Iminophosphorane-substituted Proton Sponges. Part 3.[2] Preparation and Crystal Structure of Three Salts of Protonated 1-Dimethylamino-8-triphenylphosphoranylideneammonionaphthalene

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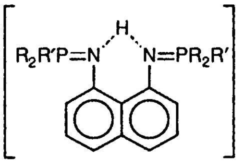
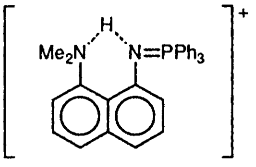
Results of the crystal structure analysis of three 1-dimethylamino-8-triphenylphosphoranylideneammonionaphthalene salts are described. The 'extra proton' has been found to bind to the nitrogen atom of the iminophosphorane group, being engaged in a strong intramolecular contact [N···N = 2.519(3), 2.543(4), 2.571(6) Å; N–H···N = 154(6), 155(6) and 147(6)° for Br^-, BF_4^- and PF_6^- salts, respectively] which is shorter in two salts than those displayed by the 1,8-bis(dimethylamino)naphthalene salts of Br^-, BF_4^- and $TeOF_5^-$, which are considered as 'proton sponges' [2.555(3), 2.562(2) and 2.574(3) Å, respectively].

The series 'Iminophosphorane-substituted Proton Sponges' comprises four publications. Part 1[1] described the crystallographic properties of neutral 1,8-diaminonaphthalene and its triphenylphosphoranylidene derivative. In Part 2,[2] the structures of three 'symmetrical' salts of type **I** (R = R′ = Ph and R = Ph, R′ = Me) were determined and discussed. Part 4 will deal with the physicochemical properties (^1H, ^{13}C, ^{15}N NMR spectra and pK_a values) and the relationship between these properties and the X-ray structure. In the present publication, salts of type **II** have been studied. These salts (**1** Br^-; **2** BF_4^-; **3** PF_6^-) were selected with two objectives: (i) to determine, in the competition for the 'proton', the relative basicities of the dimethylamino and the triphenylphosphoranylideneamino groups; and (ii) to study the influence of the anion on the molecular and crystal structure of this new class of 'proton sponge'. Previous work[2] pointed out that this effect could be important.



I



II

Table 1 Selected bond distances and angles/Å and °

	1	**2**	**3**
C(1)–C(2)	1.376(4)	1.378(4)	1.384(8)
C(1)–C(10)	1.444(3)	1.433(4)	1.427(8)
C(1)–N(11)	1.403(3)	1.413(4)	1.402(7)
C(2)–C(3)	1.403(4)	1.410(5)	1.398(9)
C(3)–C(4)	1.357(4)	1.349(5)	1.345(11)
C(4)–C(5)	1.417(4)	1.412(5)	1.412(9)
C(5)–C(6)	1.415(4)	1.417(5)	1.410(10)
C(5)–C(10)	1.429(4)	1.435(4)	1.439(9)
C(6)–C(7)	1.353(5)	1.355(6)	1.362(12)
C(7)–C(8)	1.401(5)	1.398(7)	1.370(13)
C(8)–C(9)	1.363(4)	1.370(5)	1.379(9)
C(9)–C(10)	1.429(4)	1.425(4)	1.427(8)
C(9)–N(31)	1.464(4)	1.460(4)	1.463(8)
N(11)–P(12)	1.601(2)	1.608(3)	1.618(5)
P(12)–C(13)	1.795(3)	1.791(3)	1.793(5)
P(12)–C(19)	1.797(3)	1.790(3)	1.790(6)
P(12)–C(25)	1.801(3)	1.799(3)	1.792(6)
N(31)–C(32)	1.479(5)	1.475(5)	1.479(9)
N(31)–C(33)	1.476(5)	1.470(6)	1.454(11)
C(1)–C(10)–C(5)	117.9(2)	117.2(3)	117.8(5)
C(9)–C(10)–C(5)	117.7(2)	117.9(3)	117.5(5)
C(10)–C(1)–N(11)	116.2(2)	116.7(2)	117.2(5)
C(2)–C(1)–N(11)	124.2(2)	122.9(3)	122.9(5)
C(8)–C(9)–N(31)	120.6(3)	120.7(3)	120.0(6)
C(10)–C(9)–N(31)	118.3(2)	118.4(3)	119.8(5)
C(1)–C(10)–C(9)	124.4(2)	124.9(3)	124.6(5)
C(1)–N(11)–P(12)	131.1(2)	130.7(2)	131.9(4)
N(11)–P(12)–C(13)	103.6(1)	104.4(1)	102.0(2)
N(11)–P(12)–C(19)	113.0(1)	112.7(1)	111.5(3)
N(11)–P(12)–C(25)	111.1(1)	110.7(1)	114.5(3)
C(9)–N(31)–C(32)	111.7(3)	111.2(3)	112.7(6)
C(9)–N(31)–C(33)	113.9(2)	115.1(3)	112.1(6)
C(32)–N(31)–C(33)	113.5(3)	111.7(3)	113.6(7)

Results and Discussion

The most relevant geometrical characteristics are listed in Tables 1 and 2. The molecular structures, showing the numbering system, are illustrated by ORTEP diagrams[3] in Fig. 1. The crystal structures of compounds **1** and **2** are pseudo-isomorphic (see the Experimental section), so their cations are superimposed in Fig. 1(*a*) for comparison purposes. Therefore, Fig. 1(*b*) only shows the differences between **1** and **3**. The bonding geometry within the core of the molecule is in good agreement with the values previously observed by us when two N=PPh₃ groups were the substituents at the '*peri*' positions.[2] The largest variations are associated with the relative position of the P(12) atom, the phenyl rings [Figs. 1(*a*) and (*b*)] and the twist of the dimethylamino group with respect to the naphthalene ring (Table 2). Less important variations are the N(11)–P(12) bonds, the different planarity of the naphthalene moieties [χ^2 = 538.87, 606.28 and 33.67 for **1**–**3**, respectively, *vs.* the tabulated value of 14.10] and the bending of the nitrogen atoms with respect to their mean-square planes, opposite side for compounds **1** and **2** and same side for compound **3** [ΔN(11), ΔN(31) = −0.060(2), 0.094(2); −0.110(3), 0.147(3); and 0.036(5), 0.030(5) Å]. The distortion of the naphthalene system has also been analysed by means of the torsion angles around the C(5)–C(10) bond,[4] Table 2. No significant twist of the rear-

