Crystal Structures of *meso-ortho*-Phenylenebis(methylphenylphosphine) and its Monoprotonated Tetrafluoroborate Salt

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The crystal structures of the title compounds, $C_6H_4(PMePh)_2$ (1) and $[C_6H_4(PMePhH)(PMePh)][BF_4]$ (2), have been determined by single-crystal *X*-ray diffraction methods at 295 K and refined by least squares to residuals of 0.044(1) (1 726 'observed' reflections) and 0.045(2) (1 755). Crystals of (1) are monoclinic, space group $P2_1/n$, with *a* 14.604(8), *b* 10.181(6), *c* 12.868(9) Å, β 110.94(5)°, and $Z = 4$; those of (2) are triclinic, $P\bar{1}$, with *a* 12.594(5), *b* 9.988(4), *c* 8.643(4) Å, α 81.69(3), β 87.62(3), γ 70.85(3)°, and $Z = 2$. In (1), ⟨P–C⟩ is 1.83_9 Å and ⟨C–P–C⟩ $100._7$°; in (2), the corresponding values about one of the phosphorus atoms are 1.83_5 Å and $102._2$°, but about the other, 1.78_9 Å and $110._0$°, and it is tentatively proposed that the proton is bonded to the latter. The anion in (2) is disordered.

In 1,8-bis(dimethylamino)naphthalene, the 1,8 nitrogen-atom disposition is peculiarly appropriate for the 'chelation' of a proton, and the fact that the basicity of the compound is unusually high is attributed to this cause, the protonation effectively relieving strain between the nitrogen lone pairs.[1] In a recent report,[2] the synthesis of (*RS*)-*o*-phenylenebis(methylphenylphosphine), (1), and its 1 : 1 HBF_4 salt, (2), have been described. Room-temperature ^1H n.m.r. studies of the latter in CD_2Cl_2 solution are indicative of equivalence of the two methyl groups, with chemical shifts and coupling constants being intermediate between the values expected for tertiary and quaternary species. Although the expected P · · · P separation in such species is considerably greater (*ca.* 3.2 Å) than the expected N · · · N separation in the above diamine, it was considered to be of interest to examine the crystal structures of (1) and (2), to ascertain, if possible, the disposition of the proton relative to the phosphorus atoms and its effect, if any, on the molecular stereochemistry.

EXPERIMENTAL

Crystal Data.—(1). $C_{20}H_{20}P_2$, *M* 322.3, Monoclinic, space group $P2_1/n$ (C^5_{2h}, no. 14), *a* 14.604(8), *b* 10.181(6), *c* 12.868(9) Å, β 110.94(5)°, *U* 1 787(2) Å^3, D_m 1.20(1), *Z* 4, D_c 1.20 g cm^{-3}, *F*(000) 680, monochromatic Mo-K_α radiation [also for (2)], λ 0.710 69 Å, μ 2.4 cm^{-1}, specimen size 0.13 × 0.37 × 0.37 mm.

(2). $C_{20}H_{21}BF_4P_2$, *M* 410.1, Triclinic, space group $P\bar{1}$(C^1_i, no. 2), *a* 12.594(5), *b* 9.988(4), *c* 8.643(4) Å, α 81.69(3), β 87.62(3), γ 70.85(3)°, *U* 1 016(1) Å^3, D_m 1.33(1), *Z* 2, D_c 1.34 g cm^{-3}, *F*(000) 424, μ 2.6 cm^{-1}, specimen size 0.19 × 0.34 × 0.24 mm.

