Iminophosphorane-substituted Proton Sponges. Part 2.[1] Preparation and Crystal Structure of Four Phosphoranylideneammonionaphthalene Derivatives

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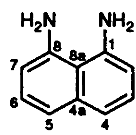
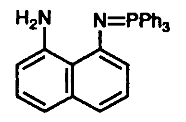
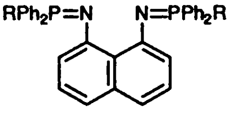
Crystal structure analysis of salts of one monosubstituted (**1**) and three *peri* disubstituted naphthalene derivatives (**2**, **3** and **4**) are described. The strong repulsion between the nitrogen lone pairs in neutral structures is replaced by an intramolecular N^+–H ··· N interaction in compounds **2**, **3** and **4** giving rise to a similar distortion in the naphthalene skeleton in each case, an inward bending of the exocyclic C_{aryl}–N bonds and a decrease of the N ··· N distance: [2.606(4)–2.533(6) Å] *versus* 2.792(3) Å found in 1,8-bis(*N,N*-dimethyl)naphthalene and 2.716(11) and 2.739(10) Å in 1,8-diaminonaphthalene. This behaviour is characteristic of proton sponges.

In Part 1 of this series,[1] we described the X-ray crystal and molecular structures of 1,8-diaminonaphthalene and 1-amino-8-triphenylphosphoranylideneaminonaphthalene.

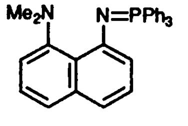




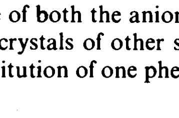
In this paper, we will discuss the structure of salts derived from symmetrical bis-iminophosphorane derivatives whilst structural features of (1-dimethylamino-8-triphenylphosphoranylideneammonionaphthalene salts) will be published in a following paper.



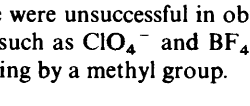
R = Ph or Me



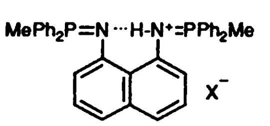
In order to have a model of the naphthalene ring and of the protonated iminophosphorane, compound **1** was selected. Two structures of the triphenyl series, **2** and **3**, and one derivative of the diphenylmethyl series **4** were studied to determine the influence of both the anion (we were unsuccessful in obtaining suitable crystals of other salts such as ClO_4^- and BF_4^-) and the substitution of one phenyl ring by a methyl group.



1; $X^- = BF_4^-$



2; $X^- = Br^-$
3; $X^- = PF_6^-$



4; $X^- = Br^-$

Results and Discussion

Selected bond distances and angles are reported in Table 1, according to the numbering system shown in Fig. 1. For comparison purposes, molecules **2** and **3**, in Fig. 1(*b*), and **4A** and **4B**, in Fig. 1(*c*), are superimposed. Due to the differences between compounds **2** and **3** (see below), Fig. 1(*d*) and 1(*e*) show stereoscopic views of the corresponding molecules.

The main geometrical differences between the mono- and disubstituted compounds (**1** *vs.* **2**–**4**) can be summarized as follows: in compound **1** no distortion from planarity was observed in the naphthalene ring [χ^2 = 5.62 *vs.* the tabulated value of 14.10 compared with χ^2 = 483.78–997.38 for compounds **2**–**4**, the N atom deviating from it 4σ 0.030(7) Å]. The conformation of the iminophosphorane group is almost perpendicular to these fused rings [Fig. 2(*a*)] and an elongation of the C–N bond is detected. In this conformation, the delocalization of the π-system of the double N–P bond into the aromatic ring is very unfavourable.

As far as the bond distances and angles are concerned (only the rigid part of the molecule was compared by means of half normal probability plots),[2] no significant differences can be found between the two independent molecules of compound **4**. In the same way the differences between compounds **2** and **3** concern the angles at the P atoms [N(11)–P(12)–C(19)/C(25) and N(31)–P(32)–C(39)], the angles at N(11) and N(31), which present inverted values, and the N(31)–P(32) distance, longer in compound **2** than in **3**, and similar to that in compound **1**. The C(9)–N(31)–P(32) and N(11)–P(12)–C(19) angles are the only differences found (pooled standard deviation, σ_p > 3.0) between compound **2** and the weighted mean values of molecules **4A** and **4B**. The presence of the methyl group, instead of the phenyl one, does not produce any significant changes in the geometry of the rigid part of the molecule. See Table 1 and Figs. 1 and 2.

The proton was always found bonded to only one nitrogen atom, not shared between both, like in some 'classical' proton sponges.[3] When the nitrogen atom is protonated, the corresponding N–P distance loses part of its double bond character [1.610(5)–1.634(3) Å *vs.* 1.596(5)–1.605(5) Å], as previously observed.[4] The P–C(phenyl) distance '*trans*' to the naphthalene ring is usually shorter than the other two, and the corresponding N–P–C angles are lower than the others, and less than the tetrahedral one. This may be due to the steric strain of the naphthalene ring.

Table 2 contains selected torsion angles related to the conformation of the iminophosphorane groups and the main

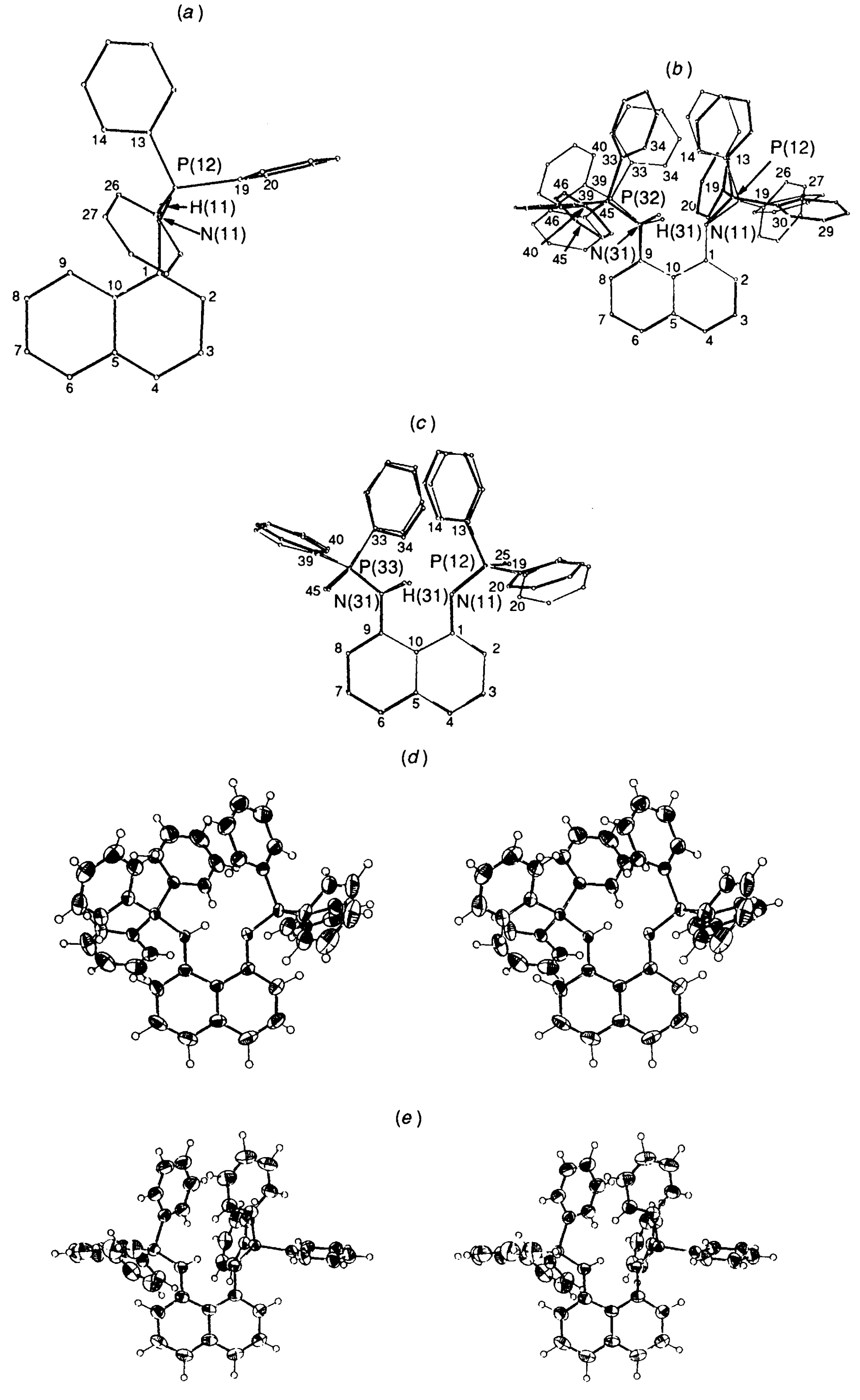


Fig. 1 Molecular structures[15] with the numbering system adopted in the crystallography work. Compounds **2** and **3**, (*b*), and the two independent molecules of compound **4**, (*c*), are superimposed for comparison purposes. Only H(11) or H(31) has been plotted. The thin lines correspond to compounds **2** and **4A**. Stereo views of **2** and **3** are shown in (*d*) and (*e*). Thermal ellipsoids for the non-hydrogen atoms are depicted at 50% probability level while hydrogen atoms are represented by spheres (radius = 0.1 Å).