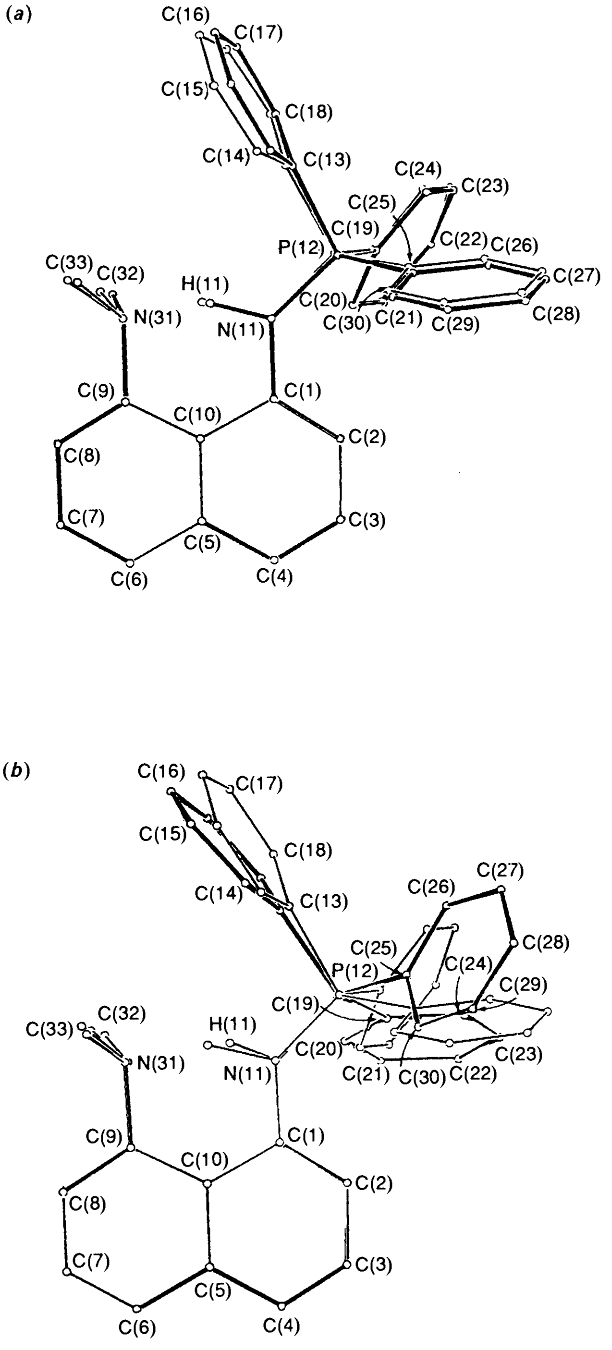


Fig. 1 Molecular structures[3] with the numbering system adopted in the crystallography work. Compounds **1** and **2**, (*a*), and compounds **1** and **3**, (*b*), are superimposed for comparison purposes. For sake of clarity only the H(31) atoms are shown. The thin lines correspond to compound **1**.

end substituent with respect to the front ones (χ_τ) was found for compound **3**.

For comparison purposes, a search in the Cambridge Structural Data Base[5] (CSD, 1991 January release) was performed looking for protonated and unprotonated 1,8-bis(dimethylamino)naphthalene derivatives (DMAN$^+$ and DMAN hereinafter). Only references where the proton was located were considered.[6–9] Two additional references[10,11] not included in the CSD were added. For these cations and those iminiphosphorane derivatives studied by us,[2] all the substituents but N(31) of **3** are splayed inward in opposite sense to that presented by the parent compound.[1]

The N(31) atoms, linked to the methyl groups, display an

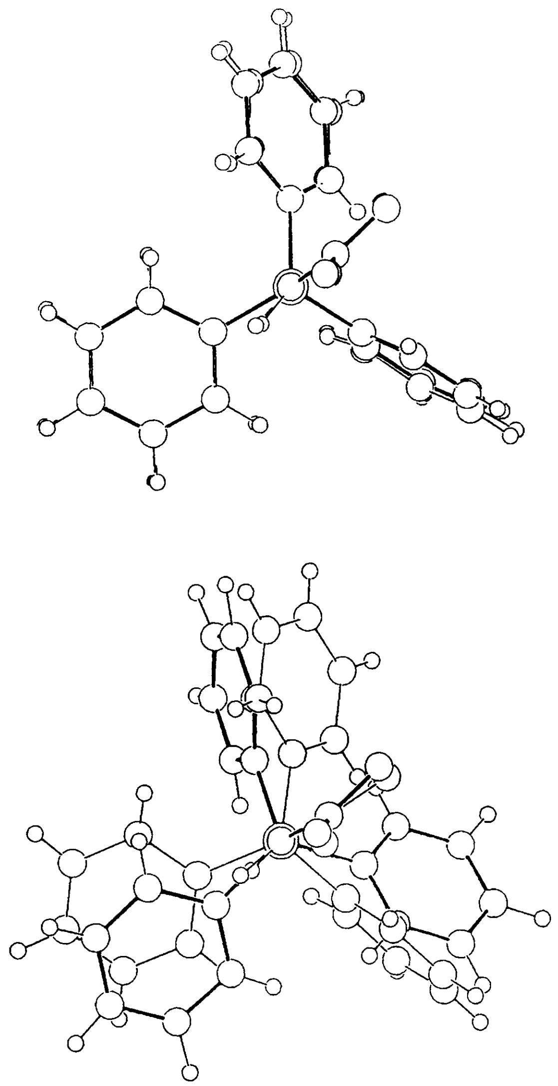


Fig. 2 Newman projections along the N(11)–P(12) bond.[3] For the sake of clarity, only the first three atoms of the naphthalene moiety are drawn. The superimposed drawing corresponds to compounds **1** and **2**, **1** and **3**, respectively. The thick lines correspond to compound **1**.

