

Effect of the Protonation and of the *ortho* Substitution on the Structure of Aryliminophosphoranes

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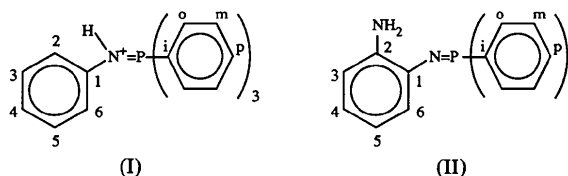
Abstract. Phenyltriphenylphosphoranylideneammonium tetrafluorophosphate, (I), $C_{24}H_{21}NP^+ \cdot BF_4^-$, $M_r = 441.21$, monoclinic, Pn , $a = 24.6077$ (18), $b = 9.0071$ (3), $c = 10.0690$ (4) Å, $\beta = 100.824$ (5)°, $V = 2192.0$ (2) Å³, $Z = 4$, $D_x = 1.337$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 15.009$ cm⁻¹, $F(000) = 912$, $T = 295$ K, $R = 0.045$ for 3641 observed reflections. 2-Amino-1-triphenylphosphoranylideneaminobenzene, (II), $C_{24}H_{21}N_2P$, $M_r = 368.42$, monoclinic, $I2/a$, $a = 30.4088$ (15), $b = 11.5561$ (3), $c = 22.9996$ (10) Å, $\beta = 101.437$ (3)°, $V = 7921.7$ (6) Å³, $Z = 16$, $D_x = 1.236$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 12.805$ cm⁻¹, $F(000) = 3104$, $T = 295$ K, $R = 0.041$ for 5873 observed reflections. The elongation of the P=N bond in (I) reflects the protonation of its N atom [1.621 (4) and 1.635 (4) Å in (I); 1.570 (2) and 1.572 (2) Å in (II)]. The endo- and exocyclic angular deformations of the benzene ring at C(1) (up to 3 and 6° respectively) could result from the electron-donor character of the iminophosphorane group and also, in (II), from the N—H...N intramolecular hydrogen bond [N...N 2.695 (3) and 2.675 (3) Å].

Introduction. The understanding of the structural features of iminophosphoranes derived from 1,8-diaminonaphthalene (Llamas-Saiz, Foces-Foces, Elguero, Molina, Alajarin & Vidal, 1991*a,b*; Llamas-Saiz, Foces-Foces, Molina, Alajarin, Vidal, Claramunt & Elguero, 1991) and from *o*-phenylenediamine, led us to determine those of the more simple compounds (I) and (II). The structure of related compounds, triphenylphosphoranylideneaminobenzene (III) [*i.e.* unprotonated compound (I)] (Böhm, Dehnicke, Beck, Hiller, Strähle, Maurer & Fenske, 1988) and *o*-phenylenediamine (1,2-diaminobenzene) (Stålhandske, 1981), were already known. Even that of cation (I) has been determined (Böhm *et al.*, 1988) but the nature of the anion, AuI_2^- gave high σ values for the atomic coordinates [up to 10 times higher than in (III)], to the point that

some distances such as N—C = 1.354 (25) Å could be grossly underestimated. The only other compound found in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) related to these compounds is the copper(I) complex (III)CuCl (Maurer, Fenske, Beck, Hiller, Strähle, Böhm & Dehnicke, 1988).

Experimental. Melting points were determined with a Kofler hot-stage microscope and are uncorrected. Spectral studies were performed with the following instruments: ¹H and ¹³C NMR, Bruker AC-200, all chemical shifts expressed in p.p.m. relative to SiMe₄. Combustion analyses were performed with a Perkin-Elmer 240C instrument and gave satisfactory results (± 0.3) for both compounds.

Compound (I): 0.71 g (0.002 mol) triphenylphosphoranylideneaminobenzene (Gololobov, Zhmurova & Kasukhin, 1981) was dissolved in 25 ml dry ethanol. 0.35 g (0.002 mol) 50% fluoroboric acid in water was weighed in 2 ml ethanol and added to the solution of triphenylphosphoranylideneaminobenzene. The mixture was stirred at room temperature for 1 h. The solvent was removed and the resulting solid was recrystallized from dichloromethane/ether yielding 0.83 g of compound (I) (89% yield); m.p. 455–456 K. ¹H NMR (CDCl₃, p.p.m.): 7.82–7.67 (*m*, 10H), 7.67–7.57 (*m*, 6H), 7.13–6.92 (*m*, 4H). ¹³C NMR (CDCl₃, p.p.m.): 119.8 (C_i) (¹J_{CP} = 102.9 Hz), 121.5 (C₂) (³J_{CP} = 6.4 Hz), 124.3 (C₄), 129.4 (C₃), 130.2 (C_m) (³J_{CP} = 13.5 Hz), 133.4 (C_o) (²J_{CP} = 11.3 Hz), 135.4 (C_p) (⁴J_{CP} = 3.0 Hz), 137.5 (C₁) (²J_{CP} = 2.4 Hz).



