{C}\equiv\text{N} < \text{Me}_2\text{N}-\text{CH}=\text{CH}-\text{C}\equiv\text{N} < \text{Me}_2\text{N}-\text{CH}=\text{N}-\text{C}\equiv\text{N} < {}^n\text{Bu}_3\text{N}^+-\text{N}^--\text{C}\equiv\text{N}$. Such a series can be used to plan rational modification of effective antihistamine drugs containing the cyano group, such as cimetidine.⁵

* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday in recognition of the long and fruitful interaction between crystallographers based in Glasgow and Zagreb.

** Author to whom correspondence should be addressed. (E-mail: ken@chem.gla.ac.uk)

In the course of examining the effect of $\text{Me}_3\text{N}(+)\text{-N}(-)$ on the hydrogen bonding properties of other stabilising groups which could be incorporated into drug molecules we have determined the structure of the phosphinyl-stabilised ylide $\text{Me}_3\text{N}(+)\text{-N}(-)\text{-P(=O)Ph}_2$ **1** from crystals of its monohydrate. The results of this analysis are presented here.

EXPERIMENTAL

Crystals of $\text{Me}_3\text{NNP(=O)Ph}_2 \cdot \text{H}_2\text{O}$ were prepared according to the method of Kameyana *et al.*⁶ The physical properties reported by these authors accord with those given here for the sample used for X-ray analysis. $^1\text{H NMR}$ (CDCl_3) (recorded on a Bruker AM200 spectrometer at 200 MHz; chemical shifts are relative to 7.25 ppm for CHCl_3) δ/ppm : 2.1 (s, 2 water-H), 3.4 (s, 9 methyl-H), 7.2–8.0 (m, 10 phenyl-H). IR(KBr) (recorded on a Nicolet Impact 410 spectrometer) $\nu_{\text{max}}/\text{cm}^{-1}$: 1150, 1110 (P=O). MS (JMS700 spectrometer in EI mode at 70eV) m/z : 274 ($\text{M}^+ - 18$). M.p. 177–178 °C.

All X-ray measurements were made at 22 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatised Mo-K α radiation, $\lambda = 0.71073$ Å, using a crystal of dimensions $0.25 \times 0.20 \times 0.10$ mm.

Crystal data: $\text{C}_{15}\text{H}_{21}\text{N}_2\text{O}_2\text{P}$, $M = 292.31$, monoclinic, space group $P2_1/c$, $a = 8.7992(5)$, $b = 14.3777(12)$, $c = 13.022(7)$ Å, $\beta = 107.667(5)^\circ$, $V = 1569.7(9)$ Å³, $Z = 4$, $D_c = 1.237$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.178$ mm⁻¹, extinction coefficient 0.0067(14).

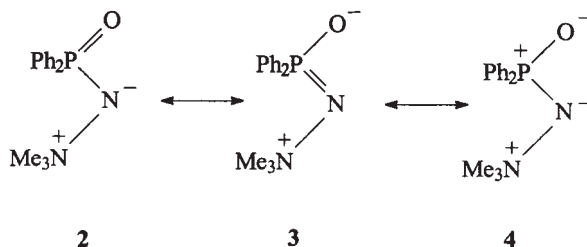
Cell dimensions are based on the setting angles of 25 reflections with $9 < \theta(\text{Mo-K}\alpha) < 20^\circ$. The intensities of 4070 reflections with $2.1 < \theta(\text{Mo-K}\alpha) < 26.3^\circ$, $-10 \leq h \leq 10$, $-2 \leq k \leq 17$ and $-2 \leq l \leq 16$ were estimated from $\omega/2\theta$ scans and corrected for Lp effects and 2.1% decomposition. Averaging gave 3176 unique reflections ($R_{\text{int}} = 0.034$); of these 1761 were deemed observed [$I > 2\sigma(I)$]. The structure was solved by direct methods⁷ and refined to convergence ($\Delta/\sigma < 0.001$ for 190 parameters) using all 3176 F^2 values with $w = [\sigma^2(F^2) + (0.0664P)^2 + 1.27P]^{-1}$ where $P = (F_{\text{obs}}^2 + 2F_{\text{calc}}^2)/3$. Final agreement indices were $R[I > 2\sigma(I)] = 0.056$ and $wR_2(\text{all data}) = 0.168$ and in the final difference map $|\Delta\rho| < 0.50$ e Å⁻³. Anisotropic U_{ij} were refined for all non-hydrogen atoms. The H atoms attached to water oxygen atom Ow were freely refined; other H-atoms were positioned from difference maps and subsequently rode on their parent C atoms. Scattering factors and anomalous dispersion corrections were those incorporated in the least-squares refinement program SHELXL97.⁸ The WINGX package⁹ was used for other calculations.

