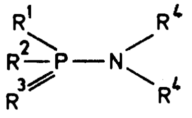
Crystal and Molecular Structure of *NN*-Di-isopropyl-*P*-phenylphosphonamidic Chloride, $PPh(Cl)(NPr^i_2)O$

By **Keith Paxton** and **Thomas A. Hamor,*** Department of Chemistry, University of Birmingham, Birmingham B15 2TT

Crystals of the title compound are monoclinic, with unit-cell dimensions $a = 7.463(5)$, $b = 13.72(1)$, $c = 13.90(1)$ Å, and $\beta = 100.35(5)°$, space group $P2_1/c$, and $Z = 4$. The structure has been determined from three-dimensional counter data and refined to R 0.045 for 1 634 observed amplitudes. The P–N bond length [1.614(2) Å] indicates a considerable degree of π bonding, and the conformation about this bond is consistent with an n–σ^* type of interaction. Comparison with structural data on related molecules shows that the π bonding is enhanced by electronegative substituents on the phosphorus atom. The two Pr^i groups are orientated differently with respect to the P–N bond. These results are discussed in relation to n.m.r. spectroscopic data which indicate that the Pr^i groups are non-equivalent at low temperature.

AMINOPHOSPHORUS compounds have interesting structural and stereochemical features which have been extensively investigated by n.m.r. spectroscopy, *X*-ray crystallography, and molecular-orbital calculations.[1] Attention has been focused on the ground-state conformation around the phosphorus–nitrogen bond, the importance of π bonding, the degree of planarity at nitrogen, and the molecular stereodynamics. Additionally, in di-isopropylamino-derivatives the possibility of a 'geared' interaction [2] between adjacent isopropyl groups has recently been considered.

Dynamic n.m.r. studies [3,4] of *NN*-di-isopropyl-*P*-phenylphosphonamidic chloride (1) and of the related *NN*-di-isopropyl-*P*-methyl-, -*P*-phenyl-, and -*P*-t-butylphosphonamidothioic chlorides have shown that the *N*-isopropyl groups are non-equivalent at low temperature. The barriers to isopropyl site exchange were found to lie in the range 39.3—52.7 kJ mol^{-1} and were considered to refer, most probably, to P–N bond rotation. The size of the barrier is such that it can be accounted for by normal steric interactions between vicinal substituents, although directional π bonding (either p–d or n–σ^*) may also contribute.[4] Alternatively, a barrier to N–C bond rotation as a result of steric interactions between the isopropyl groups (gear effect [2]) was considered [4] to be a possibility.



	R^1	R^2	R^3	R^4
(1)	Cl	Ph	O	Pr^i
(2)	F	F	B_4H_8	Me
(3)	Ph	Ph	O	Me

In order to provide a near ground-state model as a basis for the interpretation of the n.m.r. data, an *X*-ray crystallographic analysis of compound (1) was undertaken.

EXPERIMENTAL

Crystallographic Measurements.—Crystals of (1) suitable for *X*-ray analysis were kindly supplied by Dr. W. B. Jennings. A crystal of dimensions 0.4 × 0.25 × 0.15 mm was mounted about the direction of elongation (a) and, after initial examination by photographic methods, final cell dimensions and the intensity data were measured with a computer-controlled Stoe two-circle diffractometer, using Mo-K_α radiation. Reflections were scanned within the range $0.1 < (\sin\theta)/\lambda < 0.65$, and of these 1 634 having intensities greater than $2.5\sigma(I)$ were considered to be observed and were used in the structure analysis. The ω-scan technique was employed, and 120 counts of 1 s at intervals of 0.01° were taken for each reflection on layers 0—1. For reflections on layers 2—8 the scan range was calculated by use of the expression $[A + (B \sin\mu/\tan\theta')]°$ with $A = 1.0$ and $B = 0.5$, μ being the equi-inclination angle and $2\theta'$ the azimuth angle. Backgrounds were measured for 25 s at each end of the scan. Three standard reflections were re-measured after each layer of data collection in order to monitor the stability of the system. There was no significant variation in their intensities during the course of the data collection. Intensities were converted into structure amplitudes in the usual way but absorption corrections were not applied.