Compound (II): 0.52 g (0.002 mol) triphenylphosphine was dissolved in 5 ml dry ether. 0.27 g (0.002 mol) *o*-azidoaniline (Smith, Hall & Kan, 1962) was dissolved in 5 ml dry ether and was added dropwise to the solution of triphenylphosphine. The mixture was stirred at room temperature for 2 h. The resulting solid was filtered, dried and recrystallized from dry ether yielding 0.57 g of 2-amino-1-triphenylphosphoranylideneaminobenzene (78% yield); m.p. 422–423 K. ^1H NMR (CDCl_3 , p.p.m.): 7.86–7.73 (*m*, 6H), 7.56–7.39 (*m*, 9H), 6.76 (*ddd*, 1H) ($J = 1.5, 2.7, 7.3$ Hz), 6.58 (*dt*, 1H) ($J = 2.1, 7.4$ Hz), 6.43–6.35 (*m*, 2H), 4.31 (*br s*, 2H). ^{13}C NMR (CDCl_3 , p.p.m.): 113.9 (C5) ($^4J_{\text{CP}} = 1.3$ Hz), 118.0 (C4) ($^2J_{\text{CP}} = 1.2$ Hz), 119.9 (C6) ($^3J_{\text{CP}} = 9.3$ Hz), 128.5 (Cm) ($^3J_{\text{CP}} = 12.0$ Hz), 131.3 (Ci) ($^1J_{\text{CP}} = 99.6$ Hz), 131.6 (Cp) ($^4J_{\text{CP}} = 2.8$ Hz), 132.0 (C3) ($^4J_{\text{CP}} = 9.9$ Hz), 132.5 (Co) ($^2J_{\text{CP}} = 9.6$ Hz), 138.0 (C1), 141.6 (C2) ($^3J_{\text{CP}} = 20.9$ Hz).

Table 1 summarizes the data-collection conditions and the refinement parameters. The *I* cell was chosen for compound (II) because of the smaller β angle (C cell: $a = 34.311$, $b = 11.556$, $c = 23.000$ Å, $\beta = 119.7^\circ$). Final positional parameters for the non-H atoms for both structures are listed in Table 2.*

Both compounds present two independent molecules in the asymmetric unit. The existence of extra crystallographic or non-crystallographic symmetry has been checked by means of least-squares procedures (Nardelli, 1983) given the rotation and translation matrices (*R* and *T*) which bring the atomic coordinate set *B* into set *A* or *vice versa*:

$$r_A = R.r_B + T, \text{ where}$$

$$R = \begin{pmatrix} -0.8372 & 0.1559 & 0.1805 \\ 1.0906 & 0.0738 & 0.9776 \\ 0.6144 & 0.8293 & -0.2388 \end{pmatrix}, T = \begin{pmatrix} 0.3861 \\ 0.0847 \\ -0.4112 \end{pmatrix}$$

The corresponding χ^2 values for each coordinate and the theoretical value in (I) are 133.8, 116.2, 124.0 vs 38.9. In a similar way, the two independent molecules in (II) are almost related by a symmetry centre at (0.3877, -0.0067, 0.2257) ($\chi^2 = 34.0, 209.0, 125.3$ vs 35.2):

$$R = \begin{pmatrix} -0.9847 & 0.0064 & -0.0723 \\ -0.1092 & -0.9912 & 0.0922 \\ 0.1167 & -0.0037 & -1.0027 \end{pmatrix}, T = \begin{pmatrix} 0.7754 \\ -0.0133 \\ -0.4514 \end{pmatrix}$$

A careful inspection of the first calculation, in (II), revealed that the C(13)–C(18) ring is twisted around the C(13)–C(16) axis, so the C(14), C(15), C(17) and

Table 1. *Crystal analysis parameters at room temperature*

	(I)	(II)
Crystal data		
Crystal habit	Colourless prism	Dark brown prism
Crystal size (mm)	0.20 × 0.30 × 0.67	0.23 × 0.37 × 0.67
Unit-cell determination	Least-squares fit from 84 reflections ($\theta < 45^\circ$)	Least-squares fit from 83 reflections ($\theta < 45^\circ$)
Experimental data		
Technique	Philips PW1100 four-circle diffractometer; bisecting geometry; graphite-oriented monochromator; Cu <i>K</i> α	
Scan technique	$\omega/2\theta$	$\omega/2\theta$
Scan width ($^\circ$)	1.5	1.6
Detector aperture ($^\circ$)	1 × 1	1 × 1
Time per reflection (min)	1	1
θ_{max} ($^\circ$)	65	65
+ <i>h</i> , + <i>k</i> , ± <i>l</i> range	29, 11, ±11	36, 14, ±26
Number of reflections		
Measured	4256	7413
Independent	3723	6757
Observed	3641 [3 $\sigma(I)$ criterion]	5873 [3 $\sigma(I)$ criterion]
R_{int}	0.015	0.014
Standard reflections	2 reflections measured every 90 min; no variation	
Maximum–minimum transmission factors	1.135–0.745	1.095–0.733
Solution and refinement		
Solution	Direct methods	Direct methods
Refinement		
Least-squares on F_o	3 blocks	3 blocks
Parameters		
Number of variables	557 (see text)	655
Degrees of freedom	3084	5218
Ratio of freedom	6.5	9.0
Goodness of fit	1.3	1.5
H atoms	From difference synthesis	
Final (shift/e.s.d.)	0.03	0.02
Maximum shift/e.s.d.	0.41	0.38
Weighting scheme	Empirical as to give no trends in $(\omega\Delta^2 F)_{\text{vs}}(F_{\text{obs}})$ and $(\sin\theta/\lambda)$	
Maximum thermal value (Å 2)	$U_{11}[\text{F}(22)] = 0.42$ (1)	$U_{11}[\text{C}(27A)] = 0.197$ (4)
Final ΔF peaks (e Å $^{-3}$)	±0.32	±0.17
Final R, wR	0.045, 0.053	0.041, 0.047

C(18) atoms of this ring were not included in the least-squares fit just mentioned.

