N-atom configuration is notably pyramidal (Désilets *et al.*, 1987), the amide C—N bond length is significantly longer, 1·381 (7) Å. The correlation between C—N bond length and pyramidal character of the amide N atom was first pointed out by Sweet & Dahl (1970) who went on to relate lengthening of the C—N bond to greater lability of the β-lactam ring system.

The molecular packing (Fig. 2) appears to be determined by van der Waals interaction. The shortest intermolecular approach [2·30 (5) Å] is between the amide O atom and an H atom from the C10 methyl group of the molecule at $(\frac{3}{2}-x, 1-y, \frac{1}{2}+z)$.

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Structure of a Tetraphenyldiphosphine Monoxide Complex with Two Diphenylamine Molecules

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Abstract. Tetraphenyldi-λ^3,λ^5-phosphane oxide–diphenylamine (1/2), $(C_6H_5)_2PP(O)(C_6H_5)_2.2(C_6H_5)_2NH$, $M_r = 724{\cdot}8$, monoclinic, $P2_1/n$, $a = 10{\cdot}587$ (2), $b = 18{\cdot}485$ (6), $c = 10{\cdot}026$ (2) Å, $\beta = 90{\cdot}59$ (3)°, $V = 1962$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}23$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}4$ cm^{-1}, $F(000) = 764$, 294 K. Final $R = 0{\cdot}042$ for 1466 observed reflections. The structure is disordered about an inversion centre (at the centre of the P—P bond); the O atom position is thus only 'half-occupied' and equally disordered in the sites adjacent to the P atoms. The unique diphenylamine molecule takes part in an N—H···O hydrogen-bond attachment to the O atom [N···O 2·690 (6) Å]. Whereas the P—P distance [2·228 (2) Å] is within the typical range of such bonds, the P=O distance [1·345 (6) Å] is remarkably short.

Introduction. As part of a study of the adducts of monoborane species BH_2X (X = H, CN) with aminophosphines, R_2N—PR'_2, we have serendipitously isolated a complex of $Ph_2PP(O)Ph_2$ with two molecules of Ph_2NH. Attempted recrystallization of diphenyl(diphenylamino)phosphineborane under aerobic conditions produced the title compound whose structure was elucidated by X-ray analysis. Confirmation of the presence of Ph_2NH came from the electron-impact mass spectrum of the complex which showed a parent ion at $m/z = 169$ ($^{12}C_{12}{}^1H_{11}N$; base peak) at highest mass. NMR spectroscopic studies also confirmed the presence of Ph_2NH (^1H, ^{13}C) and showed the presence of the Ph_2P—$P(O)Ph_2$ species (^1H, ^{13}C, ^{31}P) [δ ^{31}P at $-21{\cdot}6$ P^{III} and at 39·2 P^V; compare $-21{\cdot}6$ and 36·9 for Ph_2P—$P(O)Ph_2$ (Fluck & Binder, 1967)].

Experimental. Using a small colourless plate crystal, accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $10 < \theta < 14°$. Crystal dimensions $0{\cdot}18 \times 0{\cdot}30 \times 0{\cdot}45$ mm; intensities of