Structure Determination.—Unique data sets measured with $2\theta_{max.}$ 50° (1) [45° (2)] yielded 3 171(1) [2 608(2)] independent reflections; 1 726 (1 755) of these respectively were considered 'observed' at the $I > 3\sigma(I)$ level and were used in the refinement after solution (heavy-atom method) and correction for absorption. Refinement was basically by 9 × 9 block-diagonal least squares but with any hydrogen-atom parameters refined in the same block as the parent non-hydrogen atom; for (2) the BF_4 parameters were treated as a single block. The thermal parameters were anisotropic for non-hydrogen atoms, isotropic for hydrogen. Final residuals *R,R'* of 0.044, 0.051(1) [0.045, 0.055(2)] were obtained with weights $w = [\sigma^2(F_o) + 0.000\ 5(F_o)^2]^{-1}$. Neutral-atom scattering factors were employed, those for P being corrected for anomalous dispersion (f', f'').[3-5] Computations were carried out with the '*X*-RAY '76' program system [6] on a CYBER 73 computer. Final atomic coordinates are in Table 1, bond lengths and angles in Table 2. Structure-factor amplitudes, thermal parameters, hydrogen-atom parameters, and phenyl-ring planes are available in Supplementary Publication No. SUP 22701 (28 pp.).† The unit-cell contents of (1) and (2) are shown in Figure 1.

Abnormal Features of (2).—The anion was refined initially as a single unit; the presence of residuals in a different map, however, suggested it to be disordered, and adoption of a disordered pair of anions, each assigned a population of 0.5 in the refinement, led to considerably improved residuals. Refinement of the structure without the phosphine hydrogen atom converged at *R* 0.045. Examination of a difference map showed significant regions of electron density of similar magnitude close to the phosphorus atoms and at similar distances from them in the 'tetrahedral' co-ordination sites; the density in these peaks was comparable to those of the other hydrogen atoms in a conventional electron-density map, and considerably enhanced relative to the values observed in the same sites of compound (1). On the other hand, the carbon-atom disposition about one of the phosphorus atoms [P(a)] was typical of a tertiary phosphine, and generally similar to the dispositions observed in (1) [*e.g.* the disposition about the other phosphorus, P(b), was quite different, the associated bond lengths being unusually short and the angular geometry much closer to tetrahedral]. Accordingly, it was concluded that the hydrogen atom was associated with P(b) and it was included and refined meaningfully in (*x,y,z*) and *U*, although the residuals remained unchanged. The convincing region of electron density about the other phosphorus atom P(a) remained and was ascribed to the phosphorus lone pair; it is not possible to unequivocally describe it as such, however, since it was possible to refine the regions of electron density at *both* hydrogen atoms meaningfully in terms of a pair of half-weighted hydrogen atoms, although again the residuals remained unaffected. Chemically, we prefer the model in which the hydrogen atom is located on P(b), since the geometry about P(b) is in keeping with a tetrahedrally

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†For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

hybridized phosphorus atom; the enhanced density of the 'lone pair' on P(a) is presumably to be ascribed to the nearness of the hydrogen atom on P(b) and its consequent polarization due to the proximity of that hydrogen atom in what is essentially an intramolecular P(a) · · · H_P(b) hydrogen bond [2.95(3) Å]. A more definitive answer to the problem in terms other than these appears to be beyond the scope of *X*-ray analysis, at least at room temperature, and may only be accessible by neutron techniques.

DISCUSSION

The unit-cell contents of (1) and (2) comprise, as expected, discrete molecules of (1) and 1 : 1 cation–anion arrays in (2), the asymmetric unit of the structure in each case comprising one of each species. The phenyl-ring geometries are unexceptional in each case, except inasmuch as they are affected by their interaction with the phosphorus atom, and accordingly discussion will be focused on those features of interest about the phosphine groups.

TABLE 1

Non-hydrogen atom fractional cell co-ordinates (× 10^4)