In spite of the high thermal values of the BF_4^- anion, no disorder models could be obtained. After performing several cycles of mixed refinement in (I) (725 parameters) and owing to the low ratio of freedom, the H atoms were kept fixed in their refined positions during the last three cycles of refinement. Computations were performed on a VAX6410 computer with the following programs: *XRAY80* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); *DIFABS* (Walker & Stuart, 1983); *SIR88* (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989); *DIRDIF* (Beurskens *et al.*, 1984); *PESOS* (Martinez-Ripoll & Cano, 1975); *PARST* (Nardelli, 1983). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Perspective views of (I) and (II), showing the molecular conformation and the numbering scheme, are depicted in Fig. 1 (Hall & Stewart, 1990). Selected bond lengths, bond angles, torsion angles and deformation parameters around the P=O bond are given in Table 3.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55155 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0527]

Table 2. Final atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j \cos(a_i, a_j).$$

Compound (I)	x	y	z	U_{eq}
Molecule A				
C(1)	0.1812 (2)	0.6067 (5)	0.0367 (4)	458 (11)
C(2)	0.2053 (2)	0.5315 (6)	-0.0572 (4)	579 (14)
C(3)	0.2313 (2)	0.6121 (8)	-0.1457 (5)	741 (20)
C(4)	0.2340 (2)	0.7624 (9)	-0.1401 (6)	790 (22)
C(5)	0.2090 (2)	0.8393 (6)	-0.0489 (5)	678 (17)
C(6)	0.1821 (2)	0.7620 (5)	0.0400 (5)	562 (14)
N(11)	0.1561 (1)	0.5209 (4)	0.1275 (3)	476 (10)
P(12)	0.13520	0.58044 (10)	0.26120	384 (2)
C(13)	0.1229 (2)	0.4212 (4)	0.3582 (4)	465 (11)
C(14)	0.0820 (2)	0.3220 (6)	0.3044 (6)	737 (19)
C(15)	0.0711 (3)	0.2003 (7)	0.3787 (9)	918 (26)
C(16)	0.0995 (3)	0.1774 (6)	0.5061 (8)	839 (24)
C(17)	0.1412 (3)	0.2747 (8)	0.5620 (6)	815 (22)
C(18)	0.1526 (2)	0.3977 (6)	0.4898 (5)	666 (16)
C(19)	0.1876 (2)	0.6931 (4)	0.3596 (4)	446 (11)
C(20)	0.2407 (2)	0.6344 (5)	0.3870 (5)	557 (13)
C(21)	0.2826 (2)	0.7124 (6)	0.4682 (6)	700 (17)
C(22)	0.2722 (2)	0.8483 (6)	0.5239 (5)	661 (16)
C(23)	0.2198 (2)	0.9054 (6)	0.4944 (6)	687 (17)
C(24)	0.1776 (2)	0.8306 (5)	0.4116 (6)	602 (15)
C(25)	0.0717 (2)	0.6811 (4)	0.2201 (4)	430 (11)
C(26)	0.0458 (2)	0.7383 (5)	0.3223 (4)	480 (12)
C(27)	-0.0032 (2)	0.8163 (5)	0.2871 (5)	552 (14)
C(28)	-0.0275 (2)	0.8353 (5)	0.1528 (5)	585 (14)
C(29)	-0.0025 (2)	0.7772 (5)	0.0521 (5)	587 (14)
C(30)	0.0471 (2)	0.6998 (5)	0.0848 (4)	493 (12)
B	0.0975 (3)	0.1715 (7)	-0.0383 (7)	786 (22)
F(1)	0.1479 (2)	0.2061 (6)	0.0310 (7)	1311 (22)
F(2)	0.0668 (3)	0.2965 (7)	-0.0318 (8)	1724 (32)
F(3)	0.0759 (4)	0.0642 (9)	0.0199 (11)	2042 (47)
F(4)	0.0928 (4)	0.1276 (11)	-0.1641 (7)	1924 (42)
Molecule B				
C(1)	0.3339 (1)	0.3697 (4)	0.1944 (4)	404 (10)
C(2)	0.2856 (2)	0.2854 (5)	0.1670 (5)	512 (13)
C(3)	0.2629 (2)	0.2268 (5)	0.2714 (5)	578 (14)
C(4)	0.2882 (2)	0.2504 (5)	0.4046 (5)	591 (14)
C(5)	0.3363 (2)	0.3317 (5)	0.4325 (4)	527 (13)
C(6)	0.3592 (2)	0.3921 (4)	0.3286 (4)	454 (11)
N(11)	0.3547 (1)	0.4309 (4)	0.0839 (3)	437 (9)
P(12)	0.40942 (4)	0.53586 (9)	0.09266 (10)	345 (2)
C(13)	0.4125 (1)	0.6023 (4)	-0.0715 (4)	408 (10)
C(14)	0.4278 (2)	0.5041 (5)	-0.1641 (4)	546 (13)
C(15)	0.4345 (2)	0.5552 (7)	-0.2897 (5)	672 (17)
C(16)	0.4249 (2)	0.7009 (7)	-0.3232 (5)	714 (18)
C(17)	0.4079 (3)	0.7996 (6)	-0.2344 (6)	710 (18)
C(18)	0.4017 (2)	0.7504 (5)	-0.1072 (5)	590 (15)
C(19)	0.4015 (2)	0.6917 (4)	0.1969 (4)	418 (10)
C(20)	0.3500 (2)	0.7617 (5)	0.1728 (5)	592 (14)
C(21)	0.3427 (2)	0.8929 (6)	0.2371 (6)	696 (17)
C(22)	0.3858 (3)	0.9566 (5)	0.3247 (6)	684 (18)
C(23)	0.4364 (2)	0.8869 (5)	0.3528 (5)	611 (15)
C(24)	0.4453 (2)	0.7546 (4)	0.2887 (4)	481 (12)
C(25)	0.4710 (1)	0.4292 (4)	0.1504 (3)	410 (10)
C(26)	0.5234 (2)	0.4968 (6)	0.1711 (5)	587 (14)
C(27)	0.5704 (2)	0.4078 (8)	0.2095 (5)	709 (19)
C(28)	0.5656 (2)	0.2582 (8)	0.2231 (5)	772 (21)
C(29)	0.5146 (2)	0.1910 (6)	0.1985 (5)	691 (18)
C(30)	0.4666 (2)	0.2763 (5)	0.1619 (4)	516 (12)
B	0.3229 (3)	0.1648 (6)	-0.1875 (5)	621 (17)
F(1)	0.3120 (2)	0.3123 (5)	-0.1744 (5)	1138 (18)
F(2)	0.3564 (5)	0.1204 (8)	-0.0769 (5)	2203 (52)
F(3)	0.2766 (4)	0.0944 (11)	-0.2107 (14)	2539 (68)
F(4)	0.3465 (2)	0.1333 (6)	-0.2958 (5)	1157 (20)
Compound (II)				
Molecule A				
C(1)	0.49882 (6)	-0.08164 (16)	0.37900 (8)	439 (5)
C(2)	0.51553 (6)	0.03087 (17)	0.39341 (9)	509 (6)
C(3)	0.54648 (8)	0.07852 (20)	0.36345 (11)	648 (8)
C(4)	0.56102 (8)	0.01737 (22)	0.31902 (12)	689 (9)
C(5)	0.54548 (8)	-0.09221 (21)	0.30483 (10)	627 (8)
C(6)	0.51477 (7)	-0.14161 (18)	0.33471 (9)	521 (6)
N(11)	0.46838 (5)	-0.12388 (14)	0.41199 (7)	499 (5)
P(12)	0.43333 (2)	-0.22345 (4)	0.39304 (2)	398 (1)
C(13)	0.39989 (6)	-0.22676 (17)	0.45004 (8)	465 (6)
C(14)	0.38830 (8)	-0.12276 (19)	0.47361 (10)	590 (7)
C(15)	0.36232 (8)	-0.12282 (22)	0.51676 (11)	669 (8)
C(16)	0.34829 (8)	-0.22569 (23)	0.53713 (10)	654 (8)
C(17)	0.36005 (8)	-0.32884 (22)	0.51468 (11)	662 (8)