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reflections with indices h −13 to 13, k 0 to 23, l 0 to 12, and with $2 < 2\theta < 54°$ were measured; ω–2θ scans; ω scan width $(0·70 + 0·35\tan\theta)°$, graphite-monochromatized Mo $K\alpha$ radiation; intensities of three reflections measured as standards every 2 h decayed by 14% over the course of the data collection; this was allowed for by appropriate scaling. 4824 reflections measured, 4277 unique, 1466 with $I > 3\sigma(I)$ labelled observed and used in structure solution and refinement; $R_{\rm int} = 0·018$. Data corrected for Lorentz and polarization effects but not for absorption. Space group $P2_1/n$ uniquely from systematic absences $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$. With $Z = 2$ in $P2_1/n$, the molecule must lie about an inversion centre and consequently the O atom bonded to P is disordered about two equivalent sites. The coordinates of the unique P atom were determined from an analysis of the three-dimensional Patterson function and the coordinates of the remaining non-H atoms found *via* the heavy-atom method. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters; the unique O atom was assigned a 0·5 occupancy factor. At an intermediate stage in the refinement, difference maps showed maxima in positions consistent with the expected locations of all H atoms; in the final rounds of calculations the H atoms were positioned on geometrical grounds (C—H, N—H 0·95 Å) and included (as riding atoms) in the structure factor calculations with an overall $B_{\rm iso}$ of 6·0 Å^2. The final cycle of refinement included 245 variable parameters. $R = 0·042$, $wR = 0·071$, goodness-of-fit 1·76, $w = 1/[\sigma^2(F_o) + 0·080(F_o)^2]$. Max. shift/e.s.d. = 0·005; density in final difference map ±0·17 e Å^{-3}; no chemically significant features. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11/73 computer using *SDP-Plus* (B. A. Frenz & Associates Inc., 1983). Atomic coordinates and details of molecular geometry are given in Tables 1 and 2 respectively.* Fig. 1 is a view of the molecule, prepared using *ORTEP*II (Johnson, 1976).

Discussion. The title compound is a hydrogen-bonded complex of one Ph$_2$P—P(O)Ph$_2$ molecule (lying about a crystallographic inversion centre at the mid-point of the P—P bond, and with the O atom consequently disordered over two sites) and two

Table 1. *Positional parameters and their estimated standard deviations*

	x	y	z	B(Å^2)*
P	0·5100 (1)	0·05612 (7)	0·4610 (1)	4·29 (2)
N	0·6510 (3)	0·1695 (2)	0·7612 (3)	5·2 (1)
O	0·5693 (6)	0·1071 (4)	0·5339 (5)	6·1 (2)
C11	0·3496 (4)	0·0772 (2)	0·4078 (4)	3·9 (1)
C12	0·2574 (5)	0·0846 (3)	0·5039 (5)	6·5 (1)
C13	0·1360 (5)	0·1050 (3)	0·4681 (6)	7·4 (1)
C14	0·1052 (4)	0·1193 (3)	0·3409 (5)	6·6 (1)
C15	0·1961 (5)	0·1129 (3)	0·2457 (5)	6·9 (1)
C16	0·3153 (4)	0·0920 (3)	0·2803 (4)	5·5 (1)
C21	0·5958 (4)	0·0415 (2)	0·3079 (4)	3·9 (1)
C22	0·5624 (4)	−0·0111 (2)	0·2141 (4)	4·7 (1)
C23	0·6336 (5)	−0·0217 (3)	0·1033 (4)	5·5 (1)
C24	0·7382 (5)	0·0199 (3)	0·0817 (5)	6·2 (1)
C25	0·7724 (4)	0·0712 (3)	0·1745 (5)	6·6 (1)
C26	0·7022 (4)	0·0814 (3)	0·2854 (4)	5·0 (1)
C31	0·5513 (4)	0·1948 (2)	0·8367 (4)	4·2 (1)
C32	0·5565 (4)	0·2038 (3)	0·9759 (4)	5·2 (1)
C33	0·4513 (5)	0·2274 (3)	1·0408 (5)	6·0 (1)
C34	0·3415 (5)	0·2432 (3)	0·9725 (6)	7·2 (1)
C35	0·3348 (5)	0·2325 (3)	0·8380 (5)	6·1 (1)
C36	0·4389 (4)	0·2096 (2)	0·7729 (4)	5·0 (1)
C41	0·7759 (4)	0·1580 (2)	0·8018 (4)	4·6 (1)
C42	0·8406 (4)	0·0981 (3)	0·7562 (4)	5·1 (1)
C43	0·9638 (4)	0·0869 (3)	0·7905 (5)	6·3 (1)
C44	1·0277 (4)	0·1347 (3)	0·8737 (4)	6·0 (1)
C45	0·9656 (5)	0·1945 (3)	0·9184 (5)	5·9 (1)
C46	0·8414 (4)	0·2071 (3)	0·8835 (5)	5·2 (1)

*Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23}]$.