Atom	Section a			Section b		
	x	*y*	*z*	*x*	*y*	*z*
(*a*) Compound (1)						
P	2 111.2(7)	0 745.1(10)	0 600.4(8)	3 962.8(8)	1 648.9(11)	0 041.6(9)
C(1)	4 250(3)	1 156(4)	3 724(3)	5 051(3)	1 529(4)	3 479(4)
C(2)	3 364(3)	0 940(4)	2 870(3)	4 966(3)	1 696(4)	2 390(3)
C(3)	3 267(2)	1 100(3)	1 759(3)	4 086(3)	1 504(3)	1 514(3)
C(4)	1 218(3)	1 037(3)	1 263(3)	3 345(3)	3 245(4)	−0 353(3)
C(5)	0 626(3)	0 083(4)	1 463(3)	2 824(3)	3 484(5)	−1 453(4)
C(6)	−0 078(3)	0 411(5)	1 899(4)	2 396(3)	4 706(5)	−1 801(4)
C(7)	−0 193(3)	1 691(5)	2 166(4)	2 465(4)	5 666(5)	−1 051(4)
C(8)	0 381(3)	2 661(5)	1 973(4)	2 963(4)	5 433(5)	0 054(4)
C(9)	1 066(3)	2 339(4)	1 520(3)	3 395(4)	4 228(4)	0 400(4)
C(10)	2 214(5)	−1 060(5)	0 615(5)	5 209(4)	2 159(8)	0 175(6)
(*b*) Compound (2) (fluorine populations: 0.5)						
P	2 376(1)	0 242(1)	1 739(1)	2 097(1)	3 395(1)	2 509(1)
C(1)	1 268(4)	0 237(6)	6 320(6)	1 194(4)	1 586(6)	6 607(6)
C(2)	1 606(4)	−0 179(5)	4 871(5)	1 426(4)	2 533(6)	5 439(6)
C(3)	1 866(3)	0 752(4)	3 682(5)	1 765(3)	2 138(4)	3 977(5)
C(4)	3 635(4)	−1 296(4)	2 252(5)	3 592(3)	2 956(4)	2 427(4)
C(5)	4 667(4)	−1 084(6)	1 976(6)	4 275(4)	2 082(5)	3 638(5)
C(6)	5 663(5)	−2 239(7)	2 310(6)	5 421(4)	1 775(6)	3 583(6)
C(7)	5 616(5)	−3 558(6)	2 916(6)	5 902(4)	2 339(5)	2 315(5)
C(8)	4 617(5)	−3 764(6)	3 206(6)	5 240(4)	3 200(5)	1 104(6)
C(9)	3 636(5)	−2 656(5)	2 890(5)	4 085(4)	3 516(5)	1 170(6)
C(10)	1 364(5)	−0 581(8)	1 244(8)	1 459(6)	5 186(6)	2 927(10)
H_P *				173(3)	339(3)	116(4)
B	−1 264(6)	3 890(8)	1 944(10)			
F(1)	−1 988(16)	3 649(18)	1 045(23)	−2 029(13)	4 264(28)	0 914(21)
F(2)	−1 713(14)	3 564(16)	3 592(16)	−1 460(22)	3 562(29)	3 151(22)
F(3)	−0 245(9)	3 298(20)	1 565(26)	−0 437(17)	2 723(22)	1 601(33)
F(4)	−1 508(14)	5 360(13)	1 638(18)	−0 833(21)	4 789(26)	2 216(29)

* (*x*, *y*, *z*), × 10^3.

(*i*) *Phosphorus–Carbon Geometries.*—In (1), all P–C(aryl) distances lie in the range 1.820(4)—1.845(3) Å; the P–CH_3 distances are not significantly different [1.843(5), 1.841(7) Å]. The angles about the phosphorus atoms vary widely, from 98.0(2) to 103.1(3)°. These values are comparable with those observed in the structure determination of tri(*o*-toyl)phosphine ($\langle$P–C$\rangle$ 1.83_5 Å, $\langle$C–P–C$\rangle$ $102._6$°).[7] In (2), the geometry about P(a) is similar ($\langle$P–C$\rangle$ 1.83_5, $\langle$C–P–C$\rangle$ $102._2$°) but about P(b) $\langle$P–C$\rangle$ is 1.78_9 Å and $\langle$C–P–C$\rangle$ $110._0$°. That the hypothesis proposed above in the discussion of the refinement concerning the location of the proton on P(b) rather than P(a) is valid is supported by comparison of this geometry with the other meagre data on protonated triarylphosphonium systems, *e.g.* in $[PPh_3H]_3[PrCl_6]$ $\langle$P–C$\rangle$ is 1.78(2) Å and $\langle$C–P–C$\rangle$ 109.7(16)°.[8]

(*ii*) *Phosphorus–Central Aryl Geometries.*—Whereas the P–C(3)–C(3) angles in (1) and (2) lie in the range 118.4(3)—118.9(3)° for the non-protonated phosphorus atoms, P(b)–C(3b)–C(3a) in (2) is considerably enlarged [121.1(3)°], and it is presumably this change which is associated with the increased 'bite' of the ligand from P · · · P 3.173(2) in (1) to 3.217(2) Å in (2).