deformation parameters.[5] The naphthalene moiety is slightly distorted around the C(5)–C(10) bond, as measured by the χ_τ parameter which shows the relative twist of one end of the bond [substituents at C(10)] with respect to the other [C(5)]. Although $\chi_{1,9}$ (atoms where the substitutions take place) tends to be greater than $\chi_{4,6}$, both distortions are not different in terms of the achieved precision. This naphthalene distortion (previously observed),[1,3] which is a consequence of the bulky substituents in the *peri*-positions, places the nitrogen atoms on different sides of the naphthalene plane. The exocyclic angles at C(1) and C(9) are distorted inward, giving rise to a decrease of the N ··· N distance (see Table 3) with respect to that observed

Table 1 Selected bond distances and angles/Å, °

	1	2	3	4	
				A	**B**
C(1)–C(2)	1.387(16)	1.390(6)	1.386(5)	1.376(9)	1.380(9)
C(1)–C(10)	1.405(16)	1.439(6)	1.433(5)	1.446(8)	1.431(8)
C(1)–N(11)	1.461(12)	1.409(5)	1.411(5)	1.405(8)	1.413(8)
C(2)–C(3)	1.428(22)	1.400(8)	1.407(6)	1.409(11)	1.408(11)
C(3)–C(4)	1.392(23)	1.349(8)	1.350(6)	1.344(13)	1.337(12)
C(4)–C(5)	1.333(24)	1.413(8)	1.404(6)	1.410(10)	1.423(10)
C(5)–C(6)	1.413(22)	1.425(8)	1.415(6)	1.440(11)	1.409(10)
C(5)–C(10)	1.431(15)	1.433(6)	1.437(5)	1.433(9)	1.435(9)
C(6)–C(7)	1.356(28)	1.342(8)	1.351(7)	1.352(11)	1.345(10)
C(7)–C(8)	1.385(24)	1.415(7)	1.414(6)	1.395(10)	1.403(10)
C(8)–C(9)	1.393(19)	1.370(6)	1.370(6)	1.388(9)	1.381(9)
C(9)–C(10)	1.406(16)	1.435(6)	1.437(5)	1.426(8)	1.430(8)
C(9)–N(31)	—	1.414(5)	1.427(5)	1.412(8)	1.417(8)
N(11)–P(12)	1.631(7)	1.598(4)	1.598(3)	1.605(5)	1.596(5)
P(12)–C(13)	1.746(12)	1.783(4)	1.796(4)	1.783(7)	1.790(7)
P(12)–C(19)	1.819(10)	1.791(5)	1.806(4)	1.806(6)	1.800(6)
P(12)–C(25)	1.770(9)	1.812(5)	1.805(3)	1.793(8)	1.793(9)
N(31)–P(32)	—	1.634(3)	1.617(3)	1.610(5)	1.615(5)
P(32)–C(33)	—	1.774(4)	1.788(4)	1.787(6)	1.784(6)
P(32)–C(39)	—	1.790(4)	1.802(4)	1.775(6)	1.790(6)
P(32)–C(45)	—	1.787(4)	1.799(4)	1.779(8)	1.792(7)
C(1)–C(10)–C(5)	118.4(11)	117.8(4)	118.2(3)	118.0(5)	118.9(5)
C(9)–C(10)–C(5)	119.3(11)	117.7(4)	116.5(3)	117.7(5)	116.9(5)
C(10)–C(1)–N(11)	118.5(9)	118.1(4)	118.7(3)	116.4(5)	117.1(5)
C(2)–C(1)–N(11)	120.0(10)	123.2(4)	122.1(3)	124.6(6)	123.3(5)
C(8)–C(9)–N(31)	—	122.4(4)	121.0(4)	122.4(5)	122.2(5)
C(10)–C(9)–N(31)	—	117.0(3)	117.8(3)	117.1(5)	117.2(5)
C(1)–C(10)–C(9)	122.3(10)	124.5(4)	125.3(3)	124.3(5)	124.2(5)
C(1)–N(11)–P(12)	123.8(6)	126.4(3)	129.2(3)	126.7(4)	127.6(4)
N(11)–P(12)–C(13)	105.4(5)	107.0(2)	107.2(2)	105.3(3)	104.9(3)
N(11)–P(12)–C(19)	112.8(4)	113.4(2)	110.3(2)	114.9(3)	114.1(3)
N(11)–P(12)–C(25)	109.6(4)	114.7(2)	117.8(2)	113.8(3)	114.6(3)
C(9)–N(31)–P(32)	—	129.5(3)	126.3(3)	127.1(4)	128.6(4)
N(31)–P(32)–C(33)	—	105.4(2)	106.6(2)	104.4(3)	104.8(3)
N(31)–P(32)–C(39)	—	112.9(2)	110.1(2)	112.1(3)	112.2(3)
N(31)–P(32)–C(45)	—	110.6(2)	111.8(2)	113.5(3)	114.0(3)

[2.792(3) Å] in 1,8-bis(*N*,*N*-dimethylamino)naphthalene[6] and [2.716(11), 2.739(10) Å] in 1,8-diaminonaphthalene.[1] This effect (common with other proton sponges)[3] may be due to the strong intramolecular hydrogen bond, $N^+–H \cdots N$ (Table 3), see below. Fig. 3 shows the Newman views along the N–P bonds. We can distinguish between two extreme geometries, the parallel one and the perpendicular one (with idealized C–N–P–Ph torsion angles of ±60, 180° *vs.* −30, 90, −150°). These geometries can be related to the hybridization state of the nitrogen atom.[7] In our case, in spite of the standard error of the hydrogen atoms, the N(31) atom shows an sp^2 hybridization, as can be deduced from the addition of the angles around it, 357(–), 360(3), 360(2), 356(3) and 360(3)°. The molecular structures of compounds **2** and **3** conflict to some extent: besides the differences between the two cations mentioned above, the P(12) atom in **3** lies on the same side of the naphthalene plane as P(32) (Fig. 2). Moreover, while the conformation presented by compounds **2** and **4** around the N–P bond corresponds to a parallel one for the unprotonated nitrogen atom and a perpendicular one for the protonated nitrogen atom ($\chi_\tau = -60$ and $-30°$ approximately, respectively) (see Table 2), compound **3** exhibits the opposite situation. Deviation from this conformation in the crystal may arise from intermolecular contacts and crystal packing effects. It is worth noticing that the iminophosphorane group which exhibits this behaviour is involved in hydrogen interactions with the anion. When the anion changes some interactions [H(29), H(46)] remain and other new ones appear [H(18), H(22), H(26)]. From the data we have at present, the substitution of a phenyl ring by a methyl group does not seem to affect the conformation of the molecule as much as the anion replacement.

The most important hydrogen bond interaction presented by structures **2**–**4** is the intramolecular bond $N^+–H \cdots N$. These contacts (Table 3) are quite short and linear, as previously observed in other sponges.[3] The proton deviates 22.6, 12.6, 12.5 and 12.6° from the lone pair direction, and the angles between the C–N–P plane and the N ··· H line are 14.5, 42.9, 35.9 and 18.7° for compounds **2**, **3**, **4A** and **4B**, respectively.

The crystal of compound **2** contains chains, two per unit cell, of Br^- and water molecules, joined together by hydrogen bonds. These chains interact with the cations through phenyl contacts (Table 3), and they are located in channels, along the *a* axis, which can be considered as an ellipsoidal cylinder of approximate traverse dimensions 7.6 × 8.1 Å, Fig. 4.[8] A search of the Cambridge Structural Database (CSD)[9] was performed in order to compare the strength and the linearity of the $Br^- \cdots H–O–H$ bonds. The data (29 entries) displayed the following mean geometry: Br ··· H = 2.43(10) Å, Br ··· O = 3.30(5) Å and Br ··· H–O = 164(12)°. In compound **4**, where the Br^- anions appear to be disordered, [Br(1)–Br(3) = 2.851(2) Å and Br(2)–Br(4) = 3.038(2) Å], two cavities, approximately torus shaped, could be detected; a Br^- anion [Br(1) or Br(2)], its centrosymmetrically related and the corresponding disordered position [Br(3) or Br(4)] are included in each cavity, the corresponding dimensions being ±6.48, ±3.34, ±2.86 Å and ±4.75, ±4.55, ±2.42 Å. The BF_4^- and

