Crystal and Molecular Structure of *NN*-Dimethyldiphenylphosphinamide

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The crystal and molecular structure of the title compound (I) has been determined by single-crystal *X*-ray diffraction. Crystals are orthorhombic, space group $P2_12_12_1$, $a = 7.670(4)$, $b = 11.141(3)$, $c = 15.644(5)$ Å, and $Z = 4$. The structure was solved from diffractometer data by the heavy-atom technique. Positional and anisotropic thermal parameters were refined by full-matrix least-squares methods to a final R factor of 6.5% for 1 005 observed reflections. The phosphorus, nitrogen, and two methyl carbon atoms are non-planar.

THE synthesis of phosphinamides has been studied extensively,[1-13] but there is little information regarding their reactions [1,4,6] and behaviour in aqueous media.[5,12] Phosphinamides are hydrolysed rapidly in acidic solutions as compared to neutral or basic conditions.[5] At present only semiquantitative information is available as to the rates of hydrolysis. Zhmurova *et al.*[12] have commented on the hydrolysis of *NN*-dimethyldiphenylphosphinamide, $\mathrm{Ph_2P(:O)\cdot NMe_2}$ (I), and diphenylphosphinamide, $\mathrm{Ph_2P(:O)\cdot NH_2}$ (II).

Hydrolysis of (I) was complete in 1—2 h in dilute hydrochloric acid, whereas, at high temperature it was complete in 2—3 min. In water at 100 °C hydrolysis of (II) occurred in 2—3 min. Data for (I) taken with the published data for the acid catalysis of benzamide [13] gives a relative rate constant (kP–N/kC–N) of *ca.* 10^5. Recently [14] phosphinamides were prepared, and their acid-catalysed hydrolysis, reactions and structure were studied. An *X*-ray diffraction study was undertaken to determine the structure of (I) independently, and to understand the bonding at phosphorus.[15]

EXPERIMENTAL

A crystal of dimensions *ca.* 0.20 × 0.25 × 0.60 mm^3 was used for data collection. The space group was determined from preliminary Weissenberg and precession photographs. Accurate lattice parameters were determined from eight independent 2θ values measured on a diffractometer.

Crystal Data.—$C_{14}H_{16}NOP$, $M = 245.11$. Orthorhombic, space group $P2_12_12_1$, $a = 7.670(4)$, $b = 11.141(3)$, $c = 15.644(5)$ Å, $U = 1\,337$ Å^3; $D_m = 1.20$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.22$ g cm^{-3}, $F(000) = 520$, Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) $= 1.94$ cm^{-1}.

Intensities of all possible independent reflections to $2\theta \leqslant 60°$ were measured by the θ—2θ scan technique on a General Electric XRD 5 diffractometer. Each reflection was scanned for 100 s, and background on each side counted for 50 s. The scan rate was 2° min^{-1} in 2θ, take-off angle 4°. Zirconium-filtered Mo-K_α radiation was used. Of 1 800 reflections measured 1 005 were considered observed by the criterion $F_o > 2\sigma(F_o)$. Standard reflections measured every 4 h showed no significant change throughout data collection. Data were corrected for Lorentz and polarization factors,[16] but not for absorption or extinction. Form factors were taken from ref. 17, hydrogen atom scattering factors from ref. 18. Anomalous terms of the form factors were not included.

Structure Determination and Refinement.—The phosphorus position was located from a three-dimensional Patterson map. Phases from the partial structure factors calculated from these positions were used for the first three-dimensional Fourier-synthesis which revealed the complete structure.

Three cycles of refinement by full-matrix least-squares refining the positional parameters reduced R to 18.2%. Three more cycles, refining positional and individual isotropic temperature factors, reduced R to 9.8%. For the final stages of refinement both the positional and individual anisotropic temperature factors were refined for non-hydrogen atoms. Phenyl hydrogen atoms were included at calculated positions (assuming C–H 1.0 Å), and given a temperature factor 0.5 Å^2 more than the carbon atoms to which they were bonded. Final refinement converged at R 6.5% and weighted factor, R', 5.3%. All parameter shifts were then $<0.1\sigma$. A final difference map showed no significant features. Throughout refinement reflections were weighted in accordance with counting statistics according to the scheme suggested in ref. 19.