Crystal data. $C_{12}H_{19}ClNOP$, $M = 259.7$, Monoclinic, $a = 7.463(5)$, $b = 13.72(1)$, $c = 13.90(1)$ Å, $\beta = 100.35(5)°$, $U = 1\,400.1$ Å^3, $Z = 4$, $D_c = 1.232$ g cm^{-3}, $F(000) = 552$. Systematic absences: $0k0$, k odd; $h0l$, l odd. Space group $P2_1/c$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 3.2 cm^{-1}.

Structure determination. The chlorine atom was located from a three-dimensional Patterson synthesis, and this served as a starting point for application of the heavy-atom phase-determining method. The first electron-density map was used only to locate the phosphorus atom. The second electron-density map which was phased on both the heavy atoms revealed the positions of the remaining atoms of the molecule (apart from H atoms). Refinement of the atomic parameters was carried out by the method of least squares. Initially isotropic thermal parameters were

---

[1] J. Emsley and D. Hall, 'The Chemistry of Phosphorus,' Harper and Row, London, 1976 and refs. therein.

[2] A. H. Cowley, R. W. Braun, and J. W. Gilje, *J. Amer. Chem. Soc.*, 1975, **97**, 434.

[3] W. B. Jennings, *Chem. Comm.*, 1971, **867**.

[4] J. Burdon, J. C. Hotchkiss, and W. B. Jennings, *J.C.S. Perkin II*, 1976, 1052.

refined and R was reduced to 0.190. Further refinement with anisotropic temperature factors reduced R to 0.095. At this stage the hydrogen atoms were located from a difference synthesis and included in the least-squares calculations with isotropic temperature factors. The refinement was terminated when all the calculated shifts were $< 0.1\sigma$ and R was 0.045 for the 1 634 observed structure amplitudes. Final atomic co-ordinates * and estimated standard deviations are listed in Table 1.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
C(1)	2 955(4)	8 752(2)	1 967(2)
C(2)	3 525(5)	9 687(3)	1 793(3)
C(3)	4 344(5)	10 265(3)	2 573(3)
C(4)	4 601(5)	9 922(3)	3 508(3)
C(5)	4 043(5)	8 997(3)	3 686(3)
C(6)	3 222(5)	8 414(3)	2 927(3)
C(7)	−1 251(5)	8 401(3)	1 390(3)
C(8)	−2 798(6)	8 508(4)	524(4)
C(9)	−1 905(8)	8 268(5)	2 346(4)
C(10)	−758(5)	6 603(2)	1 086(2)
C(11)	−889(8)	6 266(4)	34(3)
C(12)	230(7)	5 884(3)	1 825(4)
N	24(3)	7 602(2)	1 239(2)
O	3 212(3)	7 044(2)	952(2)
P	2 028(1)	7 877(1)	1 040(1)
Cl	1 694(1)	8 674(1)	−243(1)
H(2)	3 385(40)	9 917(22)	1 167(23)
H(3)	4 675(44)	10 908(27)	2 408(25)
H(4)	5 227(46)	10 322(27)	4 078(27)
H(5)	4 187(57)	8 757(29)	4 320(30)
H(6)	2 844(47)	7 822(27)	3 058(26)
H(7)	−563(37)	8 959(22)	1 422(20)
H(8A)	−2 348(52)	8 610(27)	−69(29)
H(8B)	−3 439(51)	9 113(29)	625(26)
H(8C)	−3 506(50)	7 921(30)	495(26)
H(9A)	−960(67)	8 168(33)	2 865(34)
H(9B)	−2 591(57)	8 748(32)	2 460(28)
H(9C)	−2 618(57)	7 651(33)	2 344(30)
H(10)	−1 924(43)	6 691(21)	1 215(20)
H(11A)	−1 435(48)	5 691(30)	−36(25)
H(11B)	308(71)	6 156(33)	−89(31)
H(11C)	−1 531(57)	6 781(33)	−403(30)
H(12A)	−391(48)	5 237(31)	1 736(25)
H(12B)	1 448(63)	5 787(28)	1 708(28)
H(12C)	89(78)	6 066(41)	2 480(43)

The weighting scheme used in the least-squares calculations was $w = 1/[\sigma^2(F) + 0.000\,03\,F^2]$ where $\sigma(F)$ is the standard deviation in the observed amplitudes derived from counting statistics. Computations were carried out on the Birmingham University 1906A computer with the SHELX programs,[5] together with local ancillary programs.