Tables of atomic parameters, a complete geometry listing, and observed and calculated structure factors are available from the authors. The structure has been deposited in the Cambridge Structural Database (deposition number CCDC 105609).

RESULTS AND DISCUSSION

The molecular structure of **1** (Table I, Figure 1) contains a two-coordinate ylide nitrogen atom, N1, bound to tetrahedrally coordinated ni-

trogen and phosphorus atoms. The bond lengths suggest that **2** is the predominant canonical form, with **3** and **4** also contributing (Scheme I).



Scheme I.

The P–N1 bond length [1.614(3) Å] is consistent with some multiple character: it is nearly as short as the mean value¹⁰ found in cyclic phosphazenes (1.582 Å) where the P–N bonds are thought to have aromatic character, and it is comparable to the $\text{Ph}_2\text{P}(\text{O})\text{--N}$ distance of 1.605(2) Å in

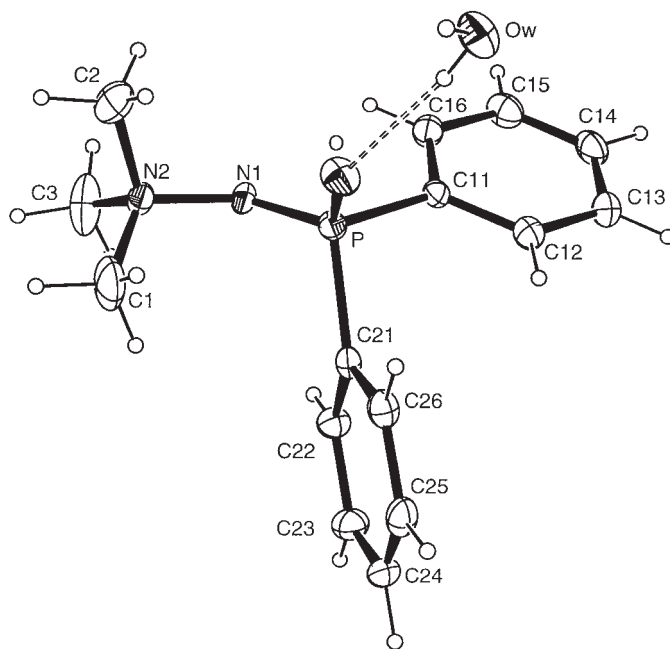


Figure 1. A view of the contents of the asymmetric unit. Here (and in Figure 2) 20% ellipsoids are shown for non-hydrogen atoms, hydrogen atoms are displayed as spheres of arbitrary radius, and hydrogen bonds are indicated by broken lines.

TABLE I
Selected distances / Å and angles / ° for **1**

Bond lengths				
P–O	1.494(2)	P–N1	1.614(3)	
P–C11	1.814(3)	P–C21	1.824(3)	
N1–N2	1.450(4)	N2–C1	1.468(6)	
N2–C3	1.473(6)	N2–C2	1.474(5)	
Bond angles				
O–P–N1	121.03(16)	O–P–C11	111.15(15)	
N1–P–C11	100.26(16)	O–P–C21	107.29(16)	
N1–P–C21	112.78(15)	C11–P–C21	102.72(15)	
N2–N1–P	120.1(2)	N1–N2–C1	115.3(3)	
N1–N2–C3	106.2(3)	C1–N2–C3	108.1(4)	
N1–N2–C2	109.6(3)	C1–N2–C2	109.9(4)	
C3–N2–C2	107.2(4)			
Torsion angles				
O–P–N1–N2	–48.9(3)	C11–P–N1–N2	–171.4(3)	
C21–P–N1–N2	80.0(3)	P–N1–N2–C1	–41.5(5)	
P–N1–N2–C3	–161.3(3)	P–N1–N2–C2	83.2(4)	
N1–P–C11–C12	–159.9(3)	N1–P–C11–C16	22.5(3)	
C11–P–C21–C22	–70.1(3)	O–P–C11–C12	70.9(3)	
C21–P–C11–C12	–43.5(3)	O–P–C21–C26	–11.2(3)	
N1–P–C21–C22	36.9(3)	C11–P–C21–C26	106.1(3)	
Hydrogen-bonds and short C–H...X (X = N or O) contacts				
D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	<(DHA)
OW–H(1W)...O	0.79(6)	2.05(6)	2.839(5)	170(6)
OW–H(2W)...O ⁱ	0.74(5)	2.12(5)	2.845(5)	171(6)
C16–H16...N1	0.93	2.56	2.938(5)	105
C22–H22...N1	0.93	2.94	3.278(5)	103
C26–H26...O	0.93	2.60	2.998(5)	106

Ph₂P(O)–N–PPh₃.¹¹ This molecule contains the only example, apart from **1**, of a structurally characterised C₂P(O)–N system in which the nitrogen atom is two-coordinate and its Ph₂P(O)–N bond is the shortest of the 30 occurrences of a C₂P(O)–N bond in the Cambridge Structural Database (CSD):¹² the remaining values are in the range 1.612–1.764 Å (mean 1.657 Å) and involve three-coordinate nitrogen.