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[16] Most programs used were from the Montana State Library for Crystallographic Computing for the IBM 1620, written by C. T. Li, G. W. Svetich, C. N. Caughlan, R. D. Witters, and K. D. Watenpaugh. Final full-matrix least-squares refinement was carried out on the Montana State University Sigma 7 computer with a modified version of W. R. Busing and H. A. Levy's UCILS R.

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TABLE 1

Atomic co-ordinates, with standard deviations in parentheses

Atom	*x*	*y*	*z*
P(1)	0.194 5(3)	0.404 5(2)	0.323 0(1)
O(2)	0.274 5(7)	0.408 4(5)	0.236 9(3)
N(3)	−0.022 3(7)	0.424 8(7)	0.329 6(5)
C(4)	−0.090 8(12)	0.548 0(6)	0.318 6(7)
C(5)	−0.132 2(11)	0.327 6(8)	0.291 2(7)
C(6)	0.281 6(11)	0.517 9(7)	0.391 3(5)
C(7)	0.257 0(11)	0.522 0(8)	0.478 5(6)
C(8)	0.339 3(11)	0.606 1(9)	0.531 0(5)
C(9)	0.439 8(14)	0.692 8(8)	0.492 2(6)
C(10)	0.464 0(14)	0.692 0(9)	0.406 7(7)
C(11)	0.390 4(12)	0.604 0(9)	0.355 9(5)
C(12)	0.229 5(10)	0.262 5(7)	0.374 3(5)
C(13)	0.363 7(11)	0.193 5(9)	0.342 0(5)
C(14)	0.397 7(11)	0.078 7(9)	0.377 9(6)
C(15)	0.303 2(14)	0.041 0(7)	0.445 0(6)
C(16)	0.172 6(12)	0.111 0(9)	0.478 8(6)
C(17)	0.136 4(10)	0.219 0(8)	0.442 7(6)
Calculated hydrogen positions			
H(1)C(7)	0.180 9	0.459 5	0.506 9
H(2)C(8)	0.319 6	0.606 1	0.594 6
H(3)C(9)	0.498 6	0.757 6	0.529 1
H(4)C(10)	0.545 5	0.758 0	0.376 6
H(5)C(11)	0.413 5	0.604 3	0.290 6
H(6)C(13)	0.438 6	0.222 1	0.290 0
H(7)C(14)	0.498 4	0.030 8	0.351 0
H(8)C(15)	0.331 1	−0.042 8	0.470 4
H(9)C(16)	0.098 8	0.078 1	0.530 2
H(10)C(17)	0.037 8	0.271 4	0.469 9

TABLE 2

Valence angles (°) with their standard deviations in parentheses

O(2)–P(1)–N(3)	117.5(4)	N(3)–P(1)–C(6)	103.8(4)
O(2)–P(1)–C(6)	111.6(4)	N(3)–P(1)–C(12)	103.9(4)
O(2)–P(1)–C(12)	111.7(4)	C(6)–P(1)–C(12)	107.5(4)
P(1)–N(3)–C(4)	118.0(5)	C(4)–N(3)–C(5)	115.1(7)
P(1)–N(3)–C(5)	115.8(6)		
P(1)–C(6)–C(7)	124.4(6)	C(7)–C(8)–C(9)	117.7(8)
P(1)–C(6)–C(11)	118.4(6)	C(8)–C(9)–C(10)	120.6(9)
C(7)–C(6)–C(11)	117.1(8)	C(9)–C(10)–C(11)	121.2(9)
C(6)–C(7)–C(8)	122.9(8)	C(10)–C(11)–C(6)	120.4(9)
P(1)–C(12)–C(13)	116.1(6)	C(13)–C(14)–C(15)	119.4(9)
P(1)–C(12)–C(17)	125.5(6)	C(14)–C(15)–C(16)	121.1(9)
C(13)–C(12)–C(17)	118.4(8)	C(15)–C(16)–C(17)	119.4(9)
C(12)–C(13)–C(14)	119.6(8)	C(16)–C(17)–C(12)	122.0(8)