Table 2 Selected torsion angles and deformation parameters/° around the C(5)–C(10) and N(11)–P(12) bonds

	1	**2**	**3**
N(11)–C(1)–C(10)–C(5)	−178.6(2)	−176.6(3)	−178.9(5)
N(11)–C(1)–C(10)–C(9)	2.7(4)	4.1(4)	2.0(8)
N(31)–C(9)–C(10)–C(1)	2.0(4)	4.3(4)	−2.0(8)
N(31)–C(9)–C(10)–C(5)	−176.7(2)	−175.1(3)	179.0(5)
C(2)–C(1)–N(11)–P(12)	7.8(4)	9.6(4)	19.9(8)
C(4)–C(5)–C(10)–C(1)	−1.7(4)	−2.6(4)	0.6(9)
C(6)–C(5)–C(10)–C(1)	178.5(3)	177.6(3)	179.8(6)
C(6)–C(5)–C(10)–C(9)	−2.7(4)	−3.0(5)	−1.1(9)
C(4)–C(5)–C(10)–C(9)	177.1(3)	176.8(3)	179.8(6)
C(1)–N(11)–P(12)–C(13)	−174.7(2)	−174.9(3)	163.4(5)
C(1)–N(11)–P(12)–C(19)	68.3(3)	67.4(3)	43.4(6)
C(1)–N(11)–P(12)–C(25)	−55.3(3)	−55.8(3)	−81.3(6)
C(8)–C(9)–N(31)–C(32)	−71.9(4)	−80.0(4)	−65.6(8)
C(8)–C(9)–N(31)–C(33)	58.4(4)	48.2(5)	63.9(8)
χ_τ	−2.2(2)	−2.8(2)	−0.2(4)
$\chi_{1,9}$	−1.2(5)	−0.6(6)	−0.9(10)
$\chi_{4,6}$	−0.2(5)	−0.2(6)	0.9(10)
χ_τ	−53.9(2)	−54.4(2)	−78.2(3)
$\chi_{25.13}$	−0.6(4)	−0.9(4)	−4.7(8)
$\chi_{25.19}$	−3.6(4)	−3.2(4)	−4.7(9)
$\chi_{13,19}$	−3.0(4)	−2.3(4)	0.0(8)

Table 3 Hydrogen interactions. Numbers stand for symmetry operations and C(1–10), C(5–10), C(13–18), C(19–24) for the centroids of the corresponding phenyl rings.

X–H···Y	Interatomic distances/Å			
	X–H	X···Y	H···Y	X–H···Y/°
1				
N(11)–H(11)···N(31)	1.20 (7)	2.519(3)	1.38(7)	154(6)
C(22)–H(22)···Br(1)$_1$	0.97(5)	3.825(4)	2.87(5)	168(4)
C(32)–H(323)···Br(1)$_2$	1.07(7)	3.983(5)	2.97(7)	158(5)
C(33)–H(332)···Br(1)	1.05(7)	3.917(5)	2.93(7)	157(5)
C(24)–H(24)–C(1–10)$_3$	0.95(4)	3.709(3)	2.94(4)	139(3)
C(16)–H(16)···C(19–24)$_4$	1.00(5)	3.757(4)	2.76(5)	173(4)
1: $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; 2: $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; 3: $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; 4: $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$				
2				
N(11)–H(11)···N(31)	1.09(6)	2.543(4)	1.51(6)	155(6)
C(22)–H(22)···F(3)$_1$	1.07(5)	3.354(6)	2.46(5)	140(3)
C(29)–H(29)···F(4)$_2$	0.92(4)	3.255(6)	2.54(4)	135(3)
C(32)–H(323)···F(2)$_3$	1.06(6)	3.474(6)	2.54(6)	146(4)
C(33)–H(332)···F(1)	1.08(5)	3.234(7)	2.36(5)	137(4)
C(24)–H(24)···C(1–10)$_4$	1.00(4)	3.801(4)	3.01(4)	137(3)
C(16)–H(16)···C(19–24)$_5$	1.03(5)	3.745(4)	2.72(5)	172(4)
1: $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; 2: $-x, -y, 1-z$; 3: $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; 4: $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; 5: $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$				
3				
N(11)–H(11)··N(31)	0.87(6)	2.571(6)	1.80(6)	147(6)
C(2)–H(2)···F(2)	1.04(8)	3.459(9)	2.77(8)	123(5)
C(7)–H(7)···F(6)$_1$	1.00(9)	3.201(13)	2.21(9)	170(7)
C(16)–H(16)···F(4)$_2$	0.99(7)	3.415(10)	2.43(7)	177(6)
C(16)–H(16)···F(3)$_2$	0.99(7)	3.364(9)	2.67(8)	128(5)
C(17)–H(17)···F(1)$_3$	1.14(7)	3.382(10)	2.65(7)	121(5)
C(20)–H(20)···F(3)$_3$	0.98(7)	3.240(10)	2.41(7)	141(6)
C(23)–H(23)···F(4)$_4$	1.02(13)	3.458(13)	2.83(14)	121(10)
C(24)–H(24)···F(5)$_5$	0.93(8)	3.227(11)	2.69(8)	117(6)
C(27)–H(27)···F(4)$_5$	1.02(9)	3.422(12)	2.78(9)	121(7)
C(28)–H(28)···F(2)$_6$	1.06(8)	3.404(11)	2.84(8)	114(5)
C(28)–H(28)···F(5)$_6$	1.06(8)	3.495(12)	2.60(7)	142(5)
C(29)–H(29)···F(6)	1.18(15)	3.581(14)	2.96(18)	113(11)
C(32)–H(322)···F(3)$_3$	1.20(9)	3.408(11)	2.76(9)	113(5)
C(33)–H(333)···F(1)$_7$	0.86(10)	3.695(12)	2.89(10)	156(9)
C(4)–H(4)···C(5–10)$_1$	1.02(8)	3.870(7)	2.89(7)	162(6)
C(14)–H(14)···C(1–10)$_6$	0.91(6)	3.750(7)	3.08(6)	132(5)
C(21)–H(21)···C(13–18)$_8$	0.95(9)	3.617(8)	3.04(9)	121(6)
1: $\frac{1}{2}-x, 1+y, \frac{1}{2}+z$; 2: $-\frac{1}{2}+x, \frac{1}{2}-y, -z$; 3: $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; 4: $\frac{1}{2}-x, -y, \frac{1}{2}+z$; 5: $\frac{1}{2}-x, -y, -\frac{1}{2}+z$; 6: $x, y, -1+z$; 7: $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$; 8: $x, y, 1+z$				

sp^3 hybridization, the mean angles are 113.0(1), 112.7(2) and 112.8(4)°, greater than the tetrahedral one. The differences between both C(9)–N(31)–Me angles (Table 2) can be ascribed to steric factors, as reflected by the C(8)–C(9)–N(31)–C(32)/C(33) torsion angles; the lower the torsion angle, the greater the bond angle. DMAN$^+$ compounds present a similar situation.

The 'proton' was always found to be bonded to the nitrogen atom of the iminophosphorane group, instead of to the nitrogen of the dimethylamino one. This situation is probably a consequence of the higher basicity of the iminophosphorane group compared with the amino one.[12]

The Newman views along the N–P bonds are shown in Fig. 2. As was previously observed,[2] the corresponding Br$^-$ and PF_6^- salts display conformations close to the parallel one ($\chi_\tau = \pm 60$ or 180°) and to the perpendicular one ($\chi_\tau = \pm 30$ or $+90$ or ± 150°), respectively[13] (Table 2). A twist of *ca.* 24° makes both conformations coincident. The sum of the internal angles around N(11) are 359(4), 359(4) and 358(6)°, showing that no pyramidalization is present in terms of the achieved precision.

