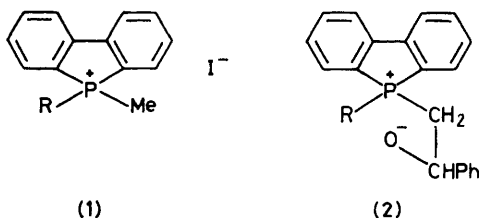


Ring Strain and the Reactivity of Dibenzophospholes and their Quaternary Salts: Crystal and Molecular Structure of 5-(*p*-Bromobenzyl)-5-phenyldibenzophospholium Bromide

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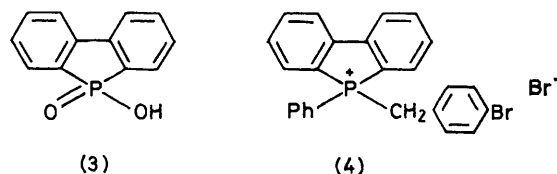
Crystals of the title compound are monoclinic, $a = 25.685(15)$, $b = 10.444(6)$, $c = 18.818(11)$, $\beta = 119.18(5)^\circ$, $Z = 8$ in space group $C2/c$, with the oxygens of water molecules present in the crystals lying along two-fold axes. The structure was determined by Patterson and electron-density methods and refined by least-squares techniques to $R = 0.066$ for 992 independent reflections. The fused ring system of the dibenzophospholium cation is almost planar and while the exocyclic C-P-C angles lie in the range 110 – 117° , the endocyclic angle is 93.9° . It is suggested that this low value is consistent with the presence of considerable ring strain, which is relieved either on phosphorane formation following nucleophilic attack at phosphorus, or on dealkylation of dibenzophospholium salts. The implications of ring strain in dibenzophospholium salts are discussed in connection with the possible aromaticity of the dibenzophospholes.

We have shown previously that dibenzophospholium salts (1; $R = \text{Me}$ or Ph) undergo alkaline hydrolysis (with ring-opening) extremely rapidly in comparison with their acyclic analogues.^{1,2} Similarly dibenzophospholium betaines (*e.g.* 2; $R = \text{Ph}$ or Bu^t) collapse rapidly in protic media to the expected Wittig reaction products whereas under the same conditions, the analogous acyclic phosphonium betaines decompose to give a range of abnormal products which arise via the intermediacy of vinylphosphonium salts derived from the betaines.^{3,4} Furthermore, certain dibenzophospholium salts undergo alkaline hydrolysis with ring expansion to form derivatives of the dibenzo[*b,d*]phosphorin system.^{2,5,6}



It has been suggested that the foregoing reactions occur as a consequence of ring strain in the dibenzophospholium salts which is relieved on formation of a trigonal bipyramidal phosphorane in which the ring system spans an apical-equatorial position; nucleophilic attack at the phosphonium centre is therefore facilitated. However, there is very little structural information on dibenzophosphole derivatives to support this argument. A number of metal complexes of 5-alkyldibenzophospholes have been studied by *X*-ray techniques⁷ as has also the phosphinic acid (3),⁸ but the structures of simple quaternary salts of the dibenzophosphole system have

not been reported. Accordingly we have carried out and now report a single-crystal *X*-ray study of the salt (4).



EXPERIMENTAL

5-p-Bromobenzyl-5-phenyldibenzophospholium Bromide (4).—5-Phenyldibenzophosphole (0.13 g, 0.5 mmol) and *p*-bromobenzyl bromide (0.2 g, excess) were heated under reflux in benzene (5 cm³) for 2 h, during which time the salt separated from the solution. After filtration and washing with benzene, the salt was recrystallised from absolute ethanol to give *crystals*, m.p. 306 – 307°C [Found: C, 58.25; H, 3.8. $\text{C}_{25}\text{H}_{19}\text{Br}_2\text{P}(0.5\text{H}_2\text{O})$ requires C, 57.85; H, 3.75%]; $\bar{\nu}_{\text{max}}$ (mull): 3460 and 3410 cm^{-1} (O-H).

Crystal Data.— $[\text{C}_{25}\text{H}_{19}\text{PBr}]^+\text{Br}^-\cdot\frac{1}{2}\text{H}_2\text{O}$, $M = 519.2$. Monoclinic, $a = 25.685(15)$, $b = 10.444(6)$, $c = 18.818(11)$, $\beta = 119.18(5)^\circ$, $U = 4407.32\text{ \AA}^3$, $D_m = 1.56$, $Z = 8$, $D_c = 1.57\text{ g cm}^{-3}$, $F(000) = 2080$. Mo- K_α radiation, $\lambda = 0.71069\text{ \AA}$; $\mu(\text{Mo-}K_\alpha) = 36.6\text{ cm}^{-1}$. Space group $C2/c$ (C_2^h , No. 15) from systematic absences.