RESULTS AND DISCUSSION

Final atomic parameters with their standard deviations are listed in Table 1, and valence angles in Table 2. Figure 1 shows the structure with bond distances, and Figure 2 bond angles at phosphorus and nitrogen. The structure projected down the *a* axis is shown in Figure 3, and a stereodiagram of the structure viewed down the *a* axis in Figure 4. Table 3 lists the equations of various least-squares planes and dihedral angles. Final observed and calculated structure factors

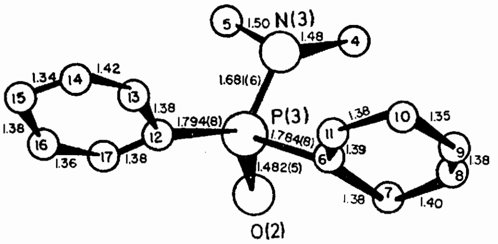

FIGURE 1 Structure and the interatomic distances of (I). The standard deviations for N–C and C–C bond distances are *ca.* 0.01 Å

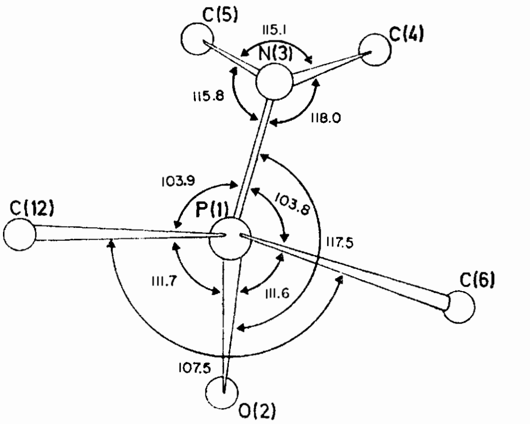

FIGURE 2 Bond angles (°) at phosphorus and nitrogen

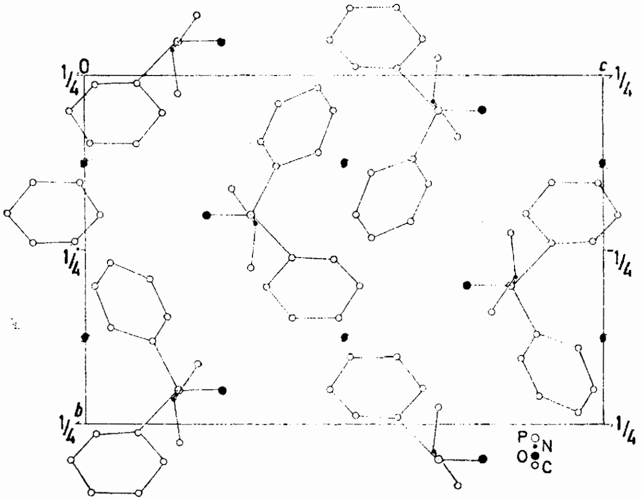

FIGURE 3 [100] Projection of the structure of (I)

TABLE 3

Equations of least-squares planes: $AX + BY + CZ = D$

Plane atoms	A/Å	B/Å	C/Å	D/Å †	S/Å^2 †
(1) P(1), N(3), C(4), C(5)	−0.138 8	−0.154 1	0.979 3	4.112	$0.687\,1 \times 10^{-1}$
(2) N(3), C(4), C(5)	−0.503 6	−0.084 9	0.859 8	4.117	0
(3) C(6)—(11)	0.795 4	−0.594 1	0.119 9	−0.970 9	$0.183\,0 \times 10^{-2}$
(4) C(12)—(17)	0.650 0	0.428 6	0.627 6	6.079	$0.607\,7 \times 10^{-3}$

Dihedral angles (°): (2)–(3) 75.7, (2)–(4) 79.9, (3)–(4) 70.3

† S = sum of squares of deviation of atoms from plane, D = origin-to-plane distance. All atoms given equal weights.

and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21663 (4 pp., 1 microfiche).*