The hydrogen interactions are detailed in Table 3 and the most relevant ones are illustrated in the packing diagrams of Fig. 3. The $[N–H\cdots N]^+$ intramolecular hydrogen bond strength is measured by the N···N distance, which is shorter than those observed by us[2] for the bis(triphenylphosphoranilydeneammonio)naphthalene salts [2.585(4), 2.606(4) Å] and falls for compounds **1** and **2** [2.519(3), 2.543(4) Å] out of the range (2.562–2.654 Å) observed for the seven DMAN$^+$ naphthalene derivatives (where the proton was located), which are considered as 'proton sponges'.[14] The last distances are significantly shorter than those for the corresponding unprotonated cases (2.756–2.792 Å).[15,16,5] The scarce information gathered from the CSD[5] concerning the sp^2N^+–H and sp^3N^+–H fragments (11 and 2 hits, respectively) concerning neutron data revealed that no significant differences could be found between both N–H bonds.

If the lone pair on N(31) is situated geometrically with regard to C(9), C(32) and C(33), then it appears that it is near the ideal position at which to form an hydrogen bond with H(11). The 'proton' deviates, φ_1 and φ_2, from the lone-pair direction

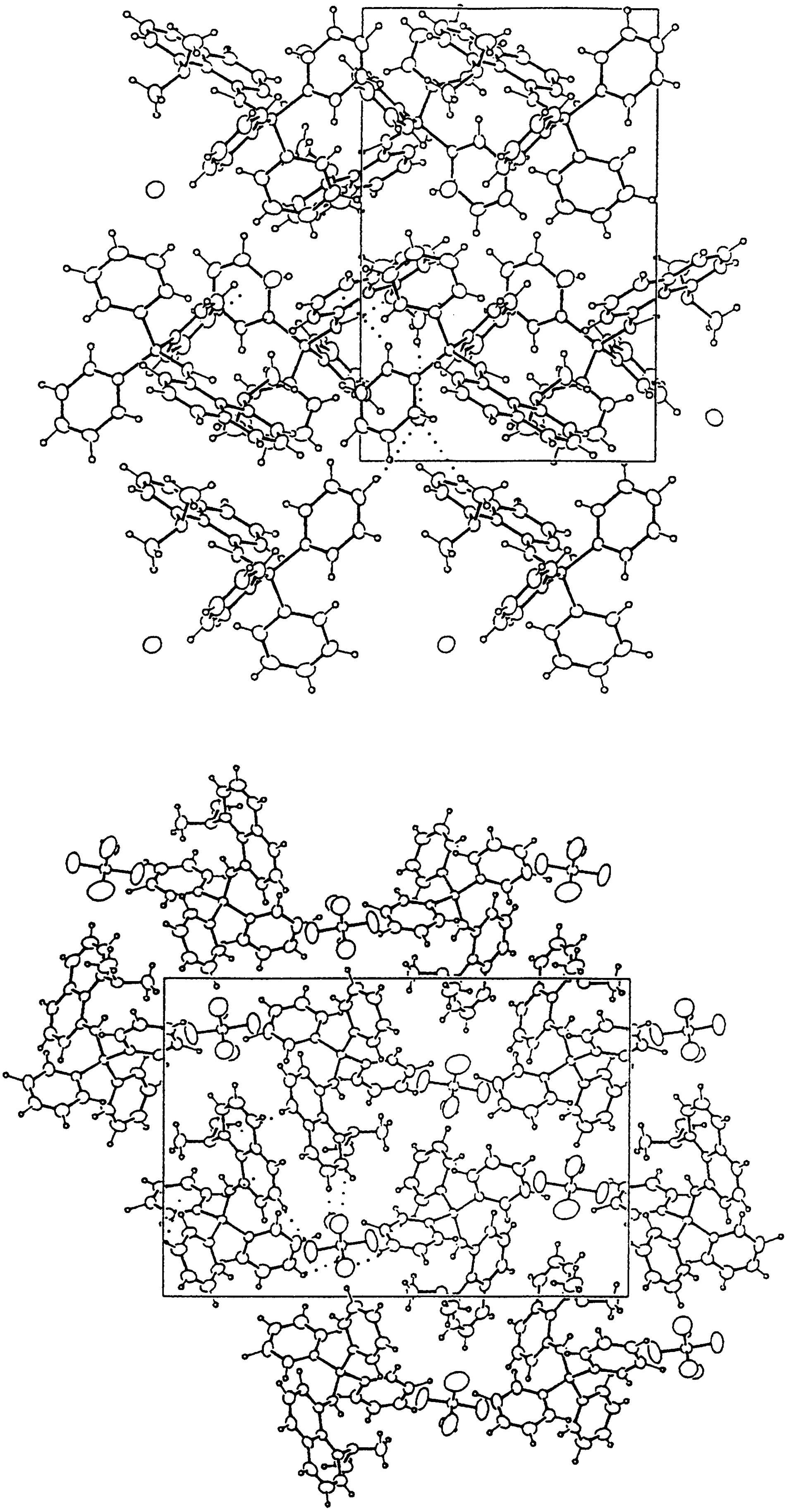


Fig. 3 Crystal packing[3] along the *c* axis (compounds **1** and **3**), showing the most relevant independent contacts. Ellipsoids are drawn at the 30% probability level while hydrogen atoms are represented by spheres (radius = 0.1 Å).