Intensities were measured on a Stöe-Stadi 2 diffractometer by the background- ω scan-background technique, to give 992 independent reflections, having $I/\sigma(I) \geq 2.5$. Lorentz and polarization factors were applied, but no absorption correction was made.

Structure Solution and Refinement.—The positions of the bromine atoms were determined from a Patterson synthesis, and the remaining non-hydrogen atoms were located from successive electron-density difference syntheses. The four oxygen atoms per unit cell lie along two-fold axes at the special positions $0, y, \frac{1}{4}$; $0, -y, \frac{3}{4}$; $\frac{1}{2}, \frac{1}{2} + y, \frac{1}{4}$; $\frac{1}{2}, \frac{1}{2} - y, \frac{3}{4}$. The structure was refined by full-matrix least-squares methods, finally with all atoms given anisotropic thermal

¹ D. W. Allen and I. T. Millar, *J. Chem. Soc. (B)*, 1969, 263.

² D. W. Allen and I. T. Millar, *J. Chem. Soc. (C)*, 1969, 252.

³ D. W. Allen, B. G. Hutley, and K. Polasik, *J.C.S. Perkin I*, 1975, 619.

⁴ D. W. Allen, P. Heatley, B. G. Hutley, and M. T. J. Mellor, *J.C.S. Perkin I*, 1976, 2529.

⁵ E. M. Richards and J. C. Tebby, *J. Chem. Soc. (C)*, 1971, 1064.

⁶ D. W. Allen and A. C. Oades, *J.C.S. Perkin I*, 1976, 2050.

⁷ D. W. Allen, F. G. Mann, I. T. Millar, H. M. Powell, and D. Watkin, *Chem. Comm.* 1969, 1004; H. M. Powell and K. M. Chui, *ibid.*, 1971, 1037; H. M. Powell, D. J. Watkin, and J. B. Wilford, *J. Chem. Soc. (A)*, 1971, 1803.

⁸ J. J. DeBoer and D. Bright, *Acta Cryst.*, 1974, **B30**, 797.

parameters and using the weighting scheme $w = 0.1277/[\sigma^2(F) + 0.046F^2]$. The scattering factors of ref. 9 were used and the refinement converged at R 0.066 for the 992 observed reflections. Final observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. 22130 (8 pp.).* Positional parameters are given in Table 1, bond lengths and valency

TABLE 1

Final positional parameters with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Br ⁻	0.062 3(1)	0.329 8(3)	0.661 7(2)
Br	0.187 2(1)	0.222 0(3)	0.332 8(2)
P	0.116 5(2)	0.669 0(6)	0.560 8(3)
O	0.000 0	0.156 1(20)	0.750 0
C(1)	0.071 9(9)	0.757 8(23)	0.593 9(12)
C(2)	0.042 6(8)	0.685 9(24)	0.629 5(10)
C(3)	0.008 4(9)	0.759 8(27)	0.654 0(10)
C(4)	0.007 7(10)	0.890 0(27)	0.652 0(17)
C(5)	0.036 9(10)	0.955 8(26)	0.618 9(15)
C(6)	0.070 2(8)	0.889 9(23)	0.589 3(12)
C(7)	0.074 9(8)	0.536 0(21)	0.500 9(12)
C(8)	0.105 5(9)	0.459 6(23)	0.461 5(11)
C(9)	0.096 7(10)	0.501 9(23)	0.385 1(14)
C(10)	0.120 9(9)	0.431 4(21)	0.347 1(12)
C(11)	0.155 0(9)	0.328 7(25)	0.386 2(12)
C(12)	0.165 0(9)	0.284 8(24)	0.461 9(14)
C(13)	0.141 6(8)	0.357 0(24)	0.500 8(11)
C(14)	0.145 9(8)	0.772 7(23)	0.516 6(10)
C(15)	0.206 6(9)	0.787 1(23)	0.565 6(12)
C(16)	0.240 1(9)	0.875 1(24)	0.546 7(13)
C(17)	0.209 2(10)	0.940 0(21)	0.473 4(13)
C(18)	0.148 4(11)	0.920 1(28)	0.421 2(12)
C(19)	0.116 4(8)	0.839 5(22)	0.441 6(12)
C(20)	0.190 0(8)	0.624 9(22)	0.645 5(12)
C(21)	0.203 1(7)	0.535 7(23)	0.707 3(11)
C(22)	0.261 4(10)	0.528 5(28)	0.765 2(12)
C(23)	0.306 2(9)	0.605 2(26)	0.761 5(13)
C(24)	0.291 7(9)	0.695 9(25)	0.700 8(11)
C(25)	0.231 1(7)	0.703 1(18)	0.641 6(10)

angles in Table 2, and the equations of some least-square planes in Table 3.

