The Chemistry of Heteroarylphosphorus Compounds, Part 16.⁺ An X-Ray Structural Study of (2-Thienyl)bis(2,2'-biphenylene)phosphorane. A Comparison with Related Methyl and Aryl bis(2,2'-biphenylene)- spiroposphoranes

David W. Allen*, Lorraine A. March, Ian W. Nowell

Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, Great Britain
and

John C. Tebby

Department of Chemistry, North Staffs Polytechnic, College Road, Stoke-on-Trent ST4 2DE,
Great Britain

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Spiroposphorane Structure, Apicophilicity of Heteroaryl Groups

Crystals of the title compound are monoclinic, $a = 18.993(11)$, $b = 8.757(5)$, $c = 13.267(8)$ Å, $\beta = 106.60(5)^\circ$, $Z = 4$ in space group Cc (C_s^4 , No. 9). The structure was determined by Patterson and electron-density methods and refined by least squares techniques to $R = 0.081$, $R' = 0.085$ for 1293 independent reflections classified as observed. The molecule is found to adopt an almost regular trigonal bipyramidal geometry in which the two biphenylene units span apical-equatorial positions and the 2-thienyl group occupies the remaining equatorial site. The 2-thienyl group, which is disordered, does not lie in the equatorial plane, and there is no indication of $C_{2p\pi} \rightarrow P_{3d\pi}$ interactions between the heteroaryl group and phosphorus. The steric requirements of the 2-thienyl group appear to be comparable with those of methyl and phenyl groups in bis(2,2'-biphenylene)spiroposphoranes.

There is now a considerable body of information on the solid state structures of pentacoordinate cyclic phosphoranes, and it has been established that the structure of such compounds in the solid state spans the range between the idealised trigonal bipyramid and rectangular pyramid, along the C_{2v} constraint of the Berry coordinate [1, 2]. It has been shown recently that in the bis(2,2'-biphenylene)-spiroposphorane series (I)–(IV), the extent of distortion along the Berry coordinate towards the rectangular pyramid increases as the steric bulk of the unique R group increases [3, 4]. Thus, for the series studied, the above distortion increases in the order $Ph \simeq Me < 1\text{-naphthyl} < 8\text{-dimethylamino-1-naphthyl}$.

- (I), R = 8-dimethylamino-1-naphthyl;
- (II), R = 1-naphthyl;
- (III), R = methyl;
- (IV), R = phenyl;
- (V), R = 2-thienyl.

For some time we have been interested in the chemistry of compounds in which a heteroaryl substituent is directly attached to phosphorus. In previous papers in this series, we have reported on

the effects of 2- and 3-furyl, 2- and 3-thienyl, 2-pyrrolyl and 1-methylpyrrol-2-yl substituents on the rate and course of reactions involving nucleophilic attack at phosphorus in phosphonium salts [5–9], phosphine oxides, phosphinate [10] and phosphonate esters [11]. There is considerable variation in the electronic effects of the above substituents, depending on the nature of the heteroatom and its position with respect to phosphorus. For example, both the 2-furyl and 2-thienyl groups markedly increase the rate of alkaline hydrolysis of phosphonium salts relative to comparable phenyl derivatives. The rate increase has been attributed to (a) the significant electron-withdrawing effects of the 2-heteroaryl groups which as a result of the pre-equilibria involved in phosphonium salt hydrolysis, lead to an increase in the steady state concentration of the anion R_4PO^- and (b) to the enhanced stability of the 2-heteroaryl carbanion relative to the phenyl (or benzyl) carbanion. Trippett [12] has recently also considered the relevance of the relative apicophilicity of the heteroaryl group in intermediate five coordinate phosphoranes. From the results of variable temperature NMR studies of phosphoranes bearing a 2-furyl group attached to phosphorus, it was concluded that the apparent apicophilicity of the 2-furyl group varied from system to system, being considerably more apicophilic than phenyl in

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some molecules, and slightly less apicophilic than phenyl in others.

As far as we are aware, there is no solid state structural information on phosphoranes bearing a heteroaryl group directly bound to phosphorus from a ring carbon. In this paper, we describe the structure of the phosphorane (V) prepared by one of us several years ago [13]. In view of the structural changes apparent in the series of phosphoranes (I)–(IV) discussed above, it was therefore of some interest to investigate the effect of the heteroaryl group on the structure of the phosphorane with particular reference to the degree of distortion from the ideal trigonal bipyramidal structure, in which each of the two five-membered rings would be expected to preferentially occupy apical-equatorial positions, leaving the heteroaryl group as an equatorial substituent. A highly apicophilic heteroaryl substituent would presumably give rise to considerable distortion of the trigonal bipyramid.