RESULTS AND DISCUSSION

A stereoscopic view of the molecule as seen in the direction of the P–N bond is shown in Figure 1. Bond lengths, bond angles, and selected torsion angles are in Table 2, and the results of mean-plane calculations are in Table 3. The packing arrangement is illustrated in Figure 2. There are no intermolecular contact distances shorter than the sum of the van der Waals radii of the atoms concerned.

The phenyl ring is planar to within the limits of experimental accuracy and the aromatic bond lengths range from 1.363 to 1.393 Å, mean 1.381 Å, slightly shorter than the accepted value of 1.394 Å.[6] The P–C(aromatic) length (1.805 Å) is similar to the corresponding lengths in NN-dimethyl-PP-diphenylphosphinic

TABLE 2

Molecular dimensions with standard deviations in parentheses

(*a*) Bond lengths (Å)

C(1)–C(2)	1.386(5)	C(10)–C(11)	1.519(5)
C(2)–C(3)	1.393(5)	C(10)–C(12)	1.516(5)
C(3)–C(4)	1.363(5)	N–C(7)	1.490(4)
C(4)–C(5)	1.372(5)	N–C(10)	1.490(4)
C(5)–C(6)	1.377(5)	P–C(1)	1.805(3)
C(1)–C(6)	1.393(4)	P–N	1.614(2)
C(7)–C(8)	1.518(5)	P–O	1.463(2)
C(7)–C(9)	1.506(6)	P–Cl	2.069(1)
C(2)–H(2)	0.91(3)	C(9)–H(9B)	0.87(4)
C(3)–H(3)	0.95(4)	C(9)–H(9C)	1.00(5)
C(4)–H(4)	1.01(4)	C(10)–H(10)	0.93(3)
C(5)–H(5)	0.93(4)	C(11)–H(11A)	0.88(4)
C(6)–H(6)	0.89(4)	C(11)–H(11B)	0.95(5)
C(7)–H(7)	0.92(3)	C(11)–H(11C)	1.00(5)
C(8)–H(8A)	0.96(4)	C(12)–H(12A)	1.00(4)
C(8)–H(8B)	0.98(4)	C(12)–H(12B)	0.96(5)
C(8)–H(8C)	0.96(4)	C(12)–H(12C)	0.97(6)
C(9)–H(9A)	0.92(5)		

(*b*) Bond angles (°) for the heavier atoms

C(2)–C(1)–C(6)	118.7(3)	N–C(10)–C(12)	111.8(3)
P–C(1)–C(2)	125.6(3)	C(11)–C(10)–C(12)	113.1(4)
P–C(1)–C(6)	115.6(3)	P–N–C(7)	119.1(2)
C(1)–C(2)–C(3)	119.8(4)	P–N–C(10)	122.8(2)
C(2)–C(3)–C(4)	120.8(4)	C(7)–N–C(10)	116.9(2)
C(3)–C(4)–C(5)	119.8(4)	N–P–C(1)	106.3(1)
C(4)–C(5)–C(6)	120.5(4)	N–P–O	115.1(1)
C(5)–C(6)–C(1)	120.5(4)	N–P–Cl	107.4(1)
N–C(7) C(8)	111.9(3)	O–P–C(1)	114.8(1)
N–C(7)–C(9)	110.6(3)	O–P–Cl	108.8(1)
C(8)–C(7)–C(9)	112.9(4)	Cl–P–C(1)	103.6(1)
N–C(10)–C(11)	111.9(3)		

(*c*) Selected torsion angles (°)