DISCUSSION

The fused ring system of the dibenzophospholium cation (Figure 1) is almost planar. The four carbons of the five-membered ring are effectively co-planar [Table 3, plane (a)] and the attached six-membered rings are inclined at angles of 2.60 and 2.84° to this plane while the phosphorus lies 0.159 Å out of it. The planes associated with the C(8)—(13) *p*-bromobenzyl and C(1)—(6) phenyl rings, make angles of 73.0 and 72.8° with plane (a) and 44.4° with each other, and presumably reflect packing requirements rather than stereochemical interactions within the cation itself. The C—P—C exocyclic bond angles lie in the range 110—117°, but the endocyclic C(14)—P—C(20) angle is only 93.9(9)°, and close to the value (93.4°) found for the phosphinic acid (3). This small value for the endocyclic angle would seem to

* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1976, Index issue.

† 'International Tables for X-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.

TABLE 2

Bond distances (Å) and angles (°), with standard deviations in parentheses

(a) Distances			
P—C(1)	1.80(2)	C(11)—C(12)	1.40(3)
P—C(7)	1.78(2)	C(12)—C(13)	1.38(3)
P—C(14)	1.75(2)	C(14)—C(15)	1.38(2)
P—C(20)	1.84(2)	C(14)—C(19)	1.42(2)
C(1)—C(2)	1.44(3)	C(15)—C(16)	1.42(3)
C(1)—C(6)	1.38(3)	C(15)—C(25)	1.53(2)
C(2)—C(3)	1.41(3)	C(16)—C(17)	1.39(3)
C(3)—C(4)	1.36(3)	C(17)—C(18)	1.40(3)
C(4)—C(5)	1.37(4)	C(18)—C(19)	1.36(3)
C(5)—C(6)	1.41(3)	C(20)—C(21)	1.40(3)
C(7)—C(8)	1.54(3)	C(20)—C(25)	1.37(3)
C(8)—C(9)	1.41(3)	C(21)—C(22)	1.36(2)
C(8)—C(13)	1.37(3)	C(22)—C(23)	1.43(3)
C(9)—C(10)	1.37(3)	C(23)—C(24)	1.39(3)
C(10)—C(11)	1.35(3)	C(24)—C(25)	1.41(2)
C(11)—Br	1.94(2)		
Br ⁻ ··· O	3.35(2)		
(b) Angles			
C(1)—P—C(7)	109.5(11)	C(11)—C(12)—C(13)	117(2)
C(1)—P—C(14)	109.9(12)	C(8)—C(13)—C(12)	120(2)
C(1)—P—C(20)	112.8(10)	P—C(14)—C(15)	111(1)
C(7)—P—C(14)	116.6(11)	P—C(14)—C(19)	129(1)
C(7)—P—C(20)	113.5(10)	C(15)—C(14)—C(19)	120(2)
C(14)—P—C(20)	93.9(9)	C(14)—C(15)—C(16)	122(2)
P—C(1)—C(2)	117(2)	C(14)—C(15)—C(25)	112(2)
P—C(1)—C(6)	120(2)	C(16)—C(15)—C(25)	126(1)
C(2)—C(1)—C(6)	123(2)	C(15)—C(16)—C(17)	116(2)
C(1)—C(2)—C(3)	115(2)	C(16)—C(17)—C(18)	122(2)
C(2)—C(3)—C(4)	123(3)	C(17)—C(18)—C(19)	121(2)
C(3)—C(4)—C(5)	121(3)	C(14)—C(19)—C(18)	119(2)
C(4)—C(5)—C(6)	121(2)	P—C(20)—C(21)	128(2)
C(1)—C(6)—C(5)	118(2)	P—C(20)—C(25)	107(1)
P—C(7)—C(8)	115(1)	C(21)—C(20)—C(25)	124(1)
C(7)—C(8)—C(9)	118(2)	C(20)—C(21)—C(22)	115(2)
C(7)—C(8)—C(13)	121(2)	C(21)—C(22)—C(23)	122(2)
C(9)—C(8)—C(13)	122(2)	C(22)—C(23)—C(24)	122(2)
C(8)—C(9)—C(10)	118(2)	C(23)—C(24)—C(25)	116(2)
C(9)—C(10)—C(11)	119(2)	C(15)—C(25)—C(20)	115(1)
Br—C(11)—C(10)	120(2)	C(15)—C(25)—C(24)	124(2)
Br—C(11)—C(12)	115(2)	C(20)—C(25)—C(24)	121(2)
C(10)—C(11)—C(12)	124(2)		