Crystal data. $C_{28}H_{19}PS$, $M_r = 418.5$. Monoclinic, $a = 18.993(11)$, $b = 8.757(5)$, $c = 13.267(8)$ Å, $\beta = 106.60(5)^\circ$, $U = 2114.6$ Å³, $D_m = 1.33$, $Z = 4$, $D_c = 1.32$ g cm⁻³, $F(000) = 872$. Mo-K α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-K}\alpha) = 2.0$ cm⁻¹. Space group Cc (C_s^4 , No. 9).

Intensity data were collected from a crystal, approximate dimensions $0.24 \times 0.32 \times 0.41$ mm, mounted with the b -axis coincident with the ω -axis of a Stöe Stadi 2 two-circle diffractometer. The background- ω scan-background technique was used to collect 2270 unique reflections of which 1293 had $I > 3\sigma(I)$ and were used for subsequent analysis. The intensities were corrected for Lorentz and polarisation factors but not for absorption.

Structure solution and refinement. The observed extinctions: $hkl, h+k=2n+1$, and $h0l, l=2n+1$, do not distinguish between the space groups C2/c and Cc. The presence of four molecules in the unit cell allows the phosphorane molecule to occupy a general position in Cc, but requires it to lie on a two-fold axis in C2/c. A trial solution was initially attempted in the non-centrosymmetric space group Cc. The x and z coordinates of the phosphorus atom were fixed at 1.0 and 0.25 respectively and the y coordinate was determined from a Patterson synthesis. Successive Fourier maps enabled the carbon atoms of the 2,2'-biphenylene units to be located and showed the 2-thienyl group to be

disordered. The 2-thienyl unit was disordered along a pseudo two-fold axis passing through the molecule and in view of this it was decided to continue refinement in the centrosymmetric space group C2/c. However, imposition of exact two-fold symmetry upon the molecule and statistical disorder upon the

Table I. Final positional parameters with standard deviations in parentheses*.

	x	y	z
P	1.000 0	0.124 7(2)	0.250 0
C(1)	0.997 5	—0.087 4	0.253 3
S(A)	0.921 6	—0.187 8	0.204 8
S(B)	1.071 3	—0.193 8	0.302 3
C(3A)	0.965 7	—0.353 9	0.225 5
C(3B)	1.027 3	—0.356 6	0.259 7
C(4A)	1.034 6	—0.340 3	0.292 4
C(4B)	0.953 9	—0.337 3	0.221 2
C(5A)	1.057 3	—0.178 5	0.298 5
C(5B)	0.935 1	—0.173 9	0.213 5
C(101)	1.088 0(4)	0.126 1(14)	0.200 1(7)
C(102)	1.141 5(5)	0.211 0(16)	0.256 1(7)
C(103)	1.208 0(6)	0.222 5(19)	0.227 2(11)
C(104)	1.214 8(6)	0.160 7(15)	0.141 7(10)
C(105)	1.159 5(6)	0.074 3(20)	0.076 7(9)
C(106)	1.096 8(7)	0.044 8(18)	0.108 4(11)
C(107)	1.059 1(5)	0.246 7(12)	0.361 3(8)
C(108)	1.126 5(4)	0.272 4(11)	0.352 2(7)
C(109)	1.174 9(6)	0.360 6(16)	0.431 4(9)
C(110)	1.153 0(7)	0.407 8(19)	0.513 4(8)
C(111)	1.085 6(7)	0.374 8(19)	0.519 4(8)
C(112)	1.036 1(6)	0.304 9(16)	0.442 2(9)
C(201)	0.918 5(6)	0.120 2(15)	0.300 8(9)
C(202)	0.855 1(5)	0.207 4(11)	0.234 9(9)
C(203)	0.792 5(6)	0.229 5(15)	0.262 9(10)
C(204)	0.787 0(7)	0.157 3(23)	0.357 2(13)
C(205)	0.843 4(7)	0.064 6(19)	0.412 8(11)
C(206)	0.907 2(5)	0.056 6(15)	0.385 3(8)
C(207)	0.946 1(4)	0.231 1(12)	0.138 4(8)
C(208)	0.871 9(6)	0.273 6(15)	0.143 0(10)
C(209)	0.826 0(5)	0.356 7(15)	0.068 3(9)
C(210)	0.847 6(7)	0.419 3(15)	—0.016 9(10)
C(211)	0.918 3(6)	0.391 6(14)	—0.024 3(9)
C(212)	0.966 2(5)	0.291 9(13)	0.051 4(8)
H(103)	1.253 8	0.284 6	0.277 5
H(104)	1.265 3	0.177 5	0.121 1
H(105)	1.164 6	0.030 8	0.003 0
H(106)	1.055 8	—0.035 9	0.066 6
H(109)	1.229 1	0.388 6	0.426 1
H(110)	1.190 0	0.473 7	0.575 0
H(111)	1.070 9	0.406 9	0.589 3
H(112)	0.979 8	0.293 7	0.443 8
H(203)	0.748 4	0.299 1	0.215 6
H(204)	0.739 4	0.175 3	0.384 9
H(205)	0.836 8	—0.003 3	0.477 4
H(206)	0.952 1	—0.006 4	0.437 1
H(209)	0.771 1	0.378 3	0.073 5
H(210)	0.809 3	0.486 7	—0.076 1
H(211)	0.936 9	0.444 2	—0.085 7
H(212)	1.019 1	0.262 2	0.041 8