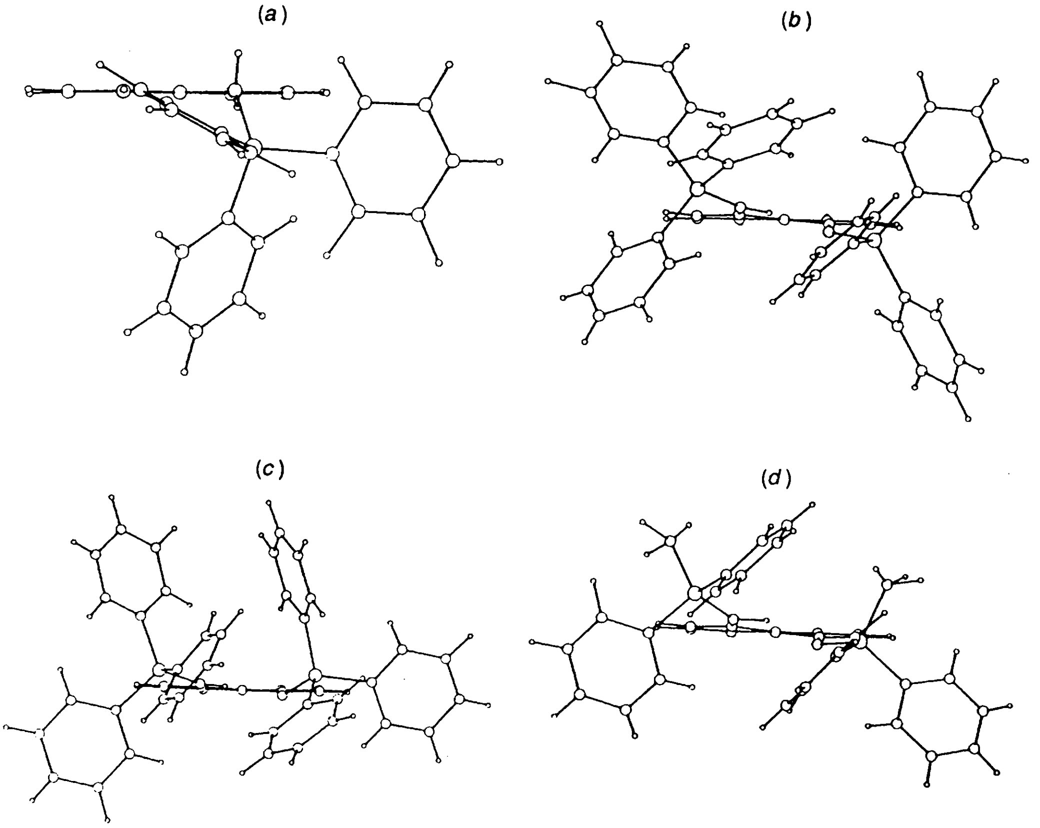


Fig. 2 Perspective view[16] of the molecules showing the naphthalene distortions and the relative situation of the iminophosphorane group for compounds **1**, **2**, **3** and **4A**

Table 2 Selected torsion angles and deformation parameters (°) around the C(5)–C(10), N(11)–P(12) and N(31)–P(32) bonds

	1	**2**	**3**	**4**	
				A	**B**
N(11)–C(1)–C(10)–C(9)	−0.3(15)	10.9(6)	7.3(6)	11.0(8)	8.6(8)
N(31)–C(9)–C(10)–C(1)	—	8.3(6)	2.3(6)	8.0(8)	8.4(8)
C(5)–C(10)–C(1)–N(11)	178.2(9)	−170.2(4)	−175.0(3)	−170.3(5)	−172.2(5)
C(5)–C(10)–C(9)–N(31)	—	−170.6(4)	−175.5(3)	−170.7(6)	−170.8(5)
C(2)–C(1)–N(11)–P(12)	−72.6(12)	1.7(6)	32.6(5)	15.7(9)	9.2(9)
C(1)–N(11)–P(12)–C(13)	−159.0(7)	175.8(3)	−163.3(3)	−177.8(5)	−177.6(5)
C(1)–N(11)–P(12)–C(19)	84.0(8)	56.9(4)	78.1(4)	−61.7(6)	−63.4(6)
C(1)–N(11)–P(12)–C(25)	−36.2(8)	−69.2(4)	−47.7(4)	62.5(6)	62.4(6)
C(8)–C(9)–N(31)–P(32)	—	−12.5(6)	−11.7(6)	−23.0(8)	−23.5(8)
C(9)–N(31)–P(32)–C(33)	—	−155.9(4)	−177.4(3)	−157.2(5)	−152.4(5)
C(9)–N(31)–P(32)–C(39)	—	83.9(4)	64.8(4)	85.9(5)	88.6(5)
C(9)–N(31)–P(32)–C(45)	—	−41.5(4)	−61.2(4)	−39.4(6)	−36.4(6)
C(4)–C(5)–C(10)–C(1)	1.8(18)	−4.1(6)	−2.3(6)	−4.7(9)	−5.4(9)
C(6)–C(5)–C(10)–C(1)	−178.9(12)	175.4(4)	179.0(4)	174.1(6)	174.6(6)
C(6)–C(5)–C(10)–C(9)	−0.4(17)	−5.6(6)	−3.1(6)	−7.1(9)	−6.2(6)
C(4)–C(5)–C(10)–C(9)	−179.6(12)	174.9(4)	175.6(4)	174.1(6)	173.9(6)
χ_{τ}	0.7(8)	−4.9(3)	−3.9(3)	−6.9(4)	−7.5(4)
$\chi_{1.9}$	−1.4(22)	−1.0(7)	−2.1(7)	−1.2(11)	−0.7(11)
$\chi_{4.6}$	0.7(22)	0.5(7)	−1.3(7)	−1.2(11)	0.0(11)
χ_{τ}	−37.1(4)	−65.5(2)	−44.3(2)	−59.0(3)	−59.5(3)
$\chi_{25.13}$	2.8(11)	−5.0(6)	−4.4(6)	−3.9(9)	−5.8(9)
$\chi_{25.19}$	−0.2(11)	−6.1(6)	−5.8(6)	−4.2(9)	−5.9(9)
$\chi_{13.19}$	−3.0(11)	−1.1(6)	−1.4(6)	−0.3(9)	0.0(9)
χ_{τ}	—	−37.8(2)	−57.9(2)	−36.9(3)	−33.4(3)
$\chi_{45.33}$	—	−5.6(6)	−3.8(6)	−2.2(7)	−4.0(7)
$\chi_{45.39}$	—	−5.4(6)	−6.0(6)	−5.3(7)	−5.0(7)
$\chi_{33.39}$	—	0.2(6)	−2.2(6)	−3.1(7)	−1.0(7)

PF_6 anions lie in quite spherical holes of radius 2.64 and 3.19 Å on average. The lowest local packing coefficients, defined as $C_k = V_{guest}/V_{hole}$, are displayed by compound **4**, where the disorder is present: C_k = 0.79, 0.63, 0.66 for compounds **1–3** and 0.43, 0.39 for **4**, respectively.

Interactions for the other compounds are also shown in Table 3. These are of three types: first, those involving the anions with hydrogen atoms in the cation. Then, those between phenyl rings of the 'T-type'[10] (hydrogen pointing towards the centroid of another ring), among which, the only intramolecular one is present in compound **3**. Finally the possible interactions between parallel phenyl rings, as C(13–18) and C(33–38) (see Fig. 2); the interplanar angles are 24.7(2), 18.4(2), 8.6(3) and 7.5(2)° and the distances between their centroids are 3.930(3), 3.916(3), 3.789(5) and 3.746(5) Å, for compounds **2**, **3** and the two molecules of **4**, respectively.

Among the interactions between the anion and the hydrogen atoms of the cation, the most interesting involves the N^+–H and the fluoroborate anion of compound **1**. A search of N^+–H ··· F_4B^- hydrogen bonds was performed in the CSD. The mean geometrical parameters obtained, for three organic compounds, were F ··· H = 1.89(16) Å, F ··· N = 2.81(12) Å and N–H ··· F = 161(12)° which are not significantly different from the values obtained for compound **1**.

Experimental

Melting points 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 are in Hz). 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 summarizes the crystal data and refinement parameters. Several crystals of compound **1** were checked but all of them presented a mosaic spread wider than usual, although less than the used scan width. All hydrogen parameters were kept fixed in the refinement of this compound. The values used for the hydrogen thermal isotropic displacement parameters were the isotropic equivalents of the atoms bonded to them. The hydrogen atoms were located on the corresponding difference synthesis using all data; however, in order to confirm the position of the proton, difference Fourier synthesis, using the completed model but H(31) and Θ up to 32° were performed. The higher peaks obtained in this way were assigned to the H(31) atoms and were used in the next stages of the refinements.

