N-(Triphenylphosphoranylidene)benzamide

BY I. BAR AND J. BERNSTEIN*

Department of Chemistry, Ben Gurion University of the Negev, Beersheva, Israel

Abstract. $C_{25}H_{20}NOP$, orthorhombic, $Pna2_1$, $a = 9.276 (3)$, $b = 14.937 (6)$, $c = 14.480 (4)$ Å, $D_m = 1.28$, $D_c = 1.26$ Mg m^{-3}. The structure was refined to $R = 0.039$ ($R_w = 0.042$). The molecule contains the first reported structure of the $\geqslant$P=N—C(=O)— group in a non-cyclic environment. The carbonyl is synplanar to the N=P bond.

Introduction. This investigation was undertaken as part of a program to study the properties and structures of phosphoranylidenes (Bittner, 1979). Spectral evidence suggested that a new novel cyclic system (I) might have formed. The structure determination, however, proved the material to be (II), which also contains some chemical features not studied earlier.
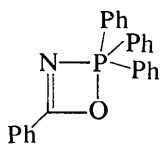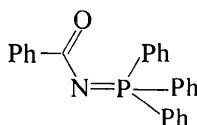
(I)   (II)

1771 reflections were measured with graphite-mono-chromatized Cu $K\alpha$ radiation and the $\theta:2\theta$ scanning technique. After correction for instrumental variations and Lp factors, 39 of these had $F_o < 2.5\sigma(F_o)$ and were considered unobserved.

The space-group ambiguity (*Pna2*$_1$ or *Pnam*) was resolved in the course of the structure solution and refinement. The structure was solved by direct methods. A starting set of four reflections was chosen by *MULTAN* (Germain, Main & Woolfson, 1971) and a multisolution tangent refinement with *SHELX* 76 (Sheldrick, 1976) was carried out. An E map based on the best of 256 solutions led to the recognition of the P and ten additional atoms. The remaining atoms were located by successive tangent refinements with phases calculated from the partial structure (Germain, Main & Woolfson, 1971). Refinement of this model on positional parameters and anisotropic temperature factors

converged at $R = 0.24$. At this stage many geometric features of the molecule were abnormal and the temperature factors of almost all the atoms were unusually high. Successive difference maps based on various parts of the molecule were used to locate a number of falsely placed atoms, after which refinement proceeded smoothly. All H atoms were located from a difference synthesis and refined isotropically together with anisotropic temperature factors for the heavy atoms. Refinement converged to $R = 0.039$, $R_w = 0.042$ |$R = 0.040$ including reflections $<2.5\sigma(F_o)$|.

Final coordinates are given in Table 1.†

Discussion. The atomic numbering is given in Fig. 1. Bond lengths and angles are in Table 2. The geometric features of all four phenyl rings are normal, although there are some wide variations in bond lengths (up to 7σ) involving C(19) to C(24). However, this variation is not systematic and we attach no special significance to it.

---

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34877 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
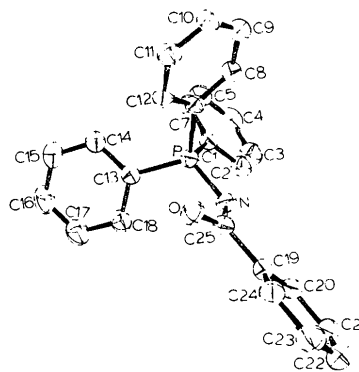

Fig. 1. Projection of the molecule with numbering of the atoms. H atoms have been omitted for clarity. Thermal ellipsoids are plotted at the 50% probability level.

---

* To whom correspondence should be addressed.