Other distances involving the P atom in **1** agree with mean values from the CSD (P=O 1.489, P-C_{ar} 1.801 Å).¹⁰ Unsurprisingly, the O and N1 atoms subtend the most obtuse angle at P [121.0(2)].

The structures of ten $\text{Me}_3\text{N-N-X}$ molecules with a variety of stabilising X groups, including nitro, sulfonyl and phosphinyl, are now known (Table II).¹³⁻¹⁷ The N-N distances fall in a narrow range [1.450(4) Å in **1** to 1.49(1) Å when X = alkyl] while the N-N-X angle appears easily deformed. The

TABLE II

Selected distances / Å and angles / ° in $\text{Me}_3\text{N-N-X}$ ylides

Reference	X	N-N	N-X	N-C	N-N-X
This work	-P(=O)Ph ₂	1.450(4)	1.614(3)	1.471(2)	120.1(2)
13	=CPhMe	1.46(1)	1.27(1)	1.50(1)	120.9(8)
13 ^a	=C ⁱ Pr ₂	1.49(1)	1.26(1)	1.49(1)	122.3(9)
13 ^a	=C ⁱ Pr ₂	1.49(1)	1.25(1)	1.52(1)	120.8(9)
13	=CMe ⁱ Pr	1.486(7)	1.277(7)	1.483(6)	124.2(5)
14	=C(C ₂₀ H ₂₄ O ₄)	1.480	1.272	1.494	120.9
15	-SO ₂ C ₆ H ₄ -Me-p	1.471(3)	1.592(2)	1.496(5)	118.0(1)
16	-C ₅ NCl ₃ (CN)	1.476	1.318	1.515	116.0
17	-C(=O)Ph	1.471(5)	1.313(6)	1.492(5)	114.2(3)
17	-NO ₂	1.470(8)	1.323(8)	1.503(6)	115.0(5)
Means		1.474(3)		1.495(4)	119(1)

^a Two independent molecules.

mean N-CH₃ distance in **1** is 0.02 Å shorter than the average value in Table II, possibly reflecting shrinkage arising from large amplitude libration of the methyl carbons atoms about the N1-N2 axis [$U(\text{C})_{\text{max}} = 0.26 \text{ \AA}^2$] obvious from Figure 1.

The conformation adopted by molecules of **1** in the crystal is such that the non-hydrogen atoms, apart from C1 and C2, lie roughly in one of two mutually perpendicular planes. The C3-N2-N1-P-C11-C12 chain has a *trans*-zigzag shape, characterised by torsion angles across N2-N1, N1-P and P-C11 which are close to 180° [the respective values are -161.3(3), -171.4(3) and -159.9(3)°]. The oxygen atom lies nearly in the plane of the C2_n (n = 1- 6) ring [O-P-C21-C26 = -11.2(3)°]. In consequence N1 is enclosed in a pocket defined by the H-atoms attached to C16 and C22 and by the N2 methyl groups, while the phosphinyl O atom has a more open envi-

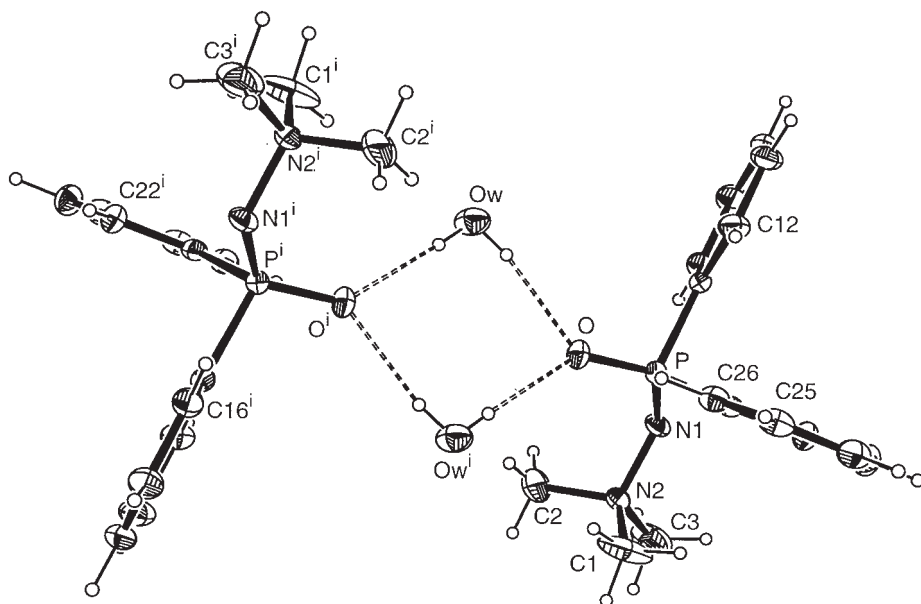


Figure 2. A view of the hydrogen bonds which link two ylide and two water molecules to form a centrosymmetric O_4H_4 ring.