Table 3 Hydrogen interactions. Numbers stand for symmetry operations and C(1–10), C(5–10), C(19–24), C(25–30), C(33–38), C(39–44) and C(45–50) for the centroids of the corresponding phenyl rings. (–) stands for fixed hydrogen atoms

	Interatomic distances/Å			
X–H ··· Y	X–H	X ··· Y	H ··· Y	X–H ··· Y/°
Compound **1**[a]				
N(11)–H(11) ··· F(4)	0.91(–)	2.880(15)	1.97(–)	171(–)
C(22)–H(22) ··· F(3)$_1$	1.05(–)	3.318(22)	2.52(–)	132(–)
C(15)–H(15)– ··· F(3)$_2$	1.04(–)	3.358(21)	2.44(–)	146(–)
C(24)–H(24) ··· F(2)$_3$	1.19(–)	3.386(18)	2.48(–)	131(–)
C(3)–H(3) ··· F(1)$_4$	1.11(–)	3.387(18)	2.32(–)	160(–)
C(20)–H(20) ··· F(1)	1.09(–)	3.474(16)	2.43(–)	161(–)
C(28)–H(28) ··· C(1–10)$_3$	1.01(–)	3.822(16)	3.09(–)	130(–)
C(23)–H(23) ··· C(5–10)$_5$	1.23(–)	3.946(15)	3.00(–)	134(–)
C(4)–H(4) ··· C(13–18)$_6$	1.11(–)	3.916(15)	3.05(–)	136(–)
C(16)–H(16) ··· C(13–18)$_7$	1.09(–)	3.826(16)	3.25(–)	114(–)
Compound **2**[b]				
N(31)–H(31) ··· N(11)	0.85(8)	2.584(4)	1.78(8)	159(9)
O(1)–H(1O1) ··· Br(7)	0.79(11)	3.357(7)	2.58(11)	168(10)
O(1)–H(2O1) ··· Br	0.67(9)	3.399(7)	2.74(9)	166(9)
O(2)–H(1O2) ··· O(1)$_1$	0.80(10)	2.997(12)	2.21(10)	166(11)
O(2)–H(2O2) ··· O(1)	0.79(14)	2.922(12)	2.21(12)	151(13)
C(21)–H(21) ··· Br$_2$	0.95(7)	3.668(6)	2.85(7)	145(6)
C(44)–H(44) ··· Br	0.96(5)	3.596(5)	2.75(5)	148(4)
C(46)–H(46) ··· O(1)	1.06(9)	3.625(8)	2.82(9)	133(6)
C(29)–H(29) ··· O(2)$_3$	0.77(7)	3.243(9)	2.49(7)	167(6)
C(47)–H(47) ··· O(2)	1.20(12)	3.595(9)	2.50(12)	152(8)
C(48)–H(48) ··· O(2)$_1$	1.18(14)	3.760(12)	2.92(14)	128(8)
C(15)–H(15) ··· C(5–10)$_4$	0.98(8)	3.797(6)	2.98(6)	142(6)
C(27)–H(27) ··· C(25–30)$_5$	0.92(8)	3.930(6)	3.07(8)	156(7)
C(6)–H(6) ··· C(33–38)$_6$	1.03(10)	3.945(6)	2.97(10)	159(7)
Compound **3**[c]				
N(31)–H(31) ··· N(11)	0.83(5)	2.606(4)	1.90(5)	143(5)
C(46)–H(46) ··· F(2)$_1$	1.00(5)	3.287(6)	2.62(5)	124(4)
C(46)–H(46) ··· F(6)$_1$	1.00(5)	3.392(8)	2.45(5)	158(4)
C(26)–H(26) ··· F(3)	0.97(5)	3.376(8)	2.61(5)	135(4)
C(18)–H(18) ··· F(4)	1.02(6)	3.314(7)	2.44(6)	144(4)
C(22)–H(22) ··· F(4)$_2$	1.01(6)	3.360(7)	2.50(6)	144(5)
C(29)–H(29) ··· F(5)$_3$	0.98(5)	3.232(7)	2.49(5)	132(3)
C(41)–H(41) ··· C(1–10)$_4$	1.05(7)	3.745(7)	2.86(7)	142(4)
C(30)–H(30) ··· C(5–10)$_5$	0.96(6)	3.746(5)	2.88(6)	151(4)
C(34)–H(34) ··· C(19–24)	0.95(5)	3.588(5)	2.86(4)	134(3)
C(17)–H(17) ··· C(45–50)$_3$	0.99(7)	3.916(6)	2.99(7)	157(5)

Table 3 (*continued*)

X–H···Y	Interatomic distances/Å			
	X–H	X···Y	H···Y	X–H···Y/°
Compound **4**[d]				
N(31A)–H(31A)···N(11A)	1.03(9)	2.534(6)	1.68(9)	138(8)
C(3A)–H(3A)···C(33–38B)$_1$	1.01(10)	3.872(9)	2.91(10)	159(8)
C(17A)–H(17A)···Br(4)$_2$	1.03(13)	3.666(13)	2.87(13)	135(9)
C(18A)–H(18A)···Br(4)$_3$	1.11(10)	3.653(8)	2.69(10)	144(7)
C(23A)–H(23A)···C(5–10B)$_1$	0.91(8)	3.735(8)	3.04(8)	135(6)
C(24A)–H(24A)···Br(2)$_3$	0.91(5)	3.783(7)	2.90(5)	163(4)
C(25A)–H(252A)···Br(2)$_3$	1.15(10)	3.771(7)	2.64(10)	169(7)
C(25A)–H(253A)···Br(4)	1.22(9)	3.594(8)	2.95(9)	113(5)
C(35A)–H(35A)···Br(2)	0.95(5)	3.631(9)	2.71(5)	164(4)
C(36A)–H(36A)···C(39–44B)$_4$	1.03(7)	3.929(9)	2.99(7)	152(5)
C(42A)–H(42A)···Br(1)$_5$	1.01(25)	3.658(12)	2.92(25)	131(17)
C(43A)–H(43A)···Br(3)$_5$	1.02(10)	3.690(11)	2.75(10)	103(7)
C(45A)–H(451A)···C(13–18B)$_6$	1.21(11)	3.493(8)	2.67(11)	124(7)
C(45A)–H(453A)···C(19–24B)$_6$	0.77(12)	3.834(9)	3.06(12)	176(11)
N(31B)–H(31B)···N(11B)	0.94(6)	2.533(6)	1.73(6)	141(6)
C(3B)–H(3B)···C(33–38A)$_5$	0.89(8)	3.817(8)	3.08(7)	142(6)
C(4B)–H(4B)···C(5–10B)$_7$	0.97(7)	4.023(8)	3.07(7)	167(5)
C(16B)–H(16B)···Br(3)$_6$	1.07(8)	3.639(11)	2.89(8)	127(5)
C(17B)–H(17B)···Br(1)$_6$	1:10(10)	3.784(9)	2.91(9)	136(6)
C(17B)–H(17B)···Br(3)$_6$	1.10(10)	3.702(11)	2.93(10)	127(6)
C(18B)–H(18B)···Br(1)	1.13(9)	3.591(8)	2.75(8)	130(5)
C(21B)–H(21B)···Br(2)$_6$	1.07(6)	3.825(8)	2.77(6)	168(5)
C(23B)–H(23B)···C(5–10A)$_6$	0.93(12)	3.641(8)	2.93(12)	135(9)
C(24B)–H(24B)···Br(1)	1.07(7)	3.755(8)	2.85(7)	142(5)
C(42B)–H(42B)···Br(2)$_8$	1.03(7)	3.719(9)	2.91(6)	135(4)
C(43B)–H(43B)···Br(4)$_8$	1.06(9)	3.978(9)	2.97(9)	159(7)
C(45B)–H(453B)···C(19–24A)$_9$	0.88(9)	4.043(8)	3.21(9)	160(7)

[a] Symmetry operations. 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: $-x, -y, -z$; 5: $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; 6: $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; 7: $1 - x, 1 - y, -z$. [b] 1: $-\frac{1}{2} + x, \frac{1}{2} - y, z$; 2: $-x, -y, -\frac{1}{2} + z$; 3: $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$; 4: $1 + x, y, z$; 5: $\frac{1}{2} + x, -\frac{1}{2} - y, z$; 6: $-x, -y, \frac{1}{2} + z$. [c] 1: $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$; 2: $x, \frac{3}{2} - y, \frac{1}{2} + z$; 3: $x, \frac{3}{2} - y, -\frac{1}{2} + z$; 4: $1 + x, y, z$; 5: $1 - x, 1 - y, -z$. [d] 1: $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; 2: $x, 1 + y, z$; 3: $-x, -y, 1 - z$; 4: $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; 5: $1 - x, 1 - y, 1 - z$; 6: $1 - x, -y, 1 - z$; 7: $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; 8: $\frac{1}{2} + x, -\frac{1}{2} - y, -\frac{1}{2} + z$; 9: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