TABLE 3

Equations of least-squares planes referred to orthogonal axes with distances (Å) of relevant atoms from the planes in square brackets

Plane (a): C(14), C(15), C(20), C(25)

$$0.4835X - 0.7168Y - 0.5025Z + 10.5202 = 0$$

$$[C(14) - 0.009, C(15) 0.016, C(20) 0.009, C(25) - 0.016, P - 0.159]$$

Plane (b): C(14)—(19)

$$0.4833X - 0.7419Y - 0.4647Z + 10.3886 = 0$$

$$[C(14) - 0.023, C(15) 0.028, C(16) - 0.010, C(17) - 0.012, C(18) 0.018, C(19) - 0.000]$$

Plane (c): C(20)—(25)

$$0.4701X - 0.6945Y - 0.5447Z + 10.8114 = 0$$

$$[C(20) 0.012, C(21) - 0.002, C(22) - 0.014, C(23) 0.019, C(24) - 0.009, C(25) - 0.007]$$

Plane (d): C(8)—(13)

$$-0.6930X - 0.5769Y - 0.4324Z + 5.0170 = 0$$

$$[C(8) 0.026, C(9) - 0.015, C(10) 0.008, C(11) - 0.010, C(12) 0.020, C(13) - 0.028, Br 0.100, C(7) 0.081]$$

Plane (e): C(1)—(6)

$$-0.4193X - 0.0547Y - 0.9062Z + 7.7753 = 0$$

$$[C(1) 0.011, C(2) - 0.027, C(3) 0.030, C(4) - 0.015, C(5) - 0.002, C(6) 0.003]$$

indicate considerable deformation of bond angles for a quaternary phosphonium centre compared with an acyclic phosphonium salt. For example,¹⁰ for the cation $\text{Ph}_3\text{P}^+\text{Me}$, the smallest angle about phosphorus is 105° . It is therefore reasonable to suppose that as a result of the deformation of bond angles at phosphorus there is appreciable ring strain in the dibenzophospholium salt which would be relieved on formation of a quinquivalent trigonal bipyramidal phosphorane, in which the endocyclic C-P-C angle would be 90° , assuming that the five-membered ring occupies apical-equatorial positions as is generally found.¹¹ Apical bond-cleavage or migration of the apical substituent to an equatorially disposed site then leads to either ring opening or ring expansion respectively with the formation of a relatively

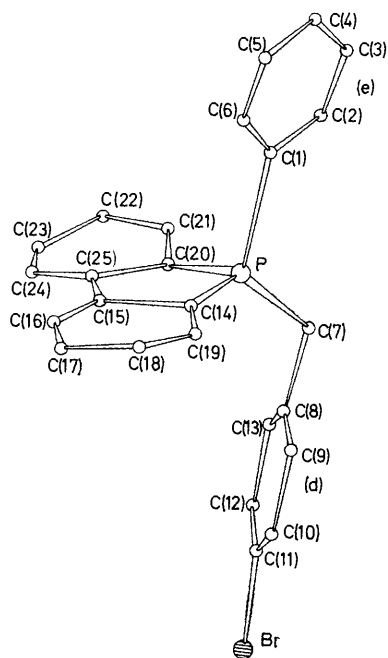


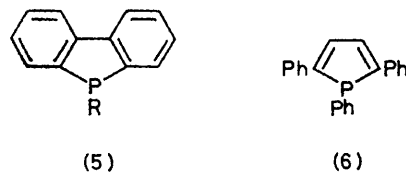
FIGURE 1 The structure of the cation

strain-free structure. The increased rate of nucleophilic attack at phosphorus in dibenzophospholium salts and the subsequent reactions undergone can therefore be accommodated in this framework.

If it is accepted that the small endocyclic angle at phosphorus in dibenzophospholium salts is indicative of ring strain, then much of the data obtained in experiments aimed at assessing the degree of delocalisation of the lone pair at phosphorus in the parent dibenzophosphole system (5; R = alkyl or aryl) and subsequently cited as evidence of phosphole aromaticity is in need of reconsideration and reinterpretation.