Table 2 (cont.)

	x	y	z	U_{eq}
C(18)	0.38552 (7)	-0.33007 (18)	0.47082 (10)	558 (7)
C(19)	0.39595 (6)	-0.20152 (15)	0.32210 (8)	451 (5)
C(20)	0.35607 (7)	-0.14032 (18)	0.31894 (10)	560 (7)
C(21)	0.32933 (8)	-0.11414 (21)	0.26400 (12)	693 (8)
C(22)	0.34218 (8)	-0.14655 (23)	0.21278 (11)	700 (8)
C(23)	0.38155 (9)	-0.20561 (22)	0.21521 (10)	680 (8)
C(24)	0.40808 (7)	-0.23410 (19)	0.26938 (9)	549 (6)
C(25)	0.45646 (7)	-0.36711 (17)	0.39082 (9)	498 (6)
C(26)	0.43361 (10)	-0.45786 (19)	0.35824 (11)	703 (9)
C(27)	0.45409 (15)	-0.56603 (22)	0.36024 (15)	1063 (16)
C(28)	0.49626 (18)	-0.58310 (35)	0.39462 (22)	1322 (21)
C(29)	0.51822 (13)	-0.49408 (40)	0.42649 (21)	1197 (18)
C(30)	0.49901 (8)	-0.38524 (25)	0.42524 (13)	778 (10)
N(31)	0.49842 (7)	0.09376 (17)	0.43597 (9)	675 (7)
Molecule B				
C(1)	0.25683 (6)	0.04718 (16)	0.12980 (8)	445 (5)
C(2)	0.23887 (6)	-0.06428 (17)	0.11558 (8)	474 (6)
C(3)	0.21066 (7)	-0.11432 (20)	0.14873 (10)	609 (7)
C(4)	0.19980 (8)	-0.05828 (23)	0.19678 (11)	676 (8)
C(5)	0.21679 (9)	0.05084 (23)	0.21133 (11)	688 (9)
C(6)	0.24464 (8)	0.10338 (19)	0.17784 (10)	584 (7)
N(11)	0.28470 (5)	0.09042 (14)	0.09352 (7)	480 (5)
P(12)	0.31934 (1)	0.19226 (4)	0.10898 (2)	381 (1)
C(13)	0.34853 (6)	0.20658 (16)	0.04843 (8)	438 (5)
C(14)	0.33436 (7)	0.14592 (19)	-0.00417 (9)	530 (6)
C(15)	0.35669 (8)	0.16051 (23)	-0.05054 (9)	653 (8)
C(16)	0.39257 (8)	0.23538 (24)	-0.04508 (9)	652 (8)
C(17)	0.40654 (7)	0.29780 (21)	0.00696 (10)	602 (7)
C(18)	0.38462 (7)	0.28315 (18)	0.05357 (9)	520 (6)
C(19)	0.36161 (6)	0.17148 (16)	0.17541 (8)	481 (6)
C(20)	0.40037 (8)	0.10992 (20)	0.17307 (12)	672 (8)
C(21)	0.43022 (9)	0.08299 (26)	0.22578 (19)	966 (13)
C(22)	0.42115 (13)	0.11496 (32)	0.27948 (16)	1060 (14)
C(23)	0.38326 (13)	0.17321 (30)	0.28170 (11)	959 (13)
C(24)	0.35324 (9)	0.20297 (22)	0.23027 (9)	668 (8)
C(25)	0.29493 (7)	0.33374 (17)	0.11470 (8)	486 (6)
C(26)	0.31929 (9)	0.42829 (18)	0.14100 (10)	617 (8)
C(27)	0.29846 (15)	0.53530 (23)	0.14053 (16)	884 (14)
C(28)	0.25420 (17)	0.54792 (33)	0.11428 (21)	1155 (19)
C(29)	0.23012 (15)	0.45548 (39)	0.08944 (23)	1220 (19)
C(30)	0.25007 (9)	0.34743 (28)	0.08898 (15)	833 (11)
N(31)	0.25234 (8)	-0.12331 (19)	0.06952 (9)	677 (7)