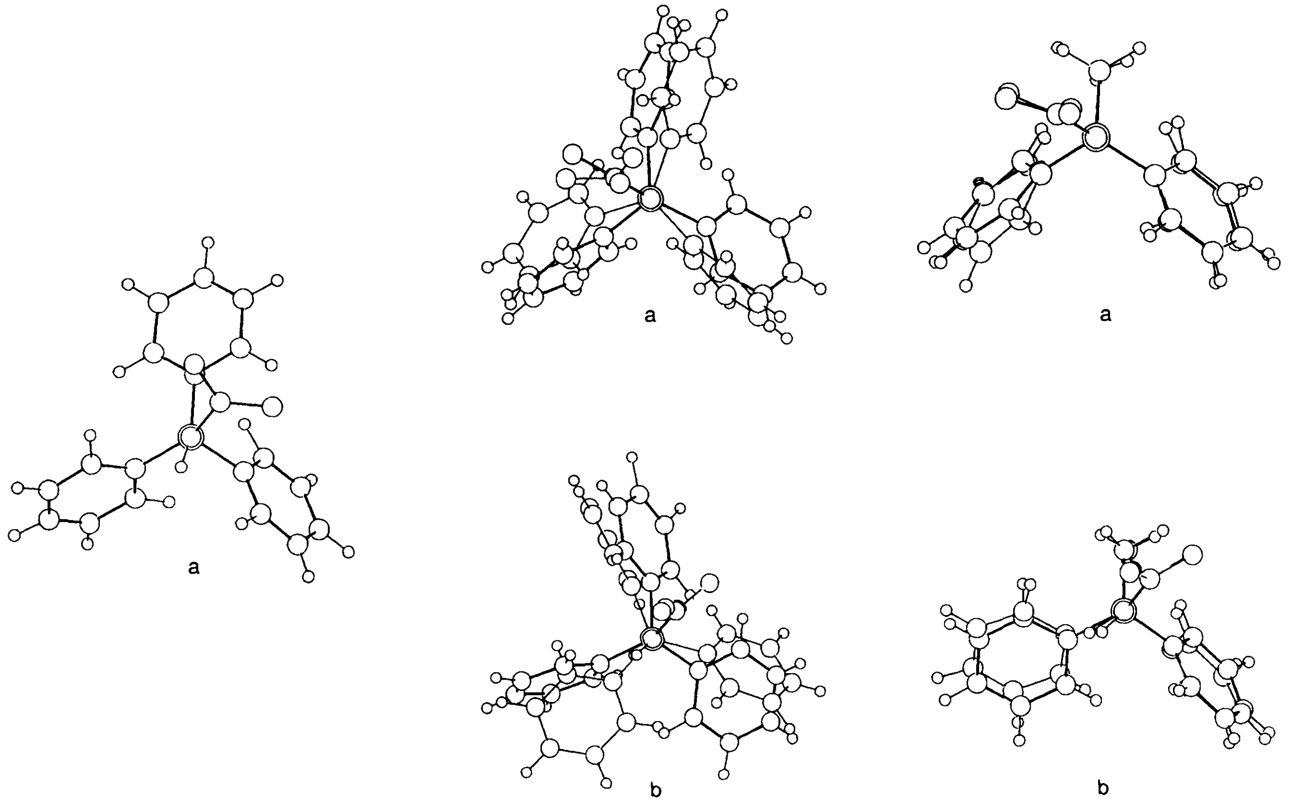


Fig. 3 Newman projections (a and b) along the N(11)–P(12) and N(31)–P(32) bonds, respectively.[15] For the sake of clarity, only the first three atoms of the naphthalene moiety are drawn. Superimposed drawings correspond to compounds **2** and **3**, **4A** and **4B**, respectively. The thick lines correspond to compounds **2** and **4A**.

Table 4 Crystal analysis parameters at room temperature

	1	**2**	**3**	**4**
Crystal data				
Formula	$C_{28}H_{23}NP^+BF_4^-$	$C_{46}H_{37}N_2P_2^+Br^-{\cdot}2H_2O$	$C_{46}H_{37}N_2P_2^+PF_6^-$	$C_{36}H_{33}N_2P_2^+Br^-$
Crystal habit	Colourless prism	Brown prism	Yellow plate	Brown prism
Crystal size/mm	0.36 × 0.23 × 0.13	0.47 × 0.20 × 0.10	0.36 × 0.33 × 0.20	0.33 × 0.20 × 0.10
Symmetry	Monoclinic, $P2_1/n$	Orthorombic, $Pna2_1$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Unit cell determination:	Least-squares fit from 73 reflections ($\Theta < 45°$)	Least-squares fit from 97 reflections ($\Theta < 45°$)	Least-squares fit from 65 reflections ($\Theta < 45°$)	Least-squares fit from 94 reflections ($\Theta < 45°$)
Unit cell dimensions/Å, °	a = 14.3965(13) b = 12.9517(14) c = 13.4087(11) 90, 96.308(7), 90	a = 8.9852(2) b = 27.0115(15) c = 15.9751(9) 90, 90, 90	a = 9.9355(3) b = 24.6904(13) c = 16.1180(8) 90, 97.670(3), 90	a = 25.2668(11) b = 10.5558(2) c = 24.2333(9) 90, 96.518(4), 90
Packing: V/Å, Z	2485.0(4), 4	3877.2(3), 4	3918.6(3), 4	6421.5(4), 8
D_c/g cm^{-3}, M, F(000)	1.313, 491.27, 1016	1.363, 795.69, 1648	1.398, 824.72, 1704	1.315, 635.52, 2624
μ/cm^{-1}	13.783	25.529	19.569	29.043
Experimental data				
Technique		Four-circle diffractometer: Philips PW 1100, bisecting geometry Graphite oriented monochromator: CuKα $\omega/2\Theta$ scans, scan width: 1.4° Detector apertures 1 × 1°; 1 min reflex^{-1}.		
	Θ_{max} = 60°	Θ_{max} = 65°	Θ_{max} = 65°	Θ_{max} = 60°
Number of reflections:				
Independent	3699	3445	6671	9532
Observed	1709 [$3\sigma(I)$ criterion]	3221 [$3\sigma(I)$ criterion]	5550 [$3\sigma(I)$ criterion]	6274 [$3\sigma(I)$ criterion]
Standard reflections:		2 reflections every 90 min. No variation		
Max.–min. transmission factors[a]	1.637–0.738	1.114–0.774	1.131–0.679	1.195–0.846
Solution and refinement				
Solution	Direct methods	Patterson	Direct methods	Direct methods
Refinement:				
Least-squares on F_o	full-matrix	3 blocks	3 blocks	7 blocks
Parameters:				
Number of variables	316[b]	641	662	1023[a]
Degrees of freedom	1293	2580	4888	5251
Ratio of freedom	5.1	5.0	8.4	6.1
H atoms		From difference synthesis[a]		
Final shift/error	0.02	0.30	0.11	0.32
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	$U11$(F4) = 0.41(2) Å^2	$U11$(O2) = 0.116(5) Å^2	$U22$(F5) = 0.318(9) Å^2	$U33$(C16A) = 0.20(1) Å^2
Final ΔF peaks	0.40 e Å^{-3}	0.30 e Å^{-2}	0.60 e Å^{-3}	1.40 e Å^{-3} near Br(2)
Final R and R_w	0.103, 0.126	0.038, 0.040	0.063, 0.076	0.070, 0.069

[a] See text. [b] Hydrogen atoms not refined.

Several attempts to obtain good crystals of the ClO_4^- and BF_4^- salts analogous to compound **2** were unsuccessful, and so the influence of the anion could not be tested. The two independent anions in compound **4** appear to be disordered; the Br(1)–Br(3) = 2.851(2) Å and Br(2)–Br(4) = 3.038(2) Å distances are shorter than the corresponding addition of their van der Walls radii (r = 1.85 Å),[11] the population parameters being pp[Br(1)] = 0.517(4), pp[Br(3)] = 1 – pp[Br(1)], pp[Br(2)] = 0.453(4), pp[Br(4)] = 1 – pp[Br(2)]. Tables 5–8 show the atomic coordinates for the non-hydrogen atoms. 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,[12] MULTAN80,[13] XRAY80,[14] XTAL3.0,[15] PLUTO[16] and PESOS.[17] Empirical absorption correction for all compounds were performed using the program DIFABS[18] and the scattering factors were taken from the International Tables for X-Ray Crystallography.[19,*]

1-*Triphenylphosphoranilidenammonionaphthalene* **1**.—Bromine (1.59 g, 10 mmol) in dry benzene (15 cm^3) was added to a stirred solution of triphenylphosphine (2.62 g, 10 mmol) in the same solvent (30 cm^3) at 0–5 °C under nitrogen. The mixture was stirred for 1 h and then allowed to warm to room temperature. A solution of 1-aminonaphthalene (1.34 g, 10 mmol) and triethylamine (2.02 g, 20 mmol) in dry benzene was added. The reaction mixture was heated at reflux temperature for 12 h. After cooling, the precipitated triethylammonium bromide was separated by filtration and the solvent was removed from the filtrate under reduced pressure. The residual material was recrystallized from benzene to give 1-triphenylphosphoranilidenammonionaphthalene which was dissolved in ethanol (50 cm^3) to which tetrafluoroboric acid (0.88 g, 10 mmol) was added. The resulting solution was stirred at room temperature for 12 h. The solvent was removed and the residue slurried with diethyl ether, filtered, air-dried and recrystallized from dichloromethane–diethyl ether (1:1) to give **1** in 88% yield, m.p. 227–229 °C (Found: C, 68.3; H, 4.9; N, 2.7. $C_{28}H_{23}BF_4NP$ requires: C, 68.46; H, 4.72; N, 2.85); ν_{max}(Nujol)/cm^{-1} 1590(m), 1441(vs), 1393(s), 1115(vs), 1090(vs), 1015(s), 997(s), 950(m), 785(s), 734(s) and 725(s); δ_H(CDCl$_3$) 6.98 (d, 1 H, J 7.5), 7.09 (t, 1 H, J 7.8), 7.32–7.40 (m, 2 H), 7.45–7.79 (m, 15 H) and 8.04 (dd, 1 H, J 3.4, 6.2); δ_C(CDCl$_3$) 120.27

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[*] Lists of the structure factors, thermal components, hydrogen parameters and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.