It is generally accepted that in its trivalent com-

pounds, phosphorus uses mainly *p* orbitals in σ -bonding, with only a small amount of *s* character mixed in. Thus in the parent dibenzophosphole system, one would expect an endocyclic C-P-C angle of *ca.* 90° (by analogy with that found in 1-benzylphosphole¹²) which would not involve undue deformation of bond angles for a tertiary phosphine. Bond-angle strain at phosphorus



would however be introduced on quaternisation, and this factor may well be responsible for the reduced rate of quaternisation of 5-phenyldibenzophosphole relative

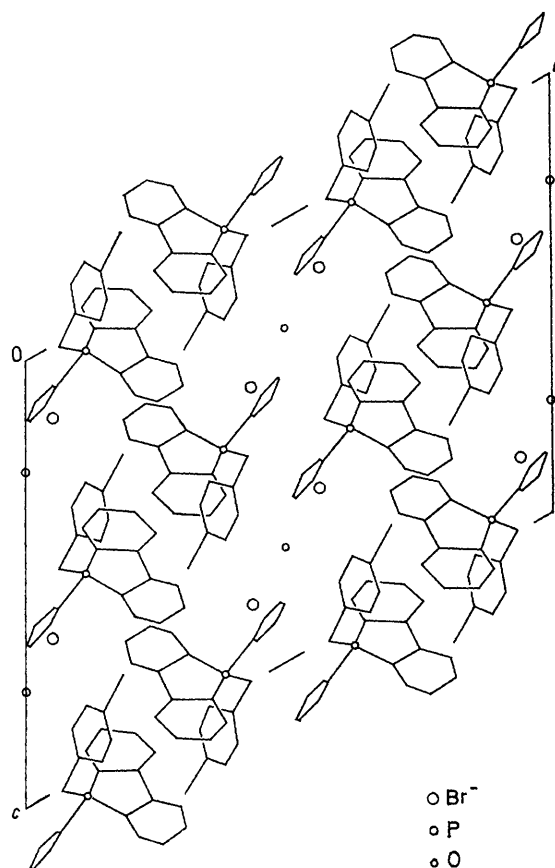


FIGURE 2 The (010) projection of the unit cell

to triphenylphosphine¹³ and also for the reduction in the P=O bond energy of 5-phenyldibenzophosphole oxide¹⁴ compared with Ph_3PO , rather than effects based

¹² P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Amer. Chem. Soc.*, 1970, **92**, 5779; P. Coggon and A. T. McPhail, *J.C.S. Dalton*, 1973, 1888.

¹³ D. W. Allen, J. R. Charlton, B. G. Hutley, and L. C. Middleton, *Phosphorus*, 1974, **5**, 9.

¹⁴ A. F. Bedford, D. M. Heinekey, I. T. Millar, and C. T. Mortimer, *J. Chem. Soc.*, 1962, 2932.

¹⁰ R. M. Wing, *J. Amer. Chem. Soc.*, 1968, **90**, 4828.

¹¹ See *e.g.*, S. Trippett, 'Organophosphorus Chemistry,' *Chem. Soc. Specialist Periodical Reports*, vols. 1-8, 1969-1977, and references therein.

on the 'aromatic' stabilisation of the dibenzophosphole system by delocalisation of the lone pair at phosphorus. Similarly, the increased rate of retrocyanoethylation of cyanoethyldibenzophospholium salts¹⁵ and the ease of electrochemical reduction of dibenzophospholium salts,¹³ compared to corresponding acyclic systems, can be explained on the basis of relief of ring strain attending conversion of the quaternary derivative to the parent phosphole.

These arguments can be similarly applied to a discussion of the chemistry of non-annelated phospholes, e.g. 1,2,5-triphenylphosphole (6), and our results support the suggestion¹⁶ that one of the likely causes of the reduced nucleophilicity of 1,2,5-triphenylphosphole compared to triphenylphosphine is the increase in ring strain in the five-membered phosphole ring on conversion from the trivalent into an intermediate quaternary state.

¹⁵ W. B. Farnham and K. Mislow, *J.C.S. Chem. Comm.* 1972, 469.

Figure 2 shows the packing of the ions and water molecules in the unit cell. Pairs of bromide ions, related by two-fold axes, are separated along the (010) direction by water molecules. The shortness of the $\text{Br}^- \cdots \text{O}$ contacts, 3.35(2) Å, points to significant interactions. The final electron-density difference map lends support to this view, as it indicates the presence of hydrogen atoms at positions suitable for attachment to the oxygen atoms and for interactions with the bromide ions.

We thank Dr. G. M. Sheldrick for a copy of his SHELX computing package, Sheffield City Polytechnic Computing Services Unit for assistance, and the S.R.C. for an equipment grant.

[7/914 Received, 26th May, 1977]

¹⁶ J. I. G. Cadogan, R. J. Scott, R. D. Gee, and I. Gosney, *J.C.S. Perkin I*, 1974, 1694.