Table 4 Crystal analysis parameters at room temperature

	1	**2**	**3**
Crystal data			
Formula	$C_{30}H_{28}N_2P^+Br^-$	$C_{30}H_{28}N_2P^+BF_4^-$	$C_{30}H_{28}N_2P^+PF_6^-$
Crystal habit	Colourless prism	Colourless prism	Colourless plate
Crystal size/mm	0.30 × 0.30 × 0.23	0.33 × 0.23 × 0.17	0.43 × 0.17 × 0.07
Symmetry	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Orthorhombic, $P2_12_12_1$
Unit cell determination:	Least-squares fit from 96 reflections ($\theta < 45^\circ$)	Least-squares fit from 60 reflections ($\theta < 45^\circ$)	Least-squares fit from 89 reflections ($\theta < 45^\circ$)
Unit cell dimensions/Å,	a = 11.3348(3)	a = 11.5221(4)	a = 23.2560(13)
	b = 17.1557(8)	b = 17.8581(9)	b = 15.4752(6)
	c = 13.0835(4)	c = 13.0051(5)	c = 7.8485(2)
	90, 91.688(3), 90	90, 91.548(4), 90	90, 90, 90
Packing: V/Å^3, Z	2543.1(2), 4	2675.0(2), 4	2824.6(2), 4
D_c/g cm^{-3}, M, F(000)	1.378, 527.44, 1088	1.327, 534.34, 1112	1.393, 592.50, 1224
μ/cm^{-1}	29.617	13.309	19.604
Experimental data			
Technique	Four-circle diffractometer: Philips PW1100, Bisecting geometry Graphite oriented monochromator: CuKα $\omega/2\theta$ scans, scan width: 1.5° Detector apertures 1 × 1°. 1 min./reflect., θ_{max} = 65		
Number of reflections:			
Independent	4352	4569	2745
Observed	3995 [$3\sigma(I)$ criterion]	3753 [$3\sigma(I)$ criterion]	2318 [$3\sigma(I)$ criterion]
Standard reflections:	2 reflections every 90 min. No variation		
Max.-min. transmission factors	1.143–0.858	1.208–0.674	1.119–0.656
Solution and refinement			
Solution	PATTERSON + DIRDIF	See text	SIR88 + DIRDIF
Refinement:			
Least-squares on F_0	Full-matrix	2 blocks	2 blocks
Parameters:			
Number of variables	419	455	473
Degrees of freedom	3576	3298	1845
Ratio of freedom	9.5	8.3	4.9
Hydrogen atoms	From difference synthesis (see text)		
Final shift/error	0.05	0.05	0.16
Weighting-scheme	Empirical as to give no trends in $\langle \omega\Delta^2F \rangle$ *vs.* $\langle \lvert F_{obs} \rvert \rangle$ and $\langle \sin\theta/\lambda \rangle$		
Max. thermal value	$U11$[C(32)] = 0.115(4) Å^2	$U33$[F(2)] = 0.219(4) Å^2	$U11$[F(6)] = 0.29(1) Å^2
Final ΔF peaks	0.50 e Å^{-3} near Br(1)	0.53 e Å^{-3} near F(2)	0.56 e Å^{-3} near F(6)
Final R and R_w	0.044, 0.049	0.059, 0.071	0.055, 0.066

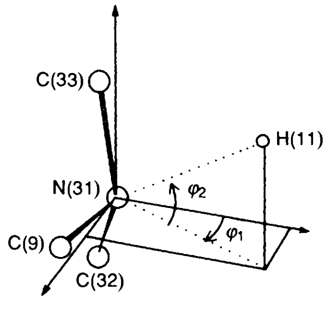


Fig. 4 N(31) ··· H(11) hydrogen bond orientation

($\varphi_1 = \varphi_2 = 0$), by 5.7, −3.3°; 8.0, −9.0° and 9.1, 0.1° for compounds **1**–**3**, respectively (Fig. 4).

The ions in the crystals are held by C–H ··· Br/F interactions and phenyl–phenyl contacts of type 'T'[17] (Table 3). Some naphthalenes, **1** and **2**, overlap through a symmetry centre, Fig. 3(*a*). The distance between their planes are 3.575(1) and 3.659(2) Å, while the glide between the respective centroids are 1.569 and 1.807 Å, respectively. Both pseudo-isomorphic salts present a similar hydrogen interaction network (Table 3). The H(332), H(323) and H(22) atoms appear to be bonded to the Br$^-$ anion in **1** whilst in **2** they interact with F(2), F(1) and F(3), respectively. An extra contact involving F(4) is present in **2**. Thus, all of the fluorine atoms are involved in this type of contact. For comparison purposes, the anion involved in the C(33) ··· Br/F interaction has been plotted in Fig. 5 showing the difference situation of the ions pairs in the three salts.

In all the salts the anions are located in isolated cavities,[18] almost spherical in shape, with radii 1.94, 2.60 and 2.92 Å approximately. The local packing coefficients, ($C_k = V_{anion}/V_{hole}$), are 0.705, 0.748 and 0.628 for **1**–**3**, respectively. If the BF_4^- and PF_6^- anions are also considered to be spheres, their estimated volumes yield radii of 2.33 and 2.61 Å, respectively. As the BF_4^- size is greater than that of the Br^- cavity, the cell constants increase their values up to 4% to accommodate the anion without modifying the packing (see above). However, although a similar radii relationship takes place between BF_4^- and PF_6^- anions, the molecules pack so as to change completely the symmetry (see Experimental). The cations are situated in such a way that all phenyl rings, and some atoms of the naphthalene moiety, are involved in hydrogen interactions (Table 3). Thus, the significant increase of the N ··· N distance could be due to the size of the anion. Although less remarkable, such influence (Br^-,[19] BF_4^- [11] and $TeOF_5^-$ [8] anions) can be noticed in DMAN$^+$ cations [2.555(3), 2.562(2) and 2.574(3) Å, respectively].

Experimental

M.p.s were determined with a Köfler hot-stage microscope and are uncorrected. Spectral studies were performed with the following instruments: IR, Nicolet FT-5DX; ^1H and ^{13}C NMR, Bruker AC-200 ($SiMe_4$ internal reference; all chemical shifts are expressed as δ values and coupling constants in Hz).