The P–N bond distance (1.681 Å) is significantly shorter than the sum of the covalent radii (1.80 Å),[20] but significantly longer than that (1.617 Å) reported by Mani *et al.*[21] The length of the P–N bond in the phosphoramidate ion, (H_3N^+–PO_3), is reported to be 1.77—1.79 Å,[22,23] while in the phosphonitrile tetramer the exocyclic P–N bond is reported to be 1.75—1.89 Å.[24] A bond order of 1.36, calculated for the P–N bond in (I) by Tyssee [14] by means of coupling constants, indicates a large amount of π-interaction of the nitrogen lone-pair electrons with the phosphorus *d* orbitals. As a result of the presence of an oxygen atom bound to phosphorus, negative charge placed on the phosphorus by interaction with nitrogen can be delocalized to the oxygen atom. This explains the shortening of the P–N bond distance to 1.681 Å and an elongation of the P=O bond distance to 1.482 Å, which is longer than the normal phosphoryl bonds (1.44 Å). If the length of a single P–N bond is taken as 1.80 Å and of a double bond as 1.47 Å, and we assume a linear relation between bond length and order, Tyssee's estimate of P–N bond-order (1.36) is in good agreement with the observed distance of 1.681 Å.

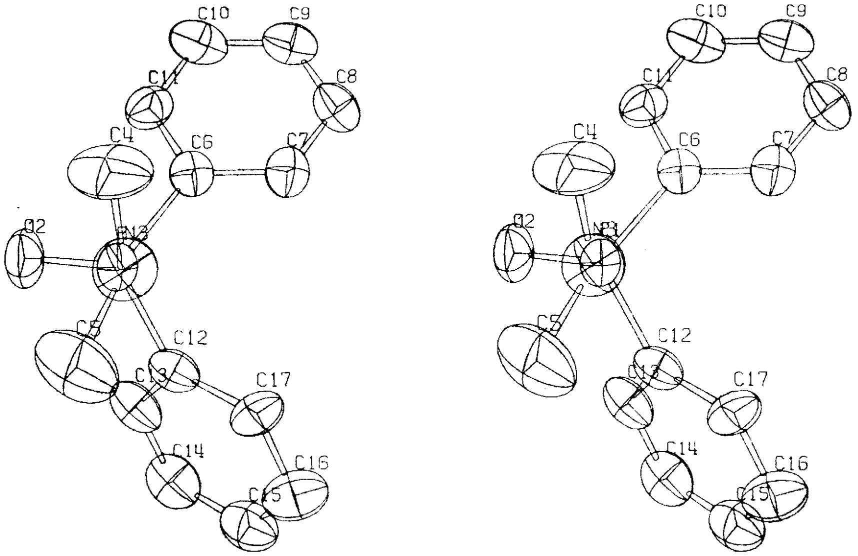

Figure 4 Stereoscopic diagram of the structure of (I) viewed down the *a* axis

Both P–C bond lengths are the same and agree well with the means in other compounds containing four-co-ordinate phosphorus.[21,25-28] That P–C(Ph) bond lengths are usually longer (1.84 Å) in compounds containing three-co-ordinate phosphorus, is due to the increase in the covalent radius of the phosphorus atom. The C–N distances (mean 1.49 Å) are as expected. The angles at phosphorus are close to tetrahedral and vary from 103.8 to 117.5°.

In each of the two phenyl rings, the C–C bond lengths agree well with each other, the mean (1.38 Å) in each phenyl group being shorter than the standard value (1.394 Å) [29] for an aromatic C–C bond. The means of the angles in the phenyl groups are 120.0°, the largest deviations being for those at the carbon atoms directly attached to phosphorus.

The phosphorus, nitrogen, and two methyl carbon atoms are non-planar; the maximum deviations of any atom from this plane is 0.23 Å. The perpendicular distance between phosphorus and the plane formed by N(3), C(4), and C(5) is 0.91 Å.

The equations for the best least-squares planes through the carbon atoms of the phenyl groups are given in Table 3. None of the carbon atoms departs significantly from its associated plane, the maximum deviation being 0.025 Å for C(8).

The dihedral angles between the plane N(3), C(4), and C(5) and the planes formed by the two phenyl groups are 75.7 and 79.9°, and that between the two phenyl groups is 70.3°.

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

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Figure 3 shows the molecular packing projected down the *a* axis. The closest intermolecular contact (3.34 Å) is between O(2) in one molecule and C(8) at $\frac{1}{2} - x, -y, \frac{1}{2} + z$. Phosphorus has no contacts <4.0 Å.

We thank Dr. Paul Haake for supplying the crystals, the National Institute of Health for a grant, and Montana State University for a grant towards computer use.

[5/1220 *Received*, 23*rd June*, 1975]