The two independent molecules in the asymmetric unit (I) have several significantly different torsion angles (C—C—N—P, C—N—P—C and N—P—C—C) and to a lesser extent ($\sigma_p = 2.5$) different P=N bonds, as well as other slight deviations from the least-squares transformation which brings molecule B into molecule A, see *Experimental* (Nardelli, 1983). The two benzene rings are planar with only slight deviations from strict planarity ($\chi^2 = 23.99$ and 5.33 for A and B respectively, vs the theoretical value of 7.81). The exocyclic N atoms deviate 0.047 (4) and 0.035 (3) Å respectively. There is a relationship between the C(6)—C(1)—N(11)—P(12) torsion angle and the C(1)—N(11) bond length: $-0.6 (6)^\circ$, 1.420 (5) Å in molecule B; $-11.4 (6)^\circ$, 1.422 (6) Å in molecule A; and $-72.6 (12)^\circ$, 1.461 (12) Å for the naphthalene derivative (Llomas-Saiz *et al.*, 1991a). This correlation could be related to the conjugation between the P=N⁺ double bond and the aromatic ring in planar systems. In A, this torsion angle is similar to the corresponding ones, $-11.5 (7)$ and $-16.7 (29)^\circ$, displayed by N-phenylimino and N-phenyliminiumtriphenylphosphorane (Böhm *et al.*, 1988). As in the naphthalene derivative, the ions are joined together by strong and almost linear N—H...F hydrogen bonds, Table 4.

A pseudo-centre of symmetry relates the two molecules in the asymmetric unit of compound (II). The main differences between them concern the twist of the C(13)–C(18) ring [N(11)–P(12)–C(13)–C(14) = 38.8 (2), 9.4 (2)°] and the C–NH₂ distances ($\sigma_P = 2.83$). This bond, in *A*, is similar to those displayed by 1,2-diaminobenzene (Stålhandske, 1981). The shortening in *B* could be owing to the greater overlapping of the N lone pair [the sums of the angles around N(31) amount to 341 (4) and 350 (4)°] with the π system of the benzene ring, as shown by the angles between them of 75 and 81°, in *A* and *B*, vs 66 and 70° in 1,2-diaminobenzene.

As a consequence of the protonation of (I), the C–N and P–N bonds appear to be significantly larger in (I) than in (II), Table 3. If the geometries of (I) and (III) are compared, the effect of the proto-