C(1)–P–N–C(7)	48.6	P–N–C(10)–C(11)	−59.6
C(1)–P–N–C(10)	−143.9	P–N–C(10)–C(12)	68.5
O–P–N–C(7)	177.0	C(2)–C(1)–P–N	−121.3
O–P–N–C(10)	−15.5	C(2)–C(1)–P–O	110.2
Cl–P–N–C(7)	−61.7	C(2)–C(1)–P–Cl	−8.2
Cl–P–N–C(10)	105.8	C(6)–C(1)–P–N	63.5
P–N–C(7)–C(8)	108.4	C(6)–C(1)–P–O	−65.0
P–N–C(7)–C(9)	−124.7	C(6)–C(1)–P–Cl	176.6

TABLE 3

Deviations (Å) of atoms from least-squares planes; x, y, and z are fractional co-ordinates relative to the cell axes

Plane(1): C(1)—C(6)

$$6.931x - 4.902y - 3.681z = -2.967$$

[C(1) 0.000, C(2) −0.001, C(3) 0.002, C(4) −0.001, C(5) −0.001, C(6) 0.002, P −0.128, N 1.199, O −1.389, Cl 0.022]

Plane (2): C(7), C(10), P

$$-1.087x + 1.903y - 13.026z = -0.076$$

[N 0.094]

---

* Lists of anisotropic thermal parameters and observed and calculated structure factors are available as Supplementary Publication No. SUP 22211 (12 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[5] G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge.

[6] *Special Publ.*, The Chemical Society, London, 1965, No. 18.

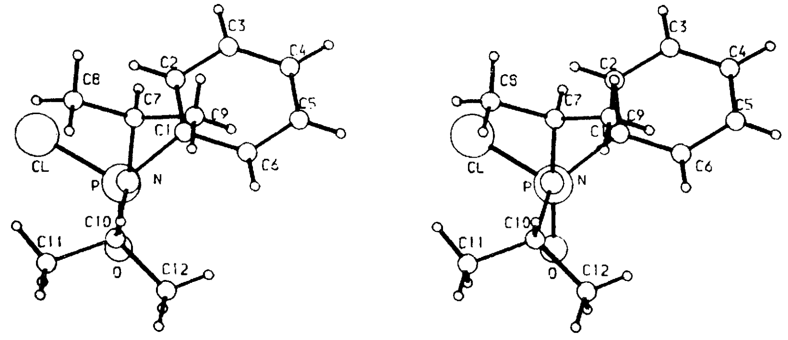


FIGURE 1 Stereoscopic view of the molecule and atom labelling

amide (1.794 and 1.784 Å),[7] triphenylphosphoranylideneketene (1.793—1.815, mean 1.805 Å),[8] and 1,2,3,4-tetraphenyl-2,4-dithiocyclodiphosphazane (1.794 and 1.797 Å).[9] The P–O bond (1.463 Å) is also similar in length to the corresponding bonds in PPh$_2$(NMe$_2$)O,[7] ifosfamide [10] (4; R = H), trofosfamide [11] (4; R = $\mathrm{CH_2CH_2CP}$), and 2,*trans*-4-dichloro-2,4-dioxo-1,3-di-t-butylcyclodiphosphazane [12] (1.482, 1.475, 1.468, and 1.448 Å respectively). Comparison of the P–Cl bond length (2.069 Å) with those in other compounds containing monochloro-substituted phosphorus atoms, however, indicates that it is slightly greater. Thus in 2,*cis*-4,*trans*-6,*trans*-8-tetrachloro-2,4,6,8-tetrakis(dimethylamino)cyclotetraphosphazatetraene,[13] 2,4,4,*trans*-6,8,8-hexachloro-2,6-bis(dimethylamino)cyclotetraphosphazatetraene,[14] *gem*-2,2,4-trichloro-4,6,6-tris(dimethylamino)cyclotriphosphazatriene,[15] and the aforementioned cyclodiphosphazane [12] the P–Cl lengths are 2.035—2.052 (mean 2.043), 2.054, 2.051, and 2.007 Å, respectively. On the other hand, the P–N bond length (1.614 Å) is somewhat shorter than most of the comparable exocyclic P–N bonds in these compounds (1.613—1.665 Å).