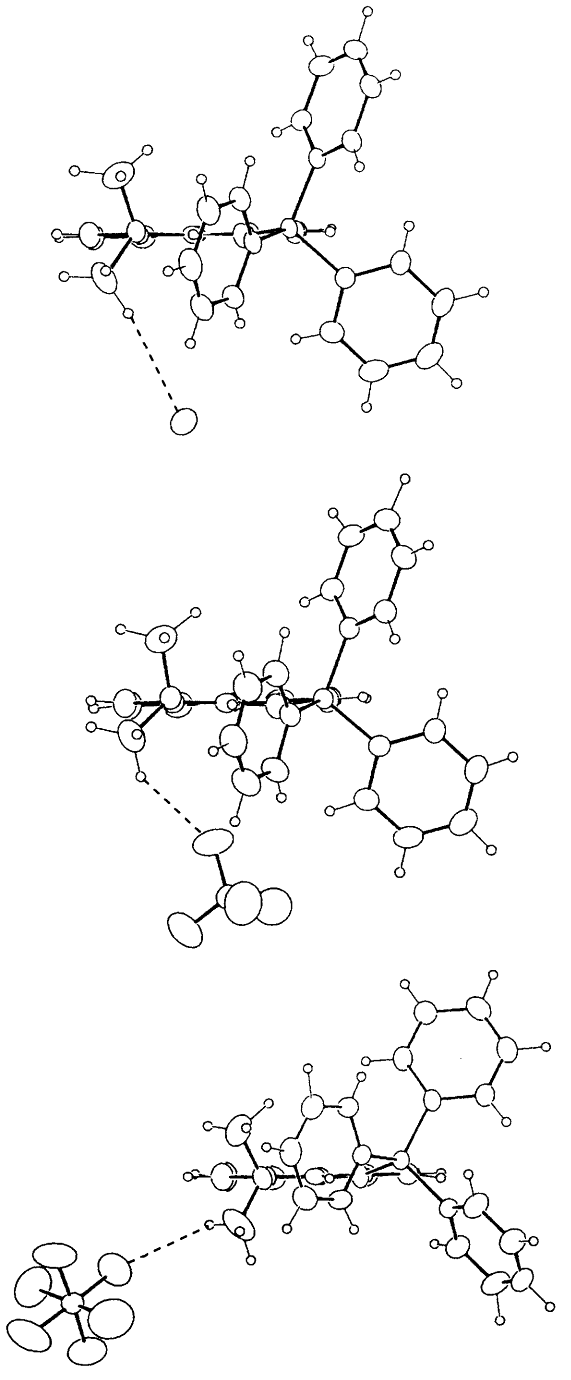


Fig. 5 Perspective view[3] of the molecules showing the naphthalene distortions and the relative situation of the iminophosphorane group for compounds **1**–**3**. Thermal ellipsoids for the non-hydrogen atoms are depicted at the 30% probability level while hydrogen atoms are represented by spheres (radius = 0.1 Å).

Table 5 Final atomic coordinates for compound **1**

Atom	*x*	*y*	*z*
C(1)	−0.077 4(2)	0.327 9(2)	0.424 8(2)
C(2)	−0.162 2(3)	0.318 4(2)	0.496 9(2)
C(3)	−0.148 6(3)	0.350 1(2)	0.595 4(2)
C(4)	−0.050 0(3)	0.390 9(2)	0.622 0(2)
C(5)	0.040 6(3)	0.402 9(2)	0.551 3(2)
C(6)	0.144 2(3)	0.444 9(2)	0.578 8(3)
C(7)	0.228 9(3)	0.458 4(2)	0.510 2(3)
C(8)	0.215 6(3)	0.431 2(2)	0.409 5(3)
C(9)	0.118 7(2)	0.388 9(2)	0.380 0(2)
C(10)	0.027 7(2)	0.372 3(1)	0.450 1(2)
N(11)	−0.085 6(2)	0.297 3(1)	0.325 4(2)
P(12)	−0.192 12(5)	0.254 60(4)	0.264 92(5)
C(13)	−0.128 1(2)	0.225 2(2)	0.147 2(2)
C(14)	−0.041 0(3)	0.167 9(2)	0.149 7(3)
C(15)	0.013 8(3)	0.148 3(2)	0.059 7(3)
C(16)	−0.017 2(3)	0.184 2(3)	−0.030 3(3)
C(17)	−0.101 2(3)	0.242 4(3)	−0.033 1(3)
C(18)	−0.157 8(3)	0.262 8(2)	0.055 4(2)
C(19)	−0.314 0(2)	0.318 6(2)	0.235 5(2)
C(20)	−0.312 3(3)	0.393 0(2)	0.276 9(2)
C(21)	−0.404 2(3)	0.444 5(2)	0.254 2(3)
C(22)	−0.495 5(3)	0.421 8(2)	0.189 7(3)
C(23)	−0.497 3(3)	0.348 8(2)	0.147 0(3)
C(24)	−0.406 8(3)	0.296 1(2)	0.169 5(2)
C(25)	−0.243 4(2)	0.171 6(2)	0.335 2(2)
C(26)	−0.362 8(3)	0.154 4(2)	0.342 1(2)
C(27)	−0.398 3(4)	0.089 7(2)	0.398 1(3)
C(28)	−0.315 8(4)	0.042 8(2)	0.446 3(3)
C(29)	−0.196 5(4)	0.060 2(2)	0.440 9(3)
C(30)	−0.160 2(3)	0.124 4(2)	0.386 2(2)
N(31)	0.103 6(2)	0.361 6(1)	0.274 5(2)
C(32)	0.074 8(5)	0.426 3(3)	0.203 4(3)
C(33)	0.200 7(3)	0.311 5(3)	0.240 2(4)
Br(1)	0.198 49(4)	0.098 38(3)	0.347 61(3)

Combustion analyses were performed with a Perkin-Elmer 240C instrument. The compounds were dried in an oven at 50 °C under vacuum for 24 h.

X-Ray Crystallography.—Table 4 contains the main characteristics of the data collection and refinement process. Due to the similarity in the unit cell parameters and space group symmetry of compounds **1** and **2**, the structure of compound **2** was solved using as an initial phasing model that obtained from just the cation coordinates of compound **1**. The corresponding difference Fourier map yielded all the anion positions. Once the refinement was completed, the pseudo-isomorphism was checked by means of full normal probability methods.[20] Apart from the scale factor between data, quite linear plots were obtained when the observed spectra were compared (correlation coefficient: $\rho = 0.993$, for all the 4349 common F_0 reflections). When the atomic coordinates were compared, the main differences were those concerning the position of the phenyl rings [(see Fig. 1(*a*)]. If U_{ij} values are analysed it is found that compound **2** (BF_4^- salt) presents higher U_{ii} values than those of the compound **1** (Br^- salt), except U_{11} for the C(27), C(28), C(29) and C(32) atoms which are more alike in both sets of data.

All the hydrogen atoms were obtained from a ΔF synthesis. The position of the 'extra proton', H(11), was unambiguously determined from difference synthesis computed using only data up to $\theta = 32°$.

The final atomic coordinates for the non-hydrogen atoms are reported in Tables 5–7. In spite of the high thermal values of the BF_4^- and PF_6^- anions, no disorder models could be obtained. Most of the calculations were performed on a VAX 6410 computer using the following set of programs: SIR88,[21] DIRDIF,[22] XRAY80,[23] XTAL3.0,[3] and PESOS.[24] Empirical absorption correction for all compounds were performed using the program DIFABS[25] and the scattering factors were taken from the *International Tables for X-Ray Crystallography*.[26,*]

Materials.—8-Amino-1-dimethylaminonaphthalene.[27] This was prepared from 1-aminonaphthalene by standard chemistry: nitration, methylation and finally, reduction.

1-*Dimethylamino*-8-*triphenylphosphoranilidenammonionaph-*

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[*] Lists of thermal components, hydrogen parameters and bond distances and bond angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.