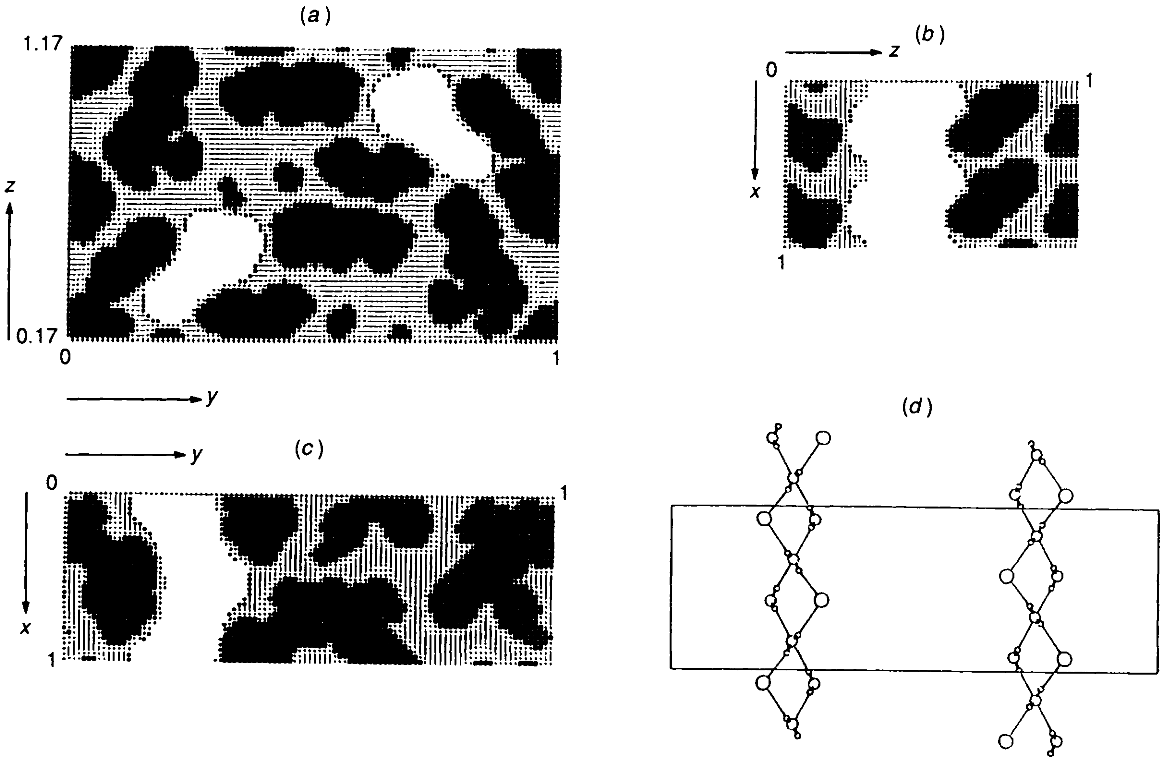

Fig. 4 The continuous channel along the *a* axis (two per unit cell) that holds the Br^- anions and water molecules in compound **2**. (*a*), (*b*) and (*c*) represent sections through $x = 0.50, y = 0.25$ and $z = 0.40$.[8] A projection along (001) (*d*) shows the chains of Br^- anions and water molecules.

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

Atom	*x*	*y*	*z*
C(1)	0.0754(6)	0.2221(9)	0.0724(7)
C(2)	0.0493(9)	0.1194(9)	0.0792(10)
C(3)	−0.0312(12)	0.0970(11)	0.1288(12)
C(4)	−0.0798(9)	0.1762(15)	0.1703(10)
C(5)	−0.0555(7)	0.2748(12)	0.1615(8)
C(6)	−0.1067(9)	0.3555(16)	0.2004(10)
C(7)	−0.0807(12)	0.4557(16)	0.1939(12)
C(8)	−0.0033(11)	0.4823(10)	0.1465(12)
C(9)	0.0493(8)	0.4063(8)	0.1053(9)
C(10)	0.0249(7)	0.3017(9)	0.1129(7)
N(11)	0.1558(5)	0.2496(5)	0.0202(5)
P(12)	0.2640(2)	0.2275(2)	0.0649(2)
C(13)	0.3309(8)	0.3127(8)	0.0015(8)
C(14)	0.2956(9)	0.4106(9)	−0.0270(12)
C(15)	0.3466(12)	0.4774(10)	−0.0804(11)
C(16)	0.4367(10)	0.4464(13)	−0.1006(10)
C(17)	0.4712(10)	0.3545(13)	−0.0726(12)
C(18)	0.4205(8)	0.2822(11)	−0.0202(10)
C(19)	0.3018(7)	0.0971(7)	0.0388(8)
C(20)	0.2700(8)	0.0528(8)	−0.0495(8)
C(21)	0.3035(8)	−0.0419(10)	−0.0758(10)
C(22)	0.3692(8)	−0.0930(9)	−0.0093(11)
C(23)	0.4039(9)	−0.0458(11)	0.0796(11)
C(24)	0.3702(8)	0.0484(9)	0.1044(10)
C(25)	0.2768(6)	0.2445(7)	0.1966(7)
C(26)	0.3259(11)	0.3274(11)	0.2397(10)
C(27)	0.3358(14)	0.3367(16)	0.3455(15)
C(28)	0.3049(13)	0.2612(16)	0.4042(11)
C(29)	0.2566(13)	0.1823(16)	0.3635(11)
C(30)	0.2426(11)	0.1700(12)	0.2595(10)
B	0.1001(9)	0.2341(10)	−0.2513(9)
F(1)	0.0821(9)	0.1412(7)	−0.2118(9)
F(2)	0.0305(8)	0.2743(12)	−0.3047(11)
F(3)	0.1580(12)	0.2172(12)	−0.3239(15)
F(4)	0.1498(14)	0.2889(11)	−0.1918(10)

(${}^1J_{PC}$ 103.2, C_i), 122.23 (C_4), 123.63 (${}^3J_{PC}$ 4.1, C_2), 124.78 (${}^4J_{PC}$ 1.4, C_8), 126.60 (C_7), 126.95 (C_6), 127.51 (${}^4J_{PC}$ 1.3, C_3), 128.09 (C_5), 129.89 (${}^3J_{PC}$ 13.6, C_m), 130.32 (${}^3J_{PC}$ 5.3, C_{8a}), 131.87 (${}^2J_{PC}$ 3.0, C_1), 133.57 (${}^2J_{PC}$ 11.0, C_O), 134.18 (C_{4a}) and 135.20 (${}^4J_{PC}$ 3.0, C_p).

Preparation of Compounds **2** *and* **4**.—Bromine (3.19 g, 20 mmol) in dry benzene (30 cm^3) was added dropwise to a stirred solution of the appropriate phosphine (20 mmol) (triphenylphosphine for compound **2** and diphenylmethylphosphine for compound **4**) in the same solvent (50 cm^3) at 0–5 °C under nitrogen. The mixture was stirred for 1 h and then allowed to warm to room temperature. A solution of 1,8-diaminonaphthalene (1.58 g, 10 mmol) and triethylamine (4.05 g, 40 mmol) in dry benzene (50 cm^3) was added. The reaction mixture was refluxed for 12 h; after cooling the separate solid was collected by filtration, washed with cold water, air-dried and recrystallized from dichloromethane–diethyl ether to give **2** or **4**.

1,8-*Bis*(*triphenylphosphoranylideneammonio*)*naphthalene bromide* **2**. (90%), m.p. 264 °C (decomp.) (Found: C, 72.6; H, 5.2; N, 3.45. $C_{46}H_{37}BrN_2P_2$ requires: C, 72.73; H, 4.91; N, 3.69); ν_{max}(Nujol)/cm^{-1} 1578(s), 1574(s), 1438(vs), 1342(s), 1308(vs), 1297(vs), 1110(vs), 817(m), 762(m), 748(s) and 727(vs); δ_H($CDCl_3$) 6.35 (d, 2 H, *J* 7.5, $H_2 + H_7$), 6.95 (t, 2 H, *J* 7.8, $H_3 + H_6$), 7.22 (d, 2 H, *J* 8.2, $H_4 + H_5$), 7.43–7.52 (m, 12 H, 12 × H_m), 7.60–7.70 (m, 18 H, 12 × H_o + 6 × H_p) and 16.42 (t, 1 H, J_{HP} 4.77, NH); δ_C($CDCl_3$) 114.64 (${}^3J_{PC}$ 8.9, $C_2 + C_7$), 120.70 (${}^3J_{PC}$ 11.6, C_{8a}), 120.73 ($C_4 + C_5$), 123.44 (${}^1J_{PC}$ 101.6, C_i), 125.39 ($C_3 + C_6$), 129.48 (${}^3J_{PC}$ 12.96, C_m), 132.47 (${}^2J_{PC}$ 10.6, C_O), 133.88 (${}^4J_{PC}$ 2.9, C_p), 136.26 (${}^4J_{PC}$ 1.1, C_{4a}) and 142.35 (dd, *J* 1.98, 2.91, $C_1 + C_8$). Crystals of **2** contain two water molecules although no water was deliberately added to the crystallization solvents.