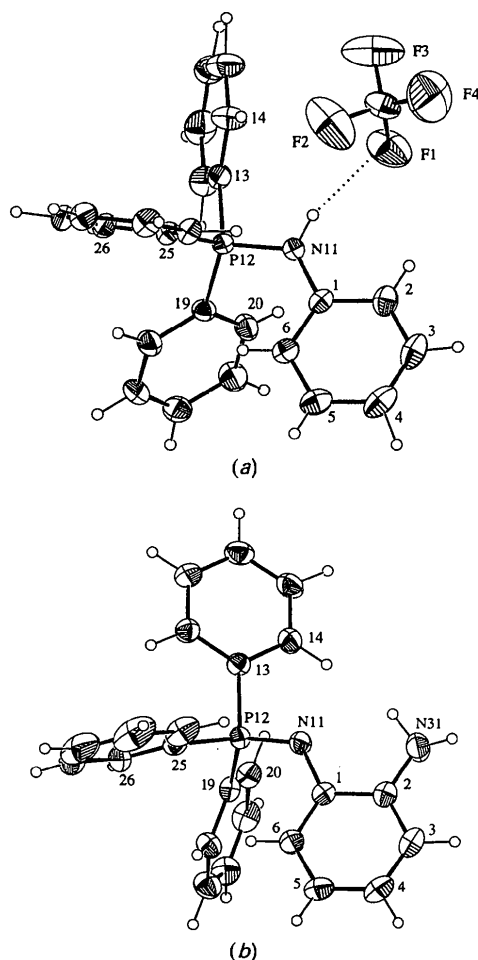


Fig. 1. A perspective view of the *A* molecules of (a) compound (I) and (b) compound (II) showing the numbering scheme. The same projections are used for plotting both molecules. (See text for differences between the two independent molecules.) Thermal ellipsoids are drawn at the 30% probability level and H atoms are represented by spheres of 0.1 Å radius.

Table 3. Selected bond distances (Å), bond angles (°), torsion angles (°) and deformation parameters (°) around the N(11)–P(12) bond

	Compound (I)		Compound (II)	
	Molecule <i>A</i>	Molecule <i>B</i>	Molecule <i>A</i>	Molecule <i>B</i>
C(1)–C(2)	1.384 (7)	1.394 (5)	1.411 (3)	1.412 (3)
C(1)–C(6)	1.399 (6)	1.392 (5)	1.396 (3)	1.394 (3)
C(1)–N(11)	1.422 (6)	1.420 (5)	1.396 (3)	1.395 (3)
C(2)–C(3)	1.395 (8)	1.384 (7)	1.386 (3)	1.382 (3)
C(3)–C(4)	1.356 (11)	1.384 (7)	1.385 (4)	1.376 (4)
C(4)–C(5)	1.384 (9)	1.377 (6)	1.368 (4)	1.379 (4)
C(5)–C(6)	1.395 (8)	1.390 (6)	1.387 (3)	1.392 (4)
N(11)–P(12)	1.621 (4)	1.635 (4)	1.570 (2)	1.572 (2)
P(12)–C(13)	1.792 (4)	1.773 (4)	1.812 (2)	1.801 (2)
P(12)–C(19)	1.787 (4)	1.786 (4)	1.812 (2)	1.807 (2)
P(12)–C(25)	1.788 (4)	1.796 (4)	1.808 (2)	1.811 (3)
C(2)–N(31)			1.400 (3)	1.388 (3)
C(6)–C(1)–N(11)	122.3 (4)	122.8 (3)	125.9 (2)	126.6 (2)
C(2)–C(1)–N(11)	117.8 (4)	118.4 (4)	116.2 (2)	116.2 (2)
C(2)–C(1)–C(6)	119.9 (4)	118.8 (4)	117.9 (2)	117.2 (2)
C(1)–C(2)–C(3)	119.2 (5)	120.5 (4)	119.8 (2)	120.5 (2)
C(2)–C(3)–C(4)	121.2 (5)	120.4 (4)	120.8 (2)	121.3 (2)
C(3)–C(4)–C(5)	120.1 (6)	119.5 (5)	120.2 (2)	119.2 (2)
C(4)–C(5)–C(6)	120.0 (5)	120.6 (4)	119.8 (2)	120.3 (2)
C(1)–C(6)–C(5)	119.5 (4)	120.2 (4)	121.5 (2)	121.5 (2)
C(1)–N(11)–P(12)	126.7 (3)	126.6 (3)	126.3 (1)	126.3 (1)
N(11)–P(12)–C(25)	112.1 (2)	110.2 (2)	115.7 (1)	115.2 (1)
N(11)–P(12)–C(19)	109.9 (2)	107.8 (2)	114.7 (1)	115.1 (1)
N(11)–P(12)–C(13)	107.5 (2)	108.9 (2)	105.2 (1)	107.7 (1)
C(1)–C(2)–N(31)			118.4 (2)	117.8 (2)
C(3)–C(2)–N(31)			121.6 (2)	121.6 (2)
C(6)–C(1)–N(11)–P(12)	–11.4 (6)	–0.6 (6)	–23.5 (3)	19.6 (3)
C(1)–N(11)–P(12)–C(13)	–166.3 (3)	–172.6 (3)	–173.7 (2)	176.7 (2)
C(1)–N(11)–P(12)–C(19)	–47.5 (4)	–55.4 (4)	–55.0 (2)	57.7 (2)
C(1)–N(11)–P(12)–C(25)	75.7 (4)	69.7 (4)	69.4 (2)	–67.5 (2)
N(11)–P(12)–C(25)–C(30)	–0.4 (4)	8.6 (4)	22.7 (2)	–18.3 (2)
N(11)–P(12)–C(19)–C(20)	–49.4 (4)	–45.4 (4)	–87.7 (2)	84.9 (2)
N(11)–P(12)–C(13)–C(14)	–64.0 (4)	–73.7 (4)	38.8 (2)	9.4 (2)
N(11)–C(1)–C(2)–N(31)			–4.3 (3)	3.6 (3)
χ_r	–46.0 (2)	–52.8 (2)	–53.1 (1)	55.6 (1)
$\chi_{25,13}$	–2.0 (5)	–2.3 (5)	–3.1 (3)	4.2 (3)
$\chi_{19,25}$	3.2 (6)	5.1 (6)	4.4 (3)	–5.2 (3)
$\chi_{13,19}$	–1.2 (5)	–2.8 (5)	–1.3 (3)	1.0 (3)