Table 2. *Interatomic distances* (Å) *and angles* (°)

P—P*	2·228 (2)	C24—C25	1·374 (7)
P—O	1·345 (6)	C25—C26	1·358 (6)
P—C11	1·817 (4)	C31—C32	1·406 (6)
P—C21	1·812 (4)	C31—C36	1·372 (6)
N—C31	1·386 (5)	C32—C33	1·367 (7)
N—C41	1·396 (5)	C33—C34	1·375 (7)
C11—C12	1·385 (6)	C34—C35	1·364 (8)
C11—C16	1·354 (6)	C35—C36	1·355 (7)
C12—C13	1·383 (7)	C41—C42	1·383 (6)
C13—C14	1·340 (8)	C41—C46	1·401 (6)
C14—C15	1·367 (7)	C42—C43	1·362 (6)
C15—C16	1·361 (7)	C43—C44	1·387 (7)
C21—C22	1·396 (6)	C44—C45	1·365 (7)
C21—C26	1·368 (6)	C45—C46	1·377 (7)
C22—C23	1·363 (6)	N···O	2·690 (6)
C23—C24	1·367 (7)	H(N)···O	1·79
P*—P—O	120·5 (3)	C23—C24—C25	119·3 (4)
P*—P—C11	102·2 (1)	C24—C25—C26	120·5 (5)
P*—P—C21	102·0 (1)	C21—C26—C25	121·2 (4)
O—P—C11	116·0 (3)	N—C31—C32	124·0 (4)
O—P—C21	109·3 (3)	N—C31—C36	118·3 (4)
C11—P—C21	105·0 (2)	C32—C31—C36	117·7 (4)
C31—N—C41	128·1 (3)	C31—C32—C33	119·1 (4)
P—C11—C12	118·7 (3)	C32—C33—C34	121·3 (5)
P—C11—C16	124·1 (3)	C33—C34—C35	119·8 (5)
C12—C11—C16	116·9 (4)	C34—C35—C36	119·1 (5)
C11—C12—C13	120·4 (4)	C31—C36—C35	122·9 (4)
C12—C13—C14	121·1 (5)	N—C41—C42	119·8 (4)
C13—C14—C15	118·8 (4)	N—C41—C46	122·2 (4)
C14—C15—C16	120·3 (4)	C42—C41—C46	117·9 (4)
C11—C16—C15	122·5 (4)	C41—C42—C43	121·0 (4)
P—C21—C22	123·3 (3)	C42—C43—C44	121·0 (5)
P—C21—C26	118·7 (3)	C43—C44—C45	118·7 (4)
C22—C21—C26	118·0 (4)	C44—C45—C46	121·0 (4)
C21—C22—C23	120·7 (4)	C41—C46—C45	120·3 (4)
C22—C23—C24	120·3 (4)	N—H(N)···O	157

*The asterisk refers to equivalent position $1-x$, $-y$, $1-z$.

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* Lists of structure factors, thermal parameters, calculated hydrogen coordinates, mean planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52201 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Ph_2NH molecules. The unique Ph_2NH molecule is hydrogen bonded to the O atom [N—H···O 2·690 (6) Å]. This hydrogen-bond distance is only slightly larger than the medium strength PO···HO distance in $Ph_3P(O).Ph_2CHOH$ [2·672 (5) Å; Lariucci, Almeida Santos & Lechat, 1986]; a stronger PO···HO hydrogen bond is found in phosphoric acid hemihydrate [2·55 (1) Å; Mighell, Smith & Brown, 1969]. In the 2:3 adduct triphenylphosphine:*p*-toluenesulfonamide (Ferguson & Glidewell, 1988), much longer N—H···O═P bonds are found [2·946 (3) and 2·957 (3) Å].