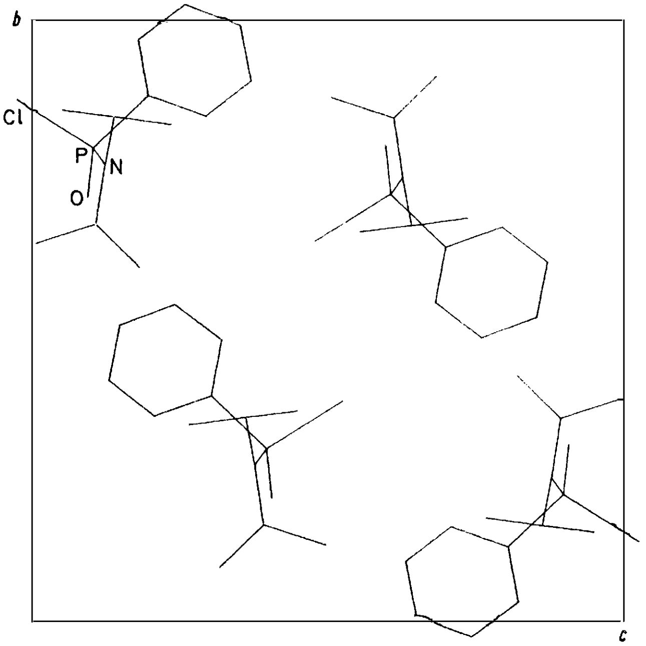
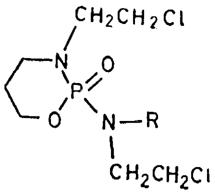


FIGURE 2 The contents of the unit cell projected along *a* *



(4)

The length of the P–N bond is of particular interest in relation to the n.m.r. studies of Jennings and his co-workers.[3,4] The accepted value for the P–N single bond length, as measured [16] in the $[\mathrm{H_3NPO_3}]$ ion, is 1.763 Å (1.769 Å corrected for thermal motion) so that the P–N bond here is shorter by *ca.* 0.15 Å. Bullen and Tucker,[13] in their description of the structure of a phosphazene $\mathrm{N_4P_4Cl_4(NMe_2)_4}$, noted that in non-geminal $\geqslant$PCl(NMe$_2$) groups the exocyclic P–N bond is shorter and the P–Cl bond longer than in geminal $\geqslant$P(NMe$_2$)$_2$ or $\geqslant$PCl$_2$ groups. It was suggested that this was due to the effect of a co-operative electron withdrawal by Cl and electron donation by N. Extrapolation of this argument leads to the conclusion that in systems PR^{1}R^{2}R^3(NR$^4_2$) the greater the electronegativities of R^1, R^2, and R^3 the shorter will be the P–N bond. Our analysis provides structural data to support this. Thus the P–N bond length in (dimethylamino)difluorophosphine–tetraborane(8) [compound (2)] is 1.593 Å,[17] in PPh$_2$(NMe$_2$)O

---

[7] Mazhar-ul-Haque and C. N. Caughlan, *J.C.S. Perkin II*, 1976, 1101.

[8] J. J. Daly and P. J. Wheatley, *J. Chem. Soc.* (*A*), 1966, 1703.

[9] M. B. Peterson and A. J. Wagner, *J.C.S. Dalton*, 1973, 106.

[10] A. Perales and S. Garcia-Blanco, *Acta Cryst.*, 1977, **B33**, 1935.

[11] A. Perales and S. Garcia-Blanco, *Acta Cryst.*, 1977, **B33**, 1939.

[12] L. Manojlović-Muir and K. W. Muir, *J.C.S. Dalton*, 1974, 2395.

[13] G. J. Bullen and P. A. Tucker, *J.C.S. Dalton*, 1972, 2437.

[14] G. J. Bullen and P. E. Dann, *J.C.S. Dalton*, 1973, 1453.

[15] F. R. Ahmed and D. R. Pollard, *Acta Cryst.*, 1972, **B28**, 513.