Table 4. Hydrogen interactions (Å, °)

C(1–6), C(19–24), C(25–30) represent the centroids of the corresponding phenyl rings

X–H...Y	X–H	X...Y	H...Y	X–H...Y
Compound (I)				
N(11) <i>A</i> –H(11) <i>A</i> ...F(1) <i>A</i>	0.85 (4)	2.992 (6)	2.18 (4)	160 (4)
N(11) <i>B</i> –H(11) <i>B</i> ...F(1) <i>B</i>	0.89 (5)	2.825 (5)	1.95 (5)	168 (5)
C(20) <i>A</i> –H(20) <i>A</i> ...C(1–6) <i>B</i>	0.76 (6)	3.593 (5)	2.89 (6)	156 (5)
C(20) <i>B</i> –H(20) <i>B</i> ...C(1–6) <i>A</i>	1.14 (5)	3.871 (5)	2.87 (5)	146 (4)
C(22) <i>B</i> –H(22) <i>B</i> ...C(1–6) <i>B'</i>	1.02 (7)	3.657 (5)	2.90 (7)	131 (4)
C(15) <i>B</i> –H(15) <i>B</i> ...C(25–30) <i>A''</i>	1.11 (7)	3.582 (6)	2.78 (7)	129 (4)
Compound (II)				
N(31) <i>A</i> –H(311) <i>A</i> ...N(11) <i>A</i>	0.98 (3)	2.695 (3)	2.20 (3)	110 (2)
N(31) <i>B</i> –H(311) <i>B</i> ...N(11) <i>B</i>	0.93 (3)	2.675 (3)	2.20 (3)	110 (2)
C(21) <i>A</i> –H(21) <i>A</i> ...C(1–6) <i>B</i>	0.94 (3)	3.699 (3)	3.03 (3)	129 (2)
C(22) <i>B</i> –H(22) <i>B</i> ...C(1–6) <i>A</i>	1.00 (4)	3.799 (3)	2.98 (4)	140 (3)
C(5) <i>A</i> –H(5) <i>A</i> ...C(19–24) <i>B''</i>	0.96 (3)	3.763 (3)	3.01 (3)	136 (2)
C(15) <i>B</i> –H(15) <i>B</i> ...C(1–6) <i>B''</i>	0.95 (3)	3.795 (5)	2.95 (2)	148 (2)
C(18) <i>B</i> –H(18) <i>B</i> ...C(1–6) <i>A'</i>	1.01 (3)	3.740 (2)	2.89 (3)	142 (2)

Symmetry code: (i) $x, 1 + y, z$; (ii) $\frac{1}{2} + x, 1 - y, -\frac{1}{2} + z$; (iii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, y, -z$; (v) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

nation results in a significant lengthening of the N–P bond [1.621 (4), 1.635 (4); 1.602 (3) Å] and in a much more marked lengthening of the N–C(Ph) bond [1.422 (6), 1.420 (5); 1.330 (5) Å].

It is worth mentioning that the most sensitive C atom is the C_{ipso} , which in ¹³C NMR spectroscopy moves from 119.8 p.p.m. in compound (I) to 131.3

p.p.m. in compound (II), a phenomenon already noted by Albright, Freeman & Schweizer (1976).

The benzene rings in (II) are less planar ($\chi^2 = 27.63$ and 45.80) than that of (I) and the N(11) and N(31) atoms deviate -0.015 (2), 0.066 (2) and -0.005 (2), -0.076 (2) Å respectively. The strain arising from the close location of both groups [2.695 (3) and 2.675 (3) vs 2.752 (2) Å in 1,2-diaminobenzene] seems to be reduced by the formation of an intramolecular hydrogen bond (Table 4) in spite of the unfavourable geometrical arrange-

ment. These distances are shorter than 2.795 Å, a value that could be expected for a regular benzene, *ortho* and symmetrically substituted (C—C = 1.395 and C—N = 1.400 Å). Both substituents extend inwards showing greater angular deformation at C(1) than those observed in (I) (Table 3) together with an increase in the C—C—N—P torsion angle. Moreover, the endocyclic angular distortions at C(1) [C(6)—C(1)—C(2) $< 120^\circ$] displayed by this type of substituent also observed in the *N*-phenylimino and *N*-phenyliminiumtriphenylphosphorane (Böhm *et al.*, 1988) would place, qualitatively, the iminophosphorane group between the electron-donor substituents of an aromatic ring, according to the Norrestam & Schepper (1981) classification.

Compounds (I) and (II) present a distorted parallel conformation around the P=N bond (C—N—P—C: $\pm 60, 180^\circ$), Table 3. The deformation parameters around a bond (Cano, Foces-Foces & Garcia-Blanco, 1979), defined as:

$$\chi_\tau = \frac{1}{NN'} \sum_{i=1}^N \sum_{j'=1}^{N'} \tau_{ij'} + \frac{(N'-N)\pi}{NN'}$$

measure the twist of the rear-end substituent with respect to the front-end one, where N and N' are the number of substituents at both ends of a bond and τ_{ij} the torsion angles, in such a way (because of their periodic character, mod 2π) that for every k' , $\tau_{jk'} > \tau_{ik'}$ when $j > i$, and for every k , $\tau_{kj'} < \tau_{ki'}$ when $j' > i'$, and with sequences i, j, \dots, N and i', j', \dots, N' numbered anticlockwise.

$$\chi_{ij} = (\tau_{jk} - \tau_{ik}) - \frac{2\pi}{N} (j - i)$$

and analogously $\chi_{i'j'}$. In this study the C(19) substituent was chosen as the angular origin.