(*iii*) *Phosphorus–Hydrogen Geometry.*—Given that it is valid to assign a population of 1.0 to the hydrogen site on P(b) in (2), P–H is found to be 1.28(3) Å. This value is shorter than the value of 1.41_4 Å observed for P–H in the PH_4^+ species in $[PH_4]I$;[9] in view of the possibly different interactions of the proton with its environment in each case, and of the different scattering models and data, it would be unwise to comment further on the significance of this observation until it is corroborated by neutron work.

(*iv*) *Substituent Dispositions.*—Consideration of Figure 2 in conjunction with molecular models shows that torsion of the phosphorus substituents about P–C(3) relative to the central ring cannot be carried out on any

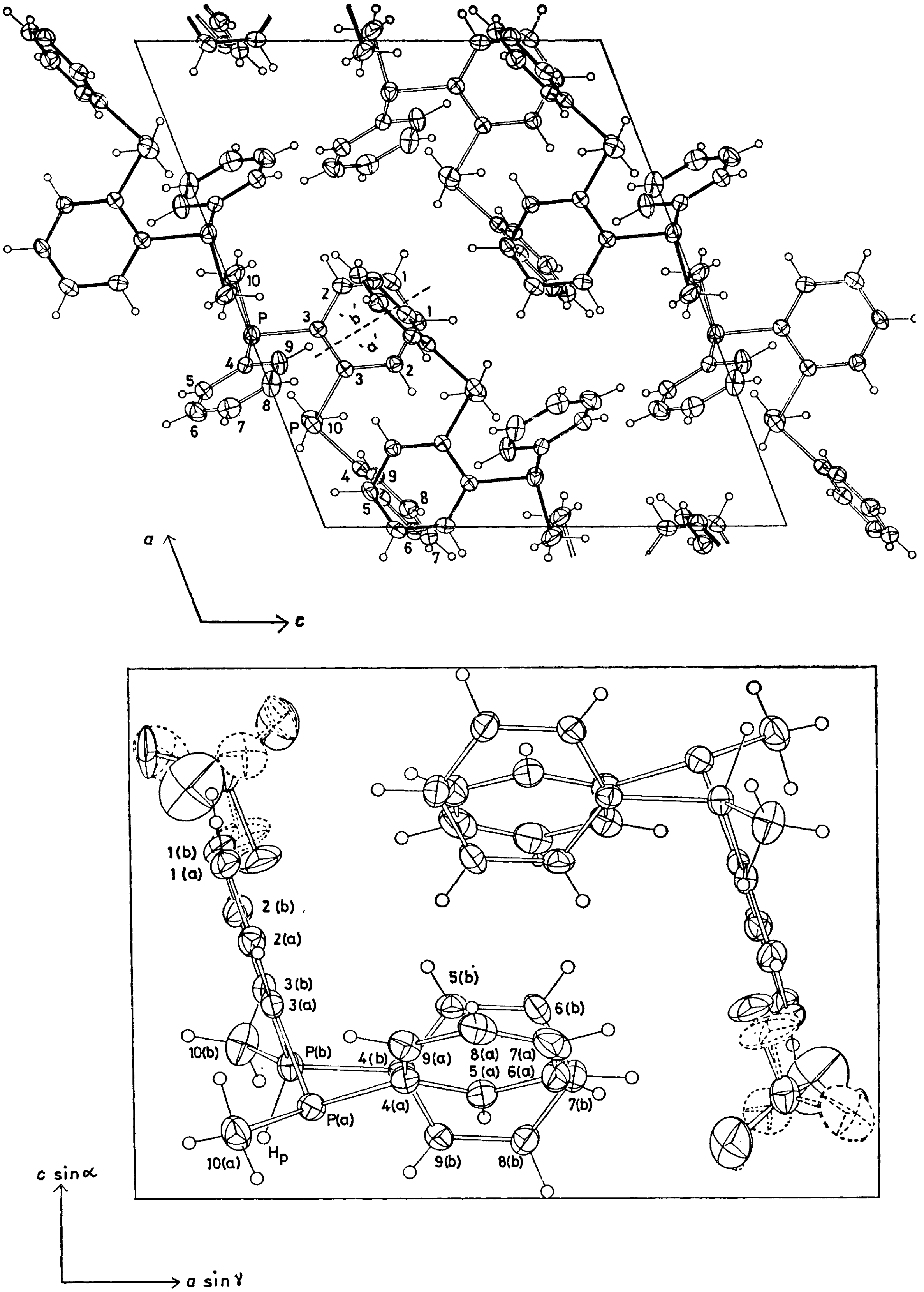

FIGURE 1 Unit-cell constants of (*a*) compound (1) showing non-hydrogen atom labelling and 20% thermal ellipsoids (hydrogen atoms being given an arbitrary radius of 0.1 Å) projected down *b*, (*b*) compound (2) displayed similarly