ronment which allows it to participate in intermolecular hydrogen bonding. As can be seen from Figure 2, two molecules of the ylide and two water molecules define a centrosymmetric O_4H_4 ring in which each phosphinyl O atom accepts hydrogen bonds from two different water molecules. This arrangement can be assigned a graph set $R^2_4(8)$ according to the Etter notation.¹⁸ It contrasts with the hydrogen bonding arrangements typical of hydrated triarylphosphine oxides: $(p\text{-Tol})_3\text{PO}$ and Ph_3PO crystallise as hemihydrates in which the water molecule lies on a two-fold axis and forms hydrogen bonds to equivalent phosphine oxide O atoms.¹⁹ This $\text{P}=\text{O} \cdots \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{P}$ motif allows each phosphine oxide O atom to accept only one hydrogen bond. Indeed, the use of Ph_3PO as a crystallisation aid seems usually to involve acceptance of a single strong hydrogen bond by the phosphine oxygen atom.²⁰ It is then tempting to suggest that the presence of the electron releasing $\text{Me}_3\text{N}-\text{N}$ group in **1** helps the phosphinyl oxygen atom to accept a second hydrogen bond. However, a CSD search for systems containing $\text{C}_2\text{P}=\text{O} \cdots \text{HO}$ (water) hydrogen bonds quickly reveals examples of the $R^2_4(8)$ graph set found in **1**, with $\text{O} \cdots \text{O}$ distances of 2.75–2.90 Å and $\text{O} \cdots \text{H}-\text{O}$ angles slightly less than 180: for instance, in triphenylphosphine oxide tetrachloropyrocatechol monohydrate the $R^2_4(8)$ phosphine oxide – water ring is augmented by donation from catechol-H to water-O,²¹ while isolated $R^2_4(8)$ rings occur in

bis{(8-chlorobenzocyclo-octatetraen-6-yl)diphenylphosphine oxide} monohydrate²² and *trans*-1,6-diphenyl-1,6-diphosphacyclodecan-1,6-dione dihydrate.²³ Thirteen $\text{C}_2\text{P=O} \cdots \text{HO}(\text{water})$ structures with reliable water H positions were located in our search of the CSD: in 8 P=O acted as a single acceptor while in 5 (including those in Refs. 21–23) it participated in two hydrogen bonds. We conclude that the choice between $\text{P=O} \cdots \text{H-O-H} \cdots \text{O=P}$ and $\text{R}_2\text{P(=O)} \cdots \text{HO}$ motifs in crystals containing $\text{C}_2\text{P=O} \cdots \text{HO}(\text{water})$ residues depends on several factors, two of the more important being the steric bulk and electronegativity of the substituents attached to the phosphorus atom.

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SAŽETAK

Kristalna struktura fosfinilom stabiliziranog ilida $\text{Me}_3\text{NNP}(=\text{O})\text{Ph}_2 \cdot \text{H}_2\text{O}$

Kenneth W. Muir, David G. Morris i Vickie Innes

Strukturne jedinice u kristalima trimetilamonio-*P,P*-difenilfosfinamidat-hidrata (1/1), $\text{Me}_3\text{NNP}(=\text{O})\text{Ph}_2 \cdot \text{H}_2\text{O}$ povezane su međusobno vodikovim vezama tako da dvije molekule $\text{Me}_3\text{NNP}(=\text{O})\text{Ph}_2$ i dvije molekule vode čine centrosimetrični prsten O_4H_4 koji pripada grafičkom skupu $R^2_4(8)$. Na taj način svaki kisikov atom iz skupine $\text{P}=\text{O}$ igra ulogu akceptora dva vodikova atoma, a ne samo jednoga, kako se obično nalazi u fosfinoksidnim hemihidratima vrste $\text{P}=\text{O} \cdots \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{P}$ koji posjeduju kristalografsku os simetrije drugog reda. Neobičajeno kratka veza $\text{P}-\text{N}$ [1,614(3) Å] u $\text{Me}_3\text{NNP}(=\text{O})\text{Ph}_2$ ukazuje na njezinu višestrukost.