Table 6 Final atomic coordinates for compound **2**

Atom	*x*	*y*	*z*
C(1)	−0.074 0(2)	0.328 5(2)	0.417 9(2)
C(2)	−0.158 5(3)	0.317 4(2)	0.489 3(2)
C(3)	−0.146 0(3)	0.347 5(2)	0.589 2(3)
C(4)	−0.050 6(3)	0.387 1(2)	0.617 1(2)
C(5)	0.037 7(3)	0.400 9(2)	0.546 2(3)
C(6)	0.137 9(4)	0.442 4(2)	0.575 5(3)
C(7)	0.220 5(4)	0.457 6(3)	0.506 3(4)
C(8)	0.209 8(3)	0.432 8(2)	0.404 5(3)
C(9)	0.115 2(3)	0.391 4(2)	0.373 1(3)
C(10)	0.026 6(3)	0.372 8(2)	0.443 0(2)
N(11)	−0.080 7(2)	0.297 7(2)	0.317 8(2)
P(12)	−0.185 76(6)	0.255 86(4)	0.257 63(5)
C(13)	−0.124 6(2)	0.225 7(2)	0.139 5(2)
C(14)	−0.043 2(3)	0.167 6(2)	0.141 6(3)
C(15)	0.009 7(4)	0.147 2(3)	0.051 5(4)
C(16)	−0.019 1(4)	0.182 6(3)	−0.039 6(3)
C(17)	−0.097 9(4)	0.239 7(3)	−0.042 5(3)
C(18)	−0.150 9(3)	0.261 9(2)	0.047 6(3)
C(19)	−0.305 5(2)	0.316 8(2)	0.228 3(2)
C(20)	−0.304 2(3)	0.389 2(2)	0.268 0(3)
C(21)	−0.395 3(3)	0.437 3(2)	0.245 3(3)
C(22)	−0.487 1(3)	0.414 1(2)	0.182 5(3)
C(23)	−0.488 5(3)	0.343 1(2)	0.142 1(3)
C(24)	−0.398 0(3)	0.293 8(2)	0.164 4(3)
C(25)	−0.235 2(3)	0.176 8(2)	0.330 3(2)
C(26)	−0.352 1(3)	0.158 8(2)	0.337 1(3)
C(27)	−0.384 1(3)	0.096 3(2)	0.392 9(3)
C(28)	−0.302 1(4)	0.052 0(2)	0.440 8(3)
C(29)	−0.185 9(4)	0.070 4(2)	0.435 2(3)
C(30)	−0.151 6(3)	0.132 7(2)	0.381 2(3)
N(31)	0.100 1(2)	0.368 4(2)	0.265 8(2)
C(32)	0.052 8(4)	0.430 0(3)	0.201 9(3)
C(33)	0.203 1(4)	0.334 5(3)	0.220 4(5)
B(1)	0.196 3(4)	0.100 7(2)	0.348 3(3)
F(1)	0.168 9(4)	0.172 7(2)	0.326 8(4)
F(2)	0.310 7(3)	0.095 1(2)	0.368 1(4)
F(3)	0.162 9(4)	0.058 2(2)	0.266 1(3)
F(4)	0.134 0(4)	0.079 2(3)	0.428 1(3)

thalene Bromide (**1**). Bromine (0.80 g, 5 mmol) in dry benzene (10 cm^3) was added dropwise to a stirred solution of triphenylphosphine (1.31 g, 5 mmol) in the same solvent (25 cm^3) at 0 °C under nitrogen. The mixture was stirred for 1 h and then allowed to warm to room temperature. A solution of 8-amino-1-dimethylaminonaphthalene (0.93 g, 5 mmol) and triethylamine (1.01 g, 10 mmol) in dry benzene (20 cm^3) was added. The reaction mixture was heated at reflux temperature for 12 h. After being cooled, the precipitated solid was collected by filtration and washed with cold water (2 × 15 cm^3). The remaining solid was filtered, air-dried and recrystallized from dichloromethane–ether (1:1) to give **1** in 56% yield, m.p. 255–257 °C (Found: C, 68.15; H, 5.6; N, 5.25. $C_{30}H_{28}BrN_2P$ requires: C, 68.31; H, 5.35; N, 5.31%); ν_{max}(Nujol)/cm^{-1} 1579(m), 1436(vs), 1288(s), 1263(m), 1130(m), 1117(s), 821(m), 772(m), 753(s), 742(s) and 727(s); δ_H(CDCl$_3$) 2.85 (s, 3 H), 2.86 (s, 3 H), 6.42 (d, 1 H, *J* 7.5), 7.10 (t, 1 H, *J* 7.9), 7.40 (d, 1 H, *J* 8.6), 7.56 (t, 1 H, *J* 7.9), 7.69–7.93 (m, 17 H) and 18.30 (s, 1 H, NH); δ_C(CDCl$_3$) 45.78 (CH$_3$N), 114.83 [$^3J_{PC}$ 7.2, C(7)], 118.81 [$^3J_{PC}$ 11.6, C(8a)], 119.88 [C(5)], 121.34 [C(2)], 122.64 [$^1J_{PC}$ 101.3, C(*i*)], 126.14 and 126.52 [C(3) and C(6)],* 128.57 [C(4)], 130.71 [$^3J_{PC}$ 12.9, C(*m*)], 132.42 [$^2J_{PC}$ 10.6, C(*o*)], 134.72 [$^4J_{PC}$ 2.9, C(*p*)], 135.71 [$^4J_{PC}$ 1.5, C(4a)], 140.20 [$^2J_{PC}$ 3.5, C(8)] and 145.63 [$^4J_{PC}$ 1.4, C(1)].

Preparation of Compounds **2** *and* **3**.—To a well-stirred solution of compound **1** (0.527 g, 1 mmol) in ethanol (15 cm^3) was added dropwise a solution of 50% aqueous tetrafluoroboric acid (0.155 cm^3, 1.25 mmol) for compound **2** or potassium hexafluorophosphate (0.23 g, 1.25 mmol) in water (5 cm^3) for compound **3**. The resultant mixture was stirred at room temperature for 2 h. The precipitated solid was collected by filtration, washed with water (3 × 10 cm^3), air-dried and recrystallized from ethanol to give **2** and **3**.