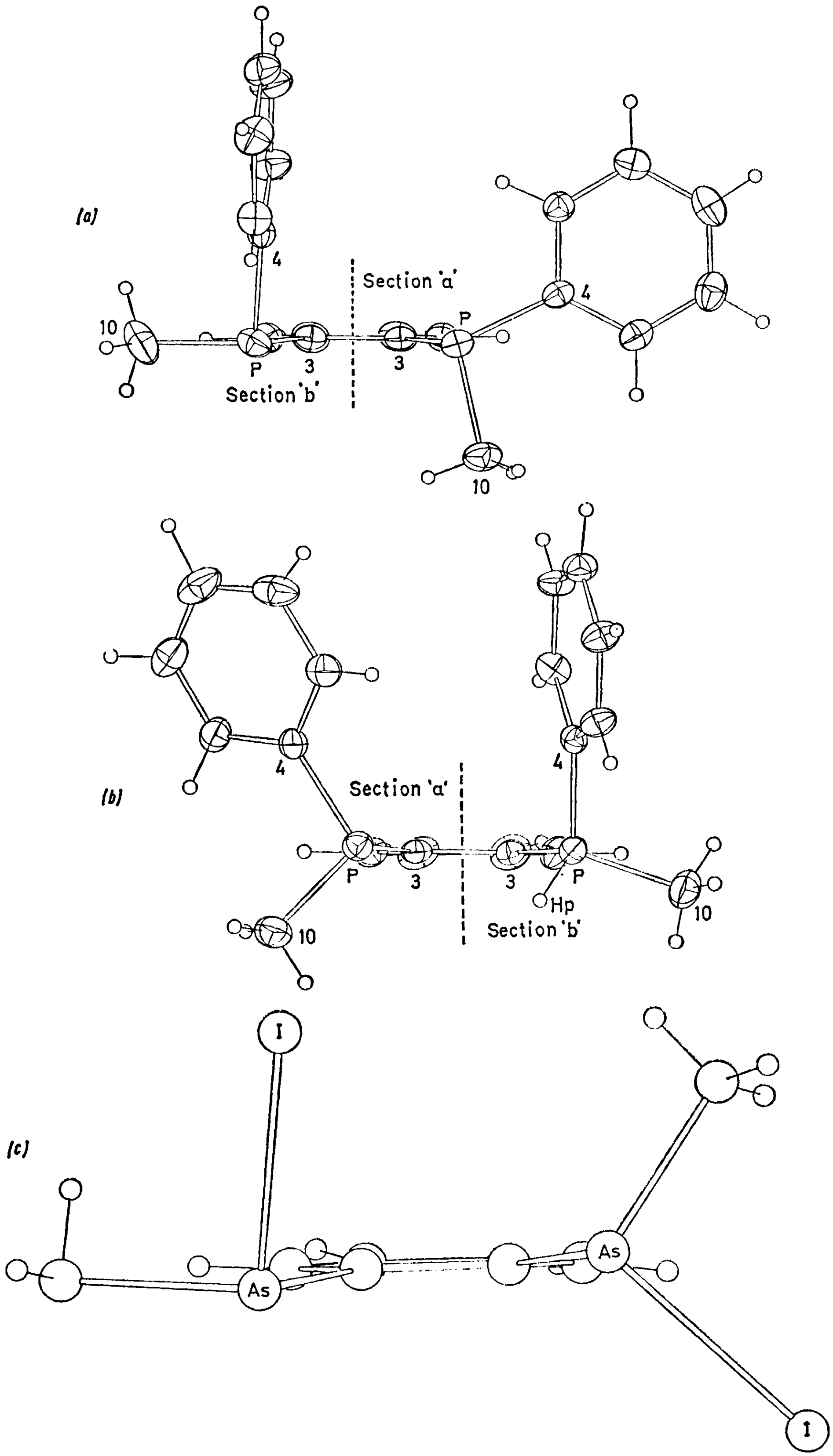

FIGURE 2 Projection of each phosphorus species in compound (2) along the C(3)→C(1) direction in the central phenyl ring to display substituent dispositions relative to that ring plane [(*a*), (*b*)], and of the molecule of *rac*-phenylenebis(iodomethylarsine) in its crystal structure (*c*)

given C(3)–P bond regardless of interactions with the substituents on the other phosphorus or the central ring itself. Minimization of these interactions requires torsion about P–C(4) to an extent dependent on the deviation of the methyl carbon from the central ring plane; Figure 2 and Table 3 show that when C(10) lies close to the ring plane, C(10)–P lies almost normal to the plane of the phenyl substituent, whereas when C(10) is removed from the plane the plane of the phenyl substituent is rotated to the limit where it and the P–C(10) bond are almost coplanar. In the latter disposition, the phenyl *ortho*-hydrogen lies close to the methyl group on the same phosphorus atom and the two nearby methyl hydrogens in consequence lie astride it. Intuitively it would be expected that a substituent disposition in which the carbon atoms on the phosphorus are displaced approximately equal distances on either side of the central ring plane and have overall pseudo-*m* symmetry (*m* normal to the ring plane) would be of lowest energy, but the above results suggest that this is not so and that an unsymmetrical disposition with its concomitant phenyl-substituent rotations may be preferred as in Figure 2(*a*). Interestingly, this disposition is also observed in the molecule of *rac*-phenylenebis(iodomethylarsine),[10] Figure 2(*c*), and it will be of interest to examine further structures of this type to assess the generality of this result. (In ref. 10, the structure of the *meso* analogue is also reported; it does *not* conform to this result, presumably as a consequence of strong charge-transfer interactions with nearby iodide ions in the lattice.)