1,8-*Bis*(*diphenylmethylphosphoranylideneammonio*)*naphthalene bromide* **4**. (87%), m.p. 223 °C (Found: C, 67.85; H, 5.1; N, 4.25. $C_{36}H_{33}BrN_2P_2$ requires: C, 68.04; H, 5.23; N, 4.41); ν_{max}(Nujol)/cm^{-1} 1579(vs), 1506(m), 1438(vs), 1404(s), 1308(vs), 1115(vs), 1047(s), 877(s), 815(m), 747(vs) and 718(vs); δ_H($CDCl_3$) 2.21 (d, 6 H, J_{HP} 12.7, CH_3P), 6.26 (d, 2 H, *J* 7.4, $H_2 + H_7$), 6.99 (t, 2 H, *J* 7.8, $H_3 + H_6$), 7.18 (d, 2 H, *J* 8.1,

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

Atom	*x*	*y*	*z*
C(1)	0.192 7(4)	−0.093 8(2)	0.437 6(3)
C(2)	0.127 0(6)	−0.139 0(2)	0.456 1(3)
C(3)	−0.003 6(6)	−0.142 4(2)	0.503 5(4)
C(4)	−0.069 0(6)	−0.101 4(2)	0.534 6(4)
C(5)	−0.010 2(5)	−0.054 1(2)	0.516 2(3)
C(6)	−0.078 0(6)	−0.010 5(2)	0.548 8(3)
C(7)	−0.023 5(6)	0.034 7(2)	0.532 6(3)
C(8)	0.099 6(5)	0.040 4(2)	0.478 2(3)
C(9)	0.166 2(4)	−0.000 1(2)	0.442 6(2)
C(10)	0.119 6(4)	−0.049 1(2)	0.464 7(3)
N(11)	0.332 5(4)	−0.089 4(1)	0.398 4(2)
P(12)	0.435 70(11)	−0.133 85(3)	0.366 94(7)
C(13)	0.591 9(4)	−0.106 7(1)	0.315 6(3)
C(14)	0.672 1(5)	−0.069 3(2)	0.356 3(3)
C(15)	0.795 4(6)	−0.048 5(2)	0.319 4(4)
C(16)	0.839 9(6)	−0.064 7(2)	0.240 5(4)
C(17)	0.763 8(7)	−0.101 4(2)	0.200 0(4)
C(18)	0.638 8(6)	−0.122 6(2)	0.236 8(3)
C(19)	0.345 1(5)	−0.174 1(2)	0.294 0(3)
C(20)	0.229 7(6)	−0.153 4(2)	0.246 1(3)
C(21)	0.163 1(7)	−0.180 3(2)	0.183 5(4)
C(22)	0.208 8(7)	−0.227 4(2)	0.167 2(4)
C(23)	0.317 8(7)	−0.249 0(2)	0.214 3(4)
C(24)	0.387 0(5)	−0.223 0(2)	0.278 7(4)
C(25)	0.517 0(5)	−0.170 8(1)	0.449 8(3)
C(26)	0.641 1(6)	−0.200 5(2)	0.432 2(4)
C(27)	0.706 3(6)	−0.228 8(2)	0.494 5(5)
C(28)	0.651 9(8)	−0.227 5(2)	0.574 1(5)
C(29)	0.530 2(9)	−0.198 4(3)	0.592 7(4)
C(30)	0.464 6(6)	−0.169 8(2)	0.531 0(3)
N(31)	0.279 8(4)	0.004 1(1)	0.381 8(2)
P(32)	0.334 49(10)	0.052 68(3)	0.329 01(7)
C(33)	0.418 3(4)	0.028 9(1)	0.236 9(3)
C(34)	0.385 2(5)	−0.018 9(2)	0.208 8(3)
C(35)	0.438 3(6)	−0.035 0(2)	0.131 8(3)
C(36)	0.520 8(8)	−0.004 8(3)	0.083 6(3)
C(37)	0.555 8(8)	0.042 6(3)	0.109 9(4)
C(38)	0.504 0(7)	0.059 5(2)	0.186 1(4)
C(39)	0.464 7(5)	0.090 0(1)	0.385 5(3)
C(40)	0.617 1(5)	0.080 8(2)	0.378 3(3)
C(41)	0.718 2(6)	0.108 2(2)	0.424 3(4)
C(42)	0.669 7(6)	0.144 2(2)	0.478 0(3)
C(43)	0.518 6(7)	0.153 2(2)	0.486 9(3)
C(44)	0.416 4(6)	0.126 8(2)	0.441 5(3)
C(45)	0.177 9(5)	0.088 3(1)	0.295 2(3)
C(46)	0.183 8(6)	0.139 3(2)	0.284 9(3)
C(47)	0.060 0(9)	0.163 4(2)	0.251 5(4)
C(48)	−0.061 7(8)	0.138 4(3)	0.228 7(4)
C(49)	−0.068 3(7)	0.086 4(3)	0.236 4(4)
C(50)	0.051 3(6)	0.062 0(2)	0.270 2(3)
Br(1)	0.080 44(6)	0.190 28(2)	0.500 0
O(1)	0.331 4(9)	0.251 2(2)	0.378 6(4)
O(2)	0.085 0(12)	0.294 8(3)	0.284 7(4)

$H_4 + H_5$), 7.53–7.68 (m, 12 H), 7.74–7.84 (m, 8 H) and 16.64 (s, 1 H, NH); δ_C($CDCl_3$) 12.08 ($^1J_{PC}$ 70.8, CH_3P), 113.19 ($^3J_{PC}$ 10.0, $C_2 + C_7$), 119.81 ($^3J_{PC}$ 11.8, C_{8a}), 120.17 ($C_4 + C_5$), 124.42 ($^1J_{PC}$ 99.0, C_i), 125.59 ($C_3 + C_6$), 129.51 ($^3J_{PC}$ 13.0, C_m), 131.46 ($^2J_{PC}$ 11.0, C_O), 133.61 ($^4J_{PC}$ 2.5, C_p), 136.47 ($^4J_{PC}$ 1.3, C_{4a}) and 143.01 (dd, *J* 2.3, 2.8, $C_1 + C_8$).

1,8-*Bis*(*triphenylphosphoranylideneammonio*)*naphthalene hexafluorophosphate* **3**. To a solution of compound **2** (1.52 g, 2 mmol), in ethanol was added a solution of potassium hexafluorophosphate (0.41 g, 2.25 mmol) in water (5 cm^3). The reaction mixture was stirred at room temperature for 3 h. The precipitated solid was collected by filtration, washed with water (3 × 10 cm^3) air-dried and recrystallized from ethanol to give **3** in 99% yield, m.p. 252 °C (Found: C, 67.2; H, 4.3; N, 3.2. $C_{46}H_{37}F_6N_2P_3$ requires: C, 66.99; H, 4.52; N, 3.40); ν_{max}(Nujol)/cm^{-1} 1572(s), 1437(vs), 1399(m), 1305(s), 1134(m), 1110(vs), 1071(m), 838(vs), 816(s), 751(s), 745(m) and 725(vs); δ_H($CDCl_3$) 6.34 (d, 2 H, *J* 7.5, $H_2 + H_7$), 6.94 (t, 2 H, *J* 7.7, $H_3 + H_6$), 7.22 (d, 2 H, *J* 7.9, $H_4 + H_5$), 7.39–7.48 (m, 12 H, 12 × H_m), 7.57–7.68 (m, 18 H, 12 × H_o + 6 × H_p) and 16.43 (s, 1 H, NH); δ_C($CDCl_3$) 114.95 ($^3J_{PC}$ 8.9, $C_2 + C_7$), 121.00 ($C_4 + C_5$), 121.05 ($^3J_{PC}$ 11.6, C_{8a}), 123.80 ($^1J_{PC}$ 101.5, C_i), 125.72 ($C_3 + C_6$), 129.75 ($^3J_{PC}$ 13.0, C_m), 132.80 ($^2J_{PC}$ 10.6, C_o), 134.13 ($^4J_{PC}$ 2.85, C_p), 136.64 ($^4J_{PC}$ 1.28, C_{4a}) and 142.82 (dd, *J* 2.1, 2.8, $C_1 + C_8$).