Table 1. *Final positional parameters for non-hydrogen* (×10⁴) *and hydrogen* (×10³) *atoms*

	x	y	z		x	y	z
P	25 (1)	−344 (0)	5167 (1)	C(22)	−5288 (6)	−34 (5)	8199 (4)
N	−1128 (3)	−375 (2)	6012 (2)	C(23)	−5562 (6)	521 (4)	7446 (4)
O	−2793 (3)	426 (2)	5166 (2)	C(24)	−4636 (5)	539 (3)	6707 (3)
C(1)	1620 (4)	−882 (2)	5635 (3)	C(25)	−2412 (2)	37 (2)	5886 (2)
C(2)	1590 (6)	−1283 (3)	6510 (4)	H(2)	68 (6)	−117 (4)	690 (4)
C(3)	2796 (6)	−1729 (4)	6836 (4)	H(3)	271 (5)	−211 (3)	754 (4)
C(4)	4037 (7)	−1766 (4)	6311 (4)	H(4)	493 (7)	−196 (4)	651 (5)
C(5)	4079 (6)	−1370 (4)	5445 (5)	H(5)	489 (5)	−139 (3)	503 (4)
C(6)	2870 (5)	−924 (3)	5114 (4)	H(6)	279 (6)	−57 (3)	442 (4)
C(7)	569 (4)	770 (2)	4821 (3)	H(8)	228 (5)	91 (3)	571 (4)
C(8)	1638 (5)	1209 (3)	5316 (3)	H(9)	294 (7)	228 (4)	566 (5)
C(9)	1952 (5)	2101 (3)	5116 (4)	H(10)	157 (6)	313 (4)	423 (4)
C(10)	1230 (6)	2539 (3)	4417 (4)	H(11)	−52 (6)	242 (3)	340 (3)
C(11)	205 (5)	2092 (3)	3894 (4)	H(12)	−94 (5)	88 (3)	381 (3)
C(12)	−137 (5)	1211 (3)	4103 (3)	H(14)	82 (5)	−50 (3)	320 (3)
C(13)	−483 (4)	−979 (2)	4179 (3)	H(15)	40 (6)	−133 (3)	192 (4)
C(14)	188 (5)	−887 (3)	3327 (3)	H(16)	−144 (6)	−247 (4)	224 (4)
C(15)	−126 (6)	−1454 (3)	2595 (3)	H(17)	−279 (7)	−247 (4)	363 (4)
C(16)	−1154 (7)	−2114 (3)	2709 (4)	H(18)	−204 (6)	−166 (3)	491 (4)
C(17)	−1864 (8)	−2193 (3)	3538 (5)	H(20)	−210 (4)	−91 (2)	744 (3)
C(18)	−1557 (5)	−1631 (3)	4278 (3)	H(21)	−387 (4)	−95 (3)	869 (3)
C(19)	−3421 (4)	11 (2)	6699 (3)	H(22)	526 (4)	95 (3)	621 (3)
C(20)	−3137 (5)	−550 (3)	7460 (3)	H(23)	−594 (4)	4 (3)	866 (3)
C(21)	−4098 (6)	−557 (4)	8198 (3)	H(24)	623 (4)	87 (3)	757 (3)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

|			
C(1)–C(2)	1·403 (7)	C(15)–C(16)	1·381 (8)
C(1)–C(6)	1·384 (6)	C(16)–C(17)	1·375 (9)
C(2)–C(3)	1·385 (8)	C(17)–C(18)	1·389 (8)
C(3)–C(4)	1·381 (9)	C(19)–C(20)	1·410 (5)
C(4)–C(5)	1·387 (9)	C(19)–C(24)	1·377 (6)
C(5)–C(6)	1·389 (7)	C(20)–C(21)	1·391 (7)
C(7)–C(8)	1·389 (6)	C(21)–C(22)	1·353 (8)
C(7)–C(12)	1·394 (6)	C(22)–C(23)	1·393 (8)
C(8)–C(9)	1·393 (6)	C(23)–C(24)	1·373 (8)
C(9)–C(10)	1·379 (7)	C(1)–P	1·815 (4)
C(10)–C(11)	1·387 (7)	C(7)–P	1·810 (4)
C(11)–C(12)	1·388 (6)	C(13)–P	1·779 (4)
C(13)–C(14)	1·388 (6)	C(19)–C(25)	1·504 (4)
C(13)–C(18)	1·401 (6)	C(25)–O	1·245 (5)
C(14)–C(15)	1·388 (7)	P–N	1·626 (3)
		N–C(25)	1·353 (5)

Mean C–H = 1·01 ± 0·11 Å.