The χ_τ parameter shows absolute values in the range 46.0 (2)– 55.6 (1)°. The greater deviation, χ_{ij} , from the ideal value of the dihedral angle between two planes with a common edge [*i.e.* N(11)—P(12)—C(19), N(11)—P(12)—C(25)] is shown by phenyl rings at C(19) and C(25), both in a synclinal conformation with respect to C(1)—N(11).

The crystal structures (I) and (II), Fig. 2, are also stabilized by weak C—H⋯(phenyl centroid) contacts of 'T' type (Desiraju, 1989), Table 4. Moreover, in (II) an interaction between the almost parallel C(13)—C(18) phenyl rings [2.2 (1)°] of molecules *A* and *B* is present [(Fig. 2(b)); the average distance between the mean square planes of these rings is 3.619 (1) Å and the glide between their centroids is 1.348 (6) Å].

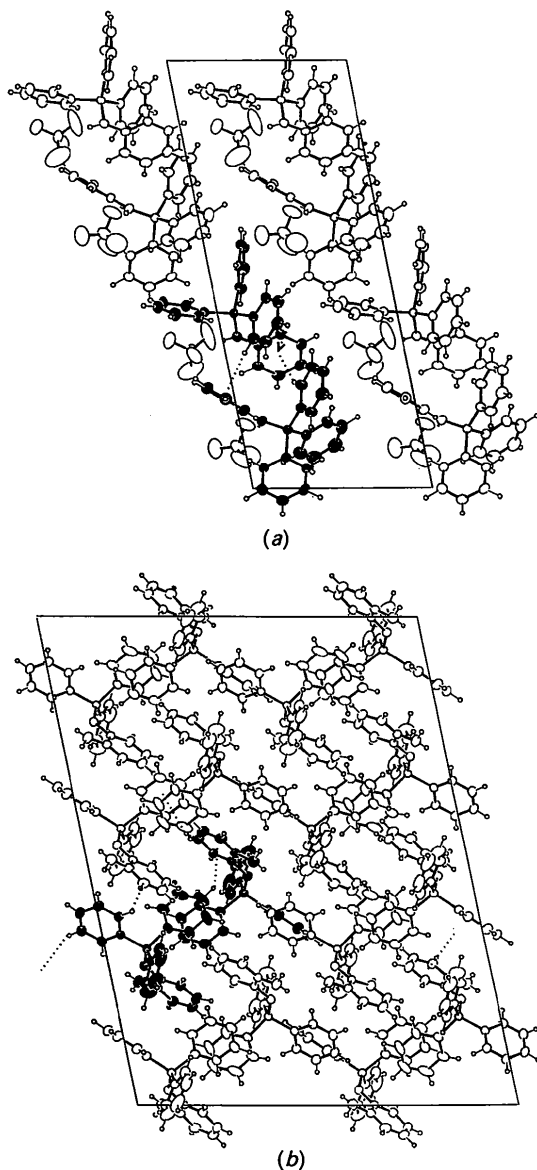


Fig. 2. The packing of (a) compound (I) and (b) compound (II) shown in a projection along the b axis to reveal the more linear C—H⋯(phenyl centroid) independent interactions (dotted lines) and the superposition of phenyl rings (II). The independent molecules in the asymmetric unit are highlighted.

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Methyl 2,4-Dideoxy-6,7,8,9,10-penta-*O*-acetyl-D-glycero- α -D-gluco-decapyranosid-3-ulose

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Abstract. $C_{21}H_{30}O_{13}$, $M_r = 490.46$, orthorhombic, $P2_12_12_1$, $a = 8.945$ (2), $b = 22.104$ (6), $c = 12.482$ (4) Å, $V = 2468$ (1) Å³, $Z = 4$, $D_x = 1.320$ (1) Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.96$ mm⁻¹, $F(000) = 1040$, room temperature, $R = 0.072$ for 1554 independent reflections with $I > 2\sigma(I)$. The pyranoid ring has the almost ideal ⁴C₁ chair conformation and is more puckered than analogous rings with the C(sp²) atom vicinal to the anomeric centre. The aliphatic chain has an extended *ap*, *ap* conformation.

Introduction. Recently we have studied the crystal structures and conformations of several pyranosides with one sp²-hybridized C atom in position 2 (vicinal

to the anomeric centre) of the pyranoid ring (Smiatecz, Myszkas & Ciunik, 1988; Ciunik, Paulsen, Luger, Smiatecz & Myszkas, 1989; Ciunik, Szweda & Smiatecz, 1991). All these compounds have a chair conformation with a large distortion towards an envelope geometry or a small one towards a half chair. These pyranoid rings are more distorted and probably more flexible than the parent compounds with all C atoms sp³ hybridized. The second conclusion is supported by observed differences between conformations of similar 2-oxyimino derivatives of pyranosides studied and between symmetry-independent molecules in two crystal structures. An inspection of carbohydrate derivatives with the C(sp²) atom in position 3 of the pyranoid ring, *i.e.*