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

Atom	*x*	*y*	*z*
C(1)	0.350 2(4)	0.527 5(2)	0.077 6(2)
C(2)	0.233 0(4)	0.514 2(2)	0.024 8(3)
C(3)	0.174 9(5)	0.462 2(2)	0.025 5(3)
C(4)	0.233 9(5)	0.423 8(2)	0.077 9(3)
C(5)	0.351 8(4)	0.434 7(2)	0.133 7(3)
C(6)	0.410 2(5)	0.393 9(2)	0.188 9(3)
C(7)	0.520 1(5)	0.404 1(2)	0.245 5(3)
C(8)	0.578 5(5)	0.456 5(2)	0.250 9(3)
C(9)	0.526 0(4)	0.497 1(2)	0.198 3(3)
C(10)	0.411 4(4)	0.487 8(1)	0.135 6(2)
N(11)	0.413 9(3)	0.578 3(1)	0.074 3(2)
P(12)	0.347 08(9)	0.636 72(4)	0.056 18(6)
C(13)	0.478 4(4)	0.681 1(2)	0.030 1(2)
C(14)	0.613 9(4)	0.666 3(2)	0.042 4(3)
C(15)	0.711 9(5)	0.701 8(2)	0.021 5(4)
C(16)	0.675 7(6)	0.751 8(2)	−0.011 1(4)
C(17)	0.541 2(6)	0.766 9(2)	−0.024 6(4)
C(18)	0.442 4(5)	0.731 9(2)	−0.003 9(3)
C(19)	0.283 2(4)	0.662 2(2)	0.148 4(2)
C(20)	0.241 2(4)	0.624 5(2)	0.204 2(3)
C(21)	0.202 2(5)	0.641 7(2)	0.279 9(3)
C(22)	0.205 7(5)	0.695 7(2)	0.299 7(3)
C(23)	0.245 1(5)	0.733 2(2)	0.245 2(3)
C(24)	0.283 4(5)	0.716 7(2)	0.169 2(3)
C(25)	0.216 3(4)	0.643 5(2)	−0.032 3(2)
C(26)	0.102 6(4)	0.675 9(2)	−0.030 3(3)
C(27)	0.014 1(4)	0.684 0(2)	−0.103 7(3)
C(28)	0.036 0(5)	0.659 5(2)	−0.177 2(3)
C(29)	0.148 9(5)	0.627 2(2)	−0.178 8(3)
C(30)	0.240 0(5)	0.619 6(2)	−0.107 4(3)
N(31)	0.581 1(3)	0.550 5(1)	0.205 8(2)
P(32)	0.687 26(10)	0.573 36(4)	0.282 63(6)
C(33)	0.714 2(4)	0.643 2(2)	0.260 8(2)
C(34)	0.607 4(5)	0.679 7(2)	0.265 1(3)
C(35)	0.624 6(5)	0.733 9(2)	0.248 1(4)
C(36)	0.746 7(6)	0.752 2(2)	0.226 5(4)
C(37)	0.851 8(5)	0.716 7(2)	0.223 2(4)
C(38)	0.836 4(5)	0.662 4(2)	0.240 8(3)
C(39)	0.846 7(4)	0.538 0(2)	0.287 5(3)
C(40)	0.891 0(5)	0.526 7(2)	0.211 2(3)
C(41)	1.014 8(6)	0.501 4(2)	0.209 9(4)
C(42)	1.092 5(5)	0.486 4(2)	0.282 5(5)
C(43)	1.050 1(5)	0.497 0(2)	0.358 9(4)
C(44)	0.925 9(5)	0.522 9(2)	0.361 4(3)
C(45)	0.617 9(4)	0.571 2(2)	0.380 2(2)
C(46)	0.692 4(5)	0.590 2(2)	0.453 5(3)
C(47)	0.629 8(7)	0.593 2(2)	0.525 9(3)
C(48)	0.495 3(7)	0.579 7(3)	0.523 8(4)
C(49)	0.421 2(6)	0561 4(3)	0.451 3(4)
C(50)	0.481 5(5)	0.557 0(2)	0.378 5(3)
P(3)	0.082 13(15)	0.848 41(6)	0.045 16(8)
F(1)	0.109 0(7)	0.903 3(2)	0.011 7(5)
F(2)	−0.042 4(5)	0.871 3(2)	0.084 1(3)
F(3)	0.046 4(7)	0.790 7(2)	0.073 7(5)
F(4)	0.203 3(5)	0.824 4(2)	0.005 7(3)
F(5)	0.176 1(6)	0.857 5(3)	0.125 1(3)
F(6)	−0.017 9(6)	0.836 2(3)	−0.037 0(4)

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Table 8 Final atomic coordinates for compound 4

	A				B		
Atom	*x*	*y*	*z*		*x*	*y*	*z*
C(1)	0.155 6(2)	−0.034 7(6)	0.317 8(2)		0.680 8(2)	0.432 5(6)	0.337 7(3)
C(2)	0.118 8(3)	−0.123 1(7)	0.296 5(3)		0.701 3(3)	0.524 3(7)	0.374 6(3)
C(3)	0.134 5(4)	−0.235 1(8)	0.271 3(3)		0.726 3(3)	0.632 6(7)	0.355 5(3)
C(4)	0.186 0(4)	−0.257 8(7)	0.265 7(3)		0.731 3(3)	0.648 9(7)	0.301 7(4)
C(5)	0.225 8(3)	−0.172 6(6)	0.287 7(3)		0.710 7(2)	0.558 4(6)	0.261 3(3)
C(6)	0.281 1(3)	−0.194 1(7)	0.281 3(3)		0.717 2(3)	0.572 5(7)	0.204 6(3)
C(7)	0.319 5(3)	−0.115 0(8)	0.304 3(3)		0.696 8(3)	0.487 1(8)	0.166 9(3)
C(8)	0.306 2(2)	−0.009 3(7)	0.334 5(3)		0.666 6(3)	0.384 4(6)	0.182 5(3)
C(9)	0.253 7(2)	0.015 6(6)	0.342 5(2)		0.658 1(2)	0.368 2(5)	0.237 3(2)
C(10)	0.211 6(2)	−0.061 0(6)	0.316 3(2)		0.682 8(2)	0.450 5(5)	0.279 5(2)
N(11)	0.142 8(2)	0.084 6(5)	0.338 3(2)		0.658 9(2)	0.317 4(5)	0.354 4(2)
P(12)	0.085 94(6)	0.128 91(17)	0.354 80(6)		0.646 13(6)	0.278 89(15)	0.415 18(6)
C(13)	0.094 5(2)	0.290 5(7)	0.375 3(3)		0.622 0(3)	0.119 5(6)	0.408 3(3)
C(14)	0.127 0(3)	0.368 5(8)	0.347 8(4)		0.645 5(3)	0.036 1(7)	0.374 8(3)
C(15)	0.129 5(5)	0.498 1(12)	0.360 0(6)		0.628 7(4)	−0.090 4(8)	0.372 5(4)
C(16)	0.099 5(6)	0.545 1(11)	0.398 0(8)		0.589 2(4)	−0.130 1(10)	0.403 0(4)
C(17)	0.067 9(5)	0.469 6(13)	0.427 3(5)		0.566 0(4)	−0.048 3(11)	0.435 1(4)
C(18)	0.064 9(3)	0.342 3(8)	0.415 3(3)		0.581 2(3)	0.077 6(8)	0.438 9(3)
C(19)	0.032 6(2)	0.127 5(6)	0.298 5(3)		0.704 0(2)	0.270 3(6)	0.465 8(2)
C(20)	0.044 4(3)	0.126 2(8)	0.243 4(3)		0.752 8(3)	0.233 6(7)	0.449 4(3)
C(21)	0.004 3(4)	0.128 4(9)	0.199 9(3)		0.796 3(3)	0.211 6(8)	0.488 4(4)
C(22)	−0.047 9(3)	0.131 4(8)	0.211 6(4)		0.790 7(4)	0.226 8(8)	0.543 9(4)
C(23)	−0.059 6(3)	0.132 8(8)	0.264 2(4)		0.743 6(4)	0.264 7(8)	0.561 1(3)
C(24)	−0.020 1(2)	0.133 5(7)	0.308 5(3)		0.699 3(3)	0.286 0(7)	0.522 5(3)
C(25)	0.063 6(3)	0.039 9(8)	0.410 8(3)		0.597 3(3)	0.376 6(8)	0.442 6(4)
N(31)	0.239 4(2)	0.114 0(5)	0.377 4(2)		0.623 9(2)	0.272 7(5)	0.254 2(2)
P(32)	0.276 47(6)	0.178 91(16)	0.428 00(7)		0.575 02(6)	0.202 15(15)	0.217 91(6)
C(33)	0.230 5(2)	0.244 7(6)	0.471 0(2)		0.531 0(2)	0.156 9(6)	0.267 1(3)
C(34)	0.197 0(3)	0.163 4(7)	0.496 0(3)		0.513 0(3)	0.251 9(8)	0.300 5(3)
C(35)	0.161 2(3)	0.210 7(9)	0.529 2(3)		0.478 1(3)	0.222 5(11)	0.338 8(4)
C(36)	0.157 2(3)	0.336 8(9)	0.538 4(3)		0.461 5(3)	0.098 5(13)	0.342 6(4)
C(37)	0.190 4(3)	0.419 7(8)	0.514 9(3)		0.478 4(3)	0.006 3(9)	0.310 8(4)
C(38)	0.227 0(3)	0.374 8(6)	0.481 1(3)		0.513 5(3)	0.034 3(8)	0.272 2(3)
C(39)	0.315 5(2)	0.304 3(7)	0.405 3(3)		0.596 3(2)	0.064 4(6)	0.183 4(3)
C(40)	0.294 6(3)	0.373 7(8)	0.359 3(3)		0.643 6(3)	0.006 8(8)	0.204 1(4)
C(41)	0.321 5(5)	0.478 3(9)	0.343 1(4)		0.659 6(4)	−0.101 4(10)	0.180 4(5)
C(42)	0.368 6(5)	0.514 1(12)	0.371 6(5)		0.629 5(4)	−0.154 4(8)	0.136 4(5)
C(43)	0.390 1(4)	0.447 2(12)	0.416 8(6)		0.583 6(4)	−0.099 0(8)	0.114 6(4)
C(44)	0.363 8(3)	0.341 5(8)	0.433 7(3)		0.566 1(3)	0.011 9(8)	0.137 8(3)
C(45)	0.318 0(3)	0.069 3(8)	0.468 4(3)		0.537 4(3)	0.302 6(7)	0.168 3(3)
Br(1)[a]	0.573 60(6)	0.183 48(15)	0.578 61(6)	Br(3)[a]	0.493 66(8)	0.356 07(18)	0.532 66(9)
Br(2)[a]	0.079 28(6)	−0.057 96(18)	0.558 78(7)	Br(4)[a]	0.015 08(9)	−0.233 82(15)	0.477 55(7)

[a] *pp*[Br(1)] = 0.517(4), *pp*[Br(3)] = 1 − *pp*[Br(1)], *pp*[Br(2)] = 0.453(4), *pp*[Br(4)] = 1 − *pp*[Br(2)]; *pp* = population parameter.

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