Table 7 Final atomic coordinates for compound **3**

Atom	*x*	*y*	*z*
C(1)	0.170 3(2)	0.354 4(4)	0.472 6(7)
C(2)	0.205 0(3)	0.296 9(4)	0.560 3(8)
C(3)	0.233 9(3)	0.322 3(5)	0.708 0(9)
C(4)	0.229 4(3)	0.403 3(5)	0.768 7(9)
C(5)	0.193 9(3)	0.464 5(4)	0.686 5(8)
C(6)	0.188 1(4)	0.549 3(5)	0.749 7(11)
C(7)	0.152 7(4)	0.607 4(5)	0.672 3(13)
C(8)	0.123 3(4)	0.585 6(4)	0.527 4(11)
C(9)	0.128 0(3)	0.504 6(4)	0.456 0(8)
C(10)	0.163 5(2)	0.440 6(4)	0.533 9(8)
N(11)	0.141 3(2)	0.332 4(3)	0.322 1(6)
P(12)	0.123 57(5)	0.240 04(7)	0.241 01(17)
C(13)	0.070 4(2)	0.270 5(3)	0.086 9(7)
C(14)	0.089 3(3)	0.319 4(5)	−0.050 1(8)
C(15)	0.050 2(3)	0.353 8(5)	−0.162 3(9)
C(16)	−0.007 9(3)	0.340 9(4)	−0.140 1(9)
C(17)	−0.026 6(3)	0.292 3(4)	−0.005 4(9)
C(18)	0.011 7(2)	0.257 2(4)	0.111 7(8)
C(19)	0.095 4(2)	0.168 5(3)	0.399 6(8)
C(20)	0.053 4(3)	0.198 8(4)	0.510 5(8)
C(21)	0.031 8(4)	0.146 1(5)	0.636 7(10)
C(22)	0.052 4(4)	0.062 3(5)	0.652 9(11)
C(23)	0.093 6(4)	0.033 4(5)	0.544 1(14)
C(24)	0.114 5(3)	0.084 4(4)	0.415 8(12)
C(25)	0.180 4(2)	0.186 8(3)	0.127 8(8)
C(26)	0.166 4(3)	0.121 5(5)	0.012 6(12)
C(27)	0.209 0(4)	0.079 1(5)	−0.074 1(12)
C(28)	0.265 4(3)	0.101 5(5)	−0.045 7(11)
C(29)	0.279 6(3)	0.165 5(6)	0.062 2(12)
C(30)	0.236 9(3)	0.209 6(5)	0.153 4(9)
N(31)	0.096 9(2)	0.484 2(3)	0.299 0(7)
C(32)	0.033 8(3)	0.485 1(6)	0.322 2(15)
C(33)	0.116 4(5)	0.536 2(6)	0.156 0(12)
P(1)	0.377 44(7)	0.160 27(10)	0.547 33(20)
F(1)	0.372 5(3)	0.226 6(5)	0.697 4(10)
F(2)	0.311 6(2)	0.141 1(6)	0.550 3(9)
F(3)	0.443 8(2)	0.174 8(5)	0.542 9(8)
F(4)	0.383 5(3)	0.092 4(6)	0.401 8(10)
F(5)	0.385 9(4)	0.089 5(5)	0.688 9(11)
F(6)	0.368 6(5)	0.228 7(6)	0.413 1(13)

1-*Dimethylamino*-8-*triphenylphosphoranylideneammonionaphthalene tetrafluoroborate* (**2**). Yield 92%; m.p. 280–281 °C (Found: 67.2; H, 5.4; N, 5.2. $C_{30}H_{28}BF_4N_2P$ requires: C, 67.43; H, 5.28; N, 5.24%); ν_{max}(Nujol)/cm^{-1} 1580(m), 1443(s), 1286(s), 1265(m), 1110(s), 1061(vs), 767(s), 750(m) and 728(s); δ_H([$^2H_6$]DMSO) 2.81 (s, 3 H), 2.82 (s, 3 H), 6.38 (d, 1 H, *J* 7.5), 7.15 (t, 1 H, *J* 7.8), 7.44 (d, 1 H, *J* 8.3), 7.62 (t, 1 H, *J* 7.8), 7.73–7.97 (m, 17 H), 18.43 (s, 1 H, NH); δ_C([$^2H_6$]DMSO) 45.35 (CH$_3$N), 114.72 [$^3J_{PC}$ 8.0, C(7)], 118.88 [$^3J_{PC}$ 12.3, C(8a)], 119.36 [C(5)], 120.39 [C(2)], 123.10 [$^1J_{PC}$ 101.4, C(*i*)], 126.39 and 126.57 [C(3) and C(6)],* 128.51 [C(4)], 130.11 [$^3J_{PC}$ 12.8, C(*m*)], 132.71 [$^2J_{PC}$ 10.9, C(*o*)], 134.43 [$^4J_{PC}$ 2.9, C(*p*)], 135.51 [$^4J_{PC}$ 1.6, C(4a)], 141.31 [$^2J_{PC}$ 3.3, C(8)] and 145.79 [$^4J_{PC}$ 1.4, C(1)].

1-*Dimethylamino*-8-*triphenylphosphoranylideneammonionaphthalene hexafluorophosphate* (**3**). Yield 87%, m.p. 291–292 °C (Found: C, 61.0; H, 4.6; N, 4.6. $C_{30}H_{28}F_6N_2P_2$ requires: C, 60.81; H, 4.76; N, 4.73%); ν_{max}(Nujol)/cm^{-1} 1578(m), 1440(vs), 1286(m), 1117(s), 1063(m), 840(vs), 769(s), 746(m) and 728(s); δ_H([$^2H_6$]DMSO) 2.50 (s, 3 H), 2.51 (s, 3 H), 6.40 (d, 1 H, *J* 7.5), 7.15 (t, 1 H, *J* 7.9), 7.44 (d, 1 H, *J* 8.3), 7.62 (t, 1 H, *J* 7.8), 7.78–7.98 (m, 17 H) and 18.43 (s, 1 H, NH); δ_C([$^2H_6$]DMSO) 45.36 (CH$_3$N), 114.73 [$^3J_{PC}$ 8.0, C(7)], 118.89 [$^3J_{PC}$ 12.3, C(8a)],

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* Assignments interchangeable.

119.36 [C(5)], 120.44 [C(2)], 123.08 [$^1J_{PC}$ 101.4, C(*i*)], 126.40 and 126.56 [C(3) and C(6)],* 128.51 [C(4)], 130.11 [$^3J_{PC}$ 12.8, C(*m*)], 132.72 [$^2J_{PC}$ 10.9, C(*o*)], 134.44 [$^4J_{PC}$ 2.8, C(*p*)], 135.53 [$^4J_{PC}$ 1.8, C(4a)], 141.26 [$^2J_{PC}$ 3.1, C(8)] and 145.84 [$^4J_{PC}$ 1.4, C(1)].

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* Assignments interchangeable.

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