The P═O bond length [1·345 (6) Å] is exceptionally short when compared with the equivalent bond lengths in, for example, $Ph_3P(O)$ [1·46 (1) Å; Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970] or the hydrogen-bonded adduct $Ph_3P(O)$.-Ph_2CHOH [1·482 (4) Å; Lariucci *et al.*, 1986] or P_4O_{10} (1·43 Å; Greenwood & Earnshaw, 1984).

The P—P bond length [2·228 (2) Å] is comparable with the values reported in various forms of elemental phosphorus [*e.g.* black, 2·244 (3) Å (Brown & Rundqvist, 1965); violet, 2·178–2·299 (3) Å (Thurn & Krebs, 1969)], in P_2I_4 [2·21 (6) Å; Leung & Waser, 1956], several P^{III}—P^{V} 2,4,6,6-tetraazadiphosphabicyclo[3.3.0]octane derivatives (2·17 to 2·25 Å; Schomburg, 1984) and bis(cyclenephosphorane) [2·264 (2) Å; Richman, Day & Holmes, 1981].

Whereas both P—P—C angles around the unique P atom are reduced from the tetrahedral angle [mean P—P—C 102·1 (1)°], the P—P—O angle has enlarged to 120·5 (3)°, and the O—P—C angles are 109·3 (3) (O—P—C21) and 116·0 (3)° (O—P—C11). In $Ph_3P(O)$ the mean O—P—C angle is close to tetrahedral 111·7 (17)°; the equivalent angles in the $Ph_3P(O).Ph_2CHOH$ adduct show greater variation [106·5 to 112·5 (2), mean 109·7°]. We consider the short P═O bond and the 120·5° P—P—O angle in the title compound to be indicative of the use of a hybridization scheme at P which is closer to sp^2 than the sp^3 schemes which can be considered to operate in $Ph_3P(O)$, the Ph_2CHOH adduct, or P_4O_{10}. This would lead to both a reduction in the P-derived electron density directed towards the phenyl groups and a stronger P═O ($p\pi$—$p\pi$) interaction. This suggestion is supported by the obersvation of longer P—C(Ph) bonds [1·817 (4) and 1·812 (4) Å] in the title compound compared with those in $Ph_3P(O)$ [mean 1·76 (1) Å] and the alcohol adduct [mean 1·785 (10) Å].

The distances and angles in the phenyl rings attached to P or N are as expected. The orientations of the phenyl rings in the molecules are defined by the interplanar angles which a ring makes with the relevant C—P—O plane or C—N—C plane; these values are 112·0 (3)° for ring C11–C16, 2·9 (3)° for C21–C26, 8·2 (3)° for C31–C36, and 40·7 (3)° for C41–C46. Apart from the intermolecular hydrogen bond there are no untoward intermolecular contacts.

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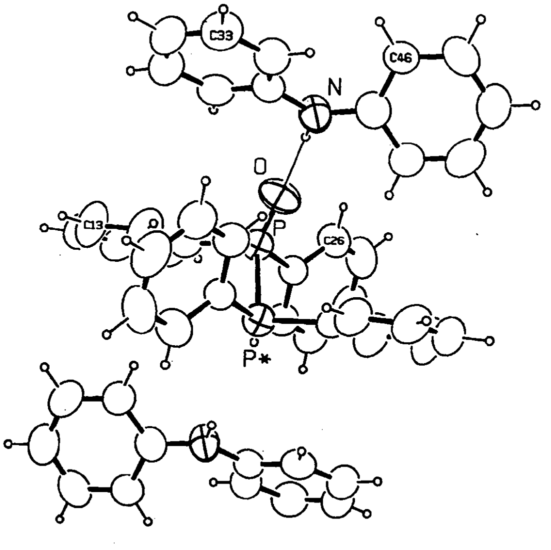

Fig. 1. A view of the PH_2P—$P(O)Ph_2.2(Ph_2NH)$ complex. A crystallographic inversion centre is at the centre of the P—P* bond; for clarity only one of the two disordered O atom sites is shown. The phenyl rings are numbered C*i*1–C*i*6 (*i* = 1–4).

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