[16] D. W. J. Cruickshank, *Acta Cryst.*, 1964, **17**, 671.

[17] M. D. La Prade and C. E. Nordman, *Inorg. Chem.*, 1969, **8**, 1669.

[compound (3)] it is 1.681 Å,[7] and in the title compound (1) with phosphorus substituents of intermediate electronegativity it is 1.614 Å. The geometry of the bonds to the nitrogen atom also parallels this sequence. In compound (2) the nitrogen atom and the three atoms linked to it are coplanar to within the limits of the experimental accuracy with the sum of the angles at N being 359.8°; in (3) the geometry of the nitrogen atom is intermediate between pyramidal and planar with the sum of the angles at N being 348.9°. In compound (1) the bonds to the nitrogen atom deviate slightly from planarity, the deviation of N from the plane of C(7), C(10), and P being 0.09 Å and the sum of the angles at nitrogen 358.8°.

The shortness of the P–N bond and the near-planarity of the bonds to the nitrogen atom are indicative of a considerable degree of π bonding which increases with increasing electronegativity of the substituents on the phosphorus atom. The nature of the π interaction in P–N (and S–N) bonds has been discussed previously,[4,18–20] generally in terms of overlap between the nitrogen lone-pair orbital with vacant *d* orbitals of the S or P atom. As a possible alternative to the p_π–d_π type of bonding, it has recently been suggested [4,20,21] that the π bonding may be due to overlap of the nitrogen lone pair with an antibonding *sp*-hybrid orbital of the P (or S) atom which is *anti* to the most electronegative substituent on the second-row element. For maximum overlap to occur in this type of bonding (n–σ^*) the conformation about the P–N (or S–N) bond must be such that the plane of atoms X, P (or S), and N (where X is the most electronegative group linked to P or S) bisects the C–N–C angle. In compound (1) the torsion angles Cl–P–N–C(7) and Cl–P–N–C(10) are −62 and 106° so that this condition holds only approximately. Such a deviation of *ca.* 22° from the ideal conformation would, however, still permit a considerable contribution from this type of bonding. The observed conformation appears to preclude any interaction between the nitrogen lone pair and the P–O bond. The observation that long P–Cl bonds tend to be associated with short P–N bonds is consistent with the overall picture of π interaction in the P–N bond which is enhanced by electronegative substituents on the phosphorus atom.

The two isopropyl groups are arranged quite differently with respect to the P–N bond. Thus methyl carbon atoms C(8) and C(9) are oriented $\pm$ anticlinal with respect to the phosphorus atom, whereas C(11) and C(12) are oriented $\mp$ synclinal. The mutual arrangement of the two $\mathrm{Pr^i}$ groups corresponds closely to the 'geared' or 'cogwheel' type of structure which has been suggested as a possible cause of the non-equivalence of these groups in the low-temperature n.m.r. spectrum.[4] A similar arrangement of $\mathrm{Pr^i}$ groups occurs in the crystal structure [22] of bis(*NN*-di-isopropyldithiocarbamato)-nickel(II), and here also a low-temperature n.m.r. study [23] indicates non-equivalence of the isopropyl groups.

The non-equivalence of the isopropyl groups may therefore arise from this effect or from a barrier to P–N bond rotation, or both. The near-planarity of the nitrogen atom indicates that the nitrogen inversion energy must be very low and would therefore be a negligible contributor to the barrier to isopropyl site exchange.

We thank Dr. W. B. Jennings for suggesting this problem and helpful discussions.

[7/1413 *Received, 2nd August*, 1977]

---

[18] D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 1962, 4118; N. L. Paddock, *Quart. Rev.*, 1964, **18**, 168.

[19] A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 5206.

[20] M. Raban and F. B. Jones, *J. Amer. Chem. Soc.*, 1971, **93**, 2692.

[21] M. Raban and D. Kost, *J. Amer. Chem. Soc.*, 1972, **94**, 3234.

[22] P. W. G. Newman and A. H. White, *J.C.S. Dalton*, 1972, 2239.

[23] R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn, and A. H. White, *Inorg. Chem.*, 1972, **11**, 2435.