C(2)–C(1)–C(6)	119·3 (4)	C(14)–C(13)–C(18)	118·6 (4)
C(1)–C(2)–C(3)	119·8 (5)	C(13)–C(14)–C(15)	121·6 (4)
C(2)–C(3)–C(4)	120·4 (5)	C(14)–C(15)–C(16)	119·3 (5)
C(3)–C(4)–C(5)	120·3 (5)	C(15)–C(16)–C(17)	119·7 (5)
C(4)–C(5)–C(6)	119·6 (5)	C(16)–C(17)–C(18)	121·6 (6)
C(1)–C(6)–C(5)	120·7 (5)	C(13)–C(18)–C(17)	119·2 (5)
C(8)–C(7)–C(12)	119·9 (4)	C(20)–C(19)–C(24)	119·2 (4)
C(7)–C(8)–C(9)	119·6 (4)	C(19)–C(20)–C(21)	119·0 (4)
C(8)–C(9)–C(10)	120·3 (4)	C(20)–C(21)–C(22)	121·3 (5)
C(9)–C(10)–C(11)	120·4 (4)	C(21)–C(22)–C(23)	119·5 (5)
C(10)–C(11)–C(12)	119·6 (4)	C(22)–C(23)–C(24)	120·5 (5)
C(7)–C(12)–C(11)	120·2 (4)	C(19)–C(24)–C(23)	120·5 (4)
C(1)–P–C(7)	106·4 (2)	C(19)–C(25)–O	119·4 (3)
C(1)–P–C(13)	106·3 (2)	C(6)–C(1)–P	120·0 (3)
C(1)–P–N	104·1 (2)	C(2)–C(1)–P	120·7 (3)
C(7)–P–N	114·7 (2)	C(18)–C(13)–P	118·5 (3)
C(13)–P–N	114·5 (2)	C(14)–C(13)–P	122·9 (3)
C(7)–P–(13)	109·9 (2)	C(8)–C(7)–P	119·4 (3)
N–C(25)–(19)	115·5 (3)	C(12)–C(7)–P	120·6 (3)
N–C(25)–O	125·1 (3)	C(20)–C(19)–C(25)	120·8 (3)
P–N–C(25)	117·8 (3)	C(24)–C(19)–C(25)	120·1 (3)

Mean C–C–H = 119·7 ± 6·2°.

The prominent feature in this structure is the presence of the $\geqslant$P=N—C(=O)— group, hitherto unreported except where one or more of the atoms is part of a cyclic system (III–VI).* In (V) and (VI) the group is constrained to an essentially antiplanar conformation about the C—N bond, while in the

(III)

(IV)

(V)

(VI)
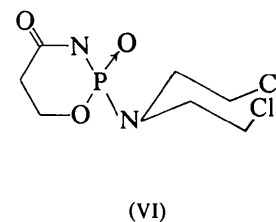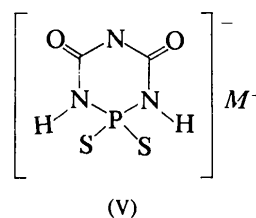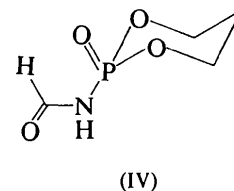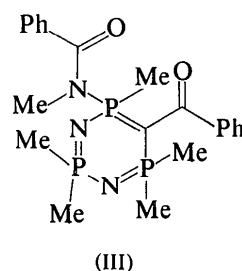
(*a*) $M^+ = NH_4^+$
(*b*) $M^+ = Tl^+$
(*c*) $M^+ = NH_4^+$, urea

---

* An additional compound containing this atom connectivity has been reported by Schmidpeter, Luber, Schomburg & Sheldrick (1976). However, the P, C and N atoms are constrained to a four-membered ring and the compound is not suitable for comparison with the others given here.