TABLE 2

Non-hydrogen atom geometry

	Compound (1)		Compound (2) [a]	
	Section a	Section b	Section a	Section b
Distances (Å)				
C(1a)–C(1b)	1.369(7)		1.377(9)	
C(1)–C(2)	1.383(5)	1.372(7)	1.383(7)	1.372(8)
C(2)–C(3)	1.395(5)	1.388(5)	1.387(6)	1.387(7)
C(3a)–C(3b)	1.403(6)		1.407(6)	
C(3)–P	1.845(3)	1.844(2)	1.854(4)	1.789(4)
P–C(4)	1.820(4)	1.840(4)	1.826(4)	1.789(4)
P–C(10)	1.843(5)	1.841(7)	1.821(9)	1.788(6)
P(a) · · · P(b)	3.173(2)		3.217(2)	
C(4)–C(5)	1.384(6)	1.369(5)	1.389(8)	1.384(6)
C(5)–C(6)	1.378(7)	1.393(7)	1.404(7)	1.374(7)
C(6)–C(7)	1.373(7)	1.351(8)	1.365(10)	1.369(7)
C(7)–C(8)	1.375(7)	1.367(7)	1.348(10)	1.368(6)
C(8)–C(9)	1.366(7)	1.379(6)	1.367(7)	1.384(7)
C(9)–C(4)	1.403(6)	1.376(6)	1.389(7)	1.369(7)
Angles (°)				
C(1)–C(1)–C(2)	119.7(4)	119.8(4)	120.2(5)	119.9(5)
C(1)–C(2)–C(3)	121.3(4)	122.1(4)	120.8(5)	120.8(5)
C(2)–C(3)–C(3)	118.8(3)	118.4(4)	118.5(4)	119.7(4)
C(3)–C(3)–P	118.9(3)	118.5(2)	118.4(3)	121.1(3)
C(2)–C(3)–P	122.3(3)	123.0(3)	123.1(4)	119.1(4)
C(3)–P–C(4)	101.0(2)	102.2(2)	102.1(4)	108.4(2)
C(3)–P–C(10)	98.0(2)	101.4(3)	101.4(3)	111.1(3)
C(4)–P–C(10)	103.1(3)	98.5(3)	102.9(3)	110.4(3)
P–C(4)–C(5)	124.8(3)	118.6(2)	117.2(4)	121.3(3)
P–C(4)–C(9)	117.7(3)	123.4(3)	124.9(4)	120.2(3)
C(5)–C(4)–C(9)	117.3(4)	118.0(4)	117.9(4)	118.4(4)
C(4)–C(5)–C(6)	120.8(4)	120.7(4)	119.6(6)	121.0(4)
C(5)–C(6)–C(7)	120.5(5)	120.5(4)	120.1(6)	119.9(4)
C(6)–C(7)–C(8)	120.0(5)	119.6(5)	120.4(5)	119.9(5)
C(7)–C(8)–C(9)	119.4(4)	120.1(5)	120.5(6)	120.1(5)
C(8)–C(9)–C(4)	122.0(4)	121.2(4)	121.5(6)	120.7(4)

Anion geometries [compound (2)] [b]

Distances (Å)			
B–F(1)	1.32(2), 1.26(2)	F(1a) · · · F(1b)	0.59(3)
B–F(2)	1.54(2), 1.09(2)	F(2a) · · · F(2b)	0.49(3)
B–F(3)	1.28(1), 1.35(2)	F(3a) · · · F(3b)	0.69(3)
B–F(4)	1.39(1), 1.24(3)	F(4a) · · · F(4b)	0.97(3)
Angles (°)			
F(1)–B–F(2)	102(1), 119(2)	F(2)–B–F(3)	122(1), 102(2)
F(1)–B–F(3)	113(1), 110(2)	F(2)–B–F(4)	107(1), 97(2)
F(1)–B–F(4)	103(1), 118(2)	F(3)–B–F(4)	108(2), 108(1)

[a] P–H_P 1.28(3) Å, H_P–P–C(3) 113(2), H_P–P–C(4) 109(1), and H_P–P–C(10) 105(1)°. [b] The two entries are for the pair of disordered components (a) and (b).

A further implication of the above is that in (1) at least, rotation about the P–C(3) bonds should be considerably hindered; an extension of the study of the ^1H n.m.r. spectrum to low temperatures (down to 185 K) in dry CH_2Cl_2 (at which point crystallization occurred) showed no significant change in the 1 : 2 : 1 triplet structure of the methyl signals. By contrast, a study of (2) in dry CH_2Cl_2 down to 180 K showed that the proton-exchange rate was slow enough below 250 K (the coalescence temperature) to enable two different phosphorus-methyl signals, quaternary and ternary, to be distinguished. The spectra will be discussed in greater detail elsewhere.[2]

TABLE 3

Deviations of C(10) from the central ring plane, δ/Å, together with the torsion angle C(10)–P–C(4)–C(*n*) (τ/°) where *n* = 5 or 9 depending on whichever atom is nearest C(10)

Molecule and section	δ[C(10)]	|τ|
1a	1.89	13.1
1b	0.05	79.2
2a	1.22	29.5
2b	0.56	73.9

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