Table 3. *Geometric features of* P—N—C—O (Å *and* deg)

	(II)	(III)	(IV)	(Va)	(Vb)	(Vc)	(VI)
P—N	1·626	1·742	1·702	1·700, 1·697	1·697, 1·692	1·692, 1·692	1·628
N—C	1·353	1·369	1·373	1·352, 1·349	1·349, 1·344	1·358, 1·356	1·385
C—O	1·245	1·242	1·243	1·231, 1·225	1·231, 1·221	1·223, 1·228	1·235
P—N—C	117·8	116·0	124·8	126·7, 125·6	126·9, 125·0	125·8, 125·7	127·1
N—C—O	125·1	119·5	120·8	123·7, 123·7	123·2, 123·8	123·3, 122·6	119·3
N—C—X*	115·5	121·5	—	116·4, 116·5	116·8, 116·2	116·8, 116·2	118·1
O—C—X*	119·4	119·0	—				122·6
Reference	(a)	(b)	(c)	(d)	(d)	(e)	(f)

References: (a) this study; (b) Oakley, Paddock, Rettig & Trotter (1977); (c) Cameron & Karolak-Wojciechowska (1977); (d) Aurivillius & Stålhandske (1975); (e) Andersson & Stålhandske (1976); (f) Camerman & Camerman (1973).

* For (II) and (III) X is C(phenyl); for (IV) X is H; for (V) X is N; for (VI) X is —CH₂—.

Table 4. *Torsion angles* (°) *and their e.s.d.'s*

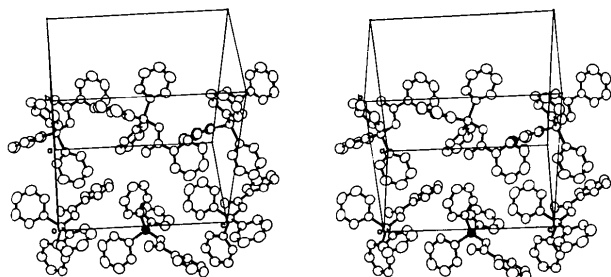|			
P—N—C(25)—O	1·3 (5)	C(14)—C(13)—P—N	165·9 (3)
C(6)—C(1)—P—N	−175·9 (3)	C(18)—C(13)—P—N	−17·4 (4)
C(2)—C(1)—P—N	6·1 (4)	C(20)—C(19)—C(25)—N	−11·5 (5)
C(8)—C(7)—P—N	82·0 (4)	C(24)—C(19)—C(25)—N	168·4 (4)
C(12)—C(7)—P—N	−93·9 (4)		

Fig. 2. Stereoplot of the structure. The reference molecule is denoted by a blackened P atom.

present compound and (III) and (IV) other conformations are possible. In this structure the group adopts an essentially synplanar conformation (Fig. 1) with a torsion angle of 1·3° while in (III) and (IV) the angles are −2·6 and 0·3° respectively.

Bond lengths and angles in this group of atoms are compared in Table 3. The P—N length is compatible with those found for P=N double bonds (Dougill, 1961; Mani, Ahmed & Barnes, 1965), while other bond lengths are essentially constant throughout the group. The P—N—C angle is comparable to that found in (III), but significantly different from the same angle in (IV); the latter increase may be due to steric effects not present in the first two compounds.

Torsion angles about various single bonds are summarized in Table 4 to give relative twists of the phenyl rings with respect to the central planar phosphoranylidene amide system.

The packing is shown in Fig. 2. There are no unusually short contacts and the structure is dominated by van der Waals forces.

References

Andersson, J.-E. & Stålhandske, C. (1976). *Acta Cryst.* B32, 587–590.

Aurivillius, B. & Stålhandske, C. (1975). *Acta Chem. Scand. Ser. A,* 29, 717–724.

Bittner, S. (1979). Private communication.

Camerman, N. & Camerman, A. (1973). *J. Am. Chem. Soc.* 95, 5038–5041.

Cameron, T. S. & Karolak-Wojciechowska, J. (1977). *Acta Cryst.* B33, 2342–2344.

Dougill, M. W. (1961). *J. Chem. Soc.* pp. 5471–5479.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A27, 368–376.

Mani, N. V., Ahmed, F. R. & Barnes, W. H. (1965). *Acta Cryst.* 19, 693–699.

Oakley, R. T., Paddock, N. L., Rettig, S. J. & Trotter, J. (1977). *Can. J. Chem.* 55, 2534–2539.

Schmidpeter, A., Luber, J., Schomburg, D. & Sheldrick, W. S. (1976). *Chem. Ber.* 109, 3581–3587.

Sheldrick, G. M. (1976). *SHELX* 76. A program for crystal structure determination. Univ. of Cambridge, England.