* C(1), S(A), C(3A), C(4A), C(5A) comprise one disordered 2-thienyl unit while C(1), S(B), C(4B), C(5B) is the second.

heterocyclic unit, did not lead to successful refinement and final stages of the analysis were carried out in the space group Cc. Two 2-thienyl units, having a common C(1) atom attached to phosphorus, were given ideal geometries and included in the least-squares refinement with common isotropic temperature factors applied to atoms related by the pseudo two-fold axis. In addition, population parameters were applied to the two units with the final refined values indicating occupancies of 48 and 52% by the C(1), S(A), C(3A), C(4A), C(5A) and C(1), S(B), C(3B), C(4B), C(5B) moieties respectively. The biphenylene hydrogen atoms were located and included in positions calculated from the geometry of the molecule (C–H 1.08 Å). A common isotropic temperature factor was applied to these hydrogens and refined to a final value of $U = 0.086(15) \text{ Å}^2$. Scattering factors were calculated using an analytical approximation [14] and the weighting scheme $w = 8.8111/[\sigma^2(F) + 0.0002 F^2]$ adopted. The C(1), phosphorus and biphenylene carbon atoms were given anisotropic temperature factors and refinement converged at $R = 0.081$, $R' = 0.085$. Final observed and calculated structure factors, thermal parameters and least-squares planes data are available on request*. The labelling scheme

Fig. 1. Labelling scheme adopted for (V). The 2-thienyl group is disordered; the two units have a common C(1) atom and the remaining atoms are designated either A or B.

* Further details of the investigations on crystal structures may be obtained from "Fachinformationszentrum Energie, Physik, Mathematik, GmbH, D-7514 Eggenstein-Leopoldshafen 2". The Registry-Nr., CSD 50331, the name of the author, and the reference should be given.

adopted is shown in Fig. 1 while final positional parameters are given in Table I, bond lengths and angles in Table II.

Discussion

The coordination polyhedron about phosphorus in (V) is that of a trigonal bipyramid in which the 2-thienyl group is equatorial and the 2,2'-biphenylene ligands span apical-equatorial positions (Fig. 2).

Fig. 2. Molecular structure of (2-thienyl)bis(2,2'-biphenylene)phosphorane, (V). Within the trigonal bipyramidal arrangement, C(101) and C(201) occupy axial positions, C(107), C(207), and C(1) are equatorial. For clarity only one of the sites for the disordered 2-thienyl group is shown, the second site being related to the one in the Figure by an approximate two-fold axis along the P–C(1) bond.

The bond angles about phosphorus are very similar to those noted for the methyl and phenyl phosphoranes (III), (IV) and indicate little distortion from the regular trigonal bipyramidal arrangement (Table III). The sum of the equatorial angles at phosphorus is 360° in all five phosphoranes [(I)–(V), Table III], but while they range from 114.7 to 123.7° in (V), in the α -naphthyl derivatives the range of values is significantly larger, being 110.9 to 132.6° , (II), and 101.8 to 151.9° , (I). The magnitude of this

a) Distances

P-C(1)	1.858	P-C(201)	1.857(13)
P-C(101)	1.966(9)	P-C(207)	1.801(9)
P-C(107)	1.907(9)	C(1)-S(B)	1.654
C(1)-S(A)	1.654	C(1)-C(5B)	1.378
C(1)-C(5A)	1.378	S(B)-C(3B)	1.667
S(A)-C(3A)	1.661	C(3B)-C(4B)	1.352
C(3A)-C(4A)	1.360	C(4B)-C(5B)	1.472
C(4A)-C(5A)	1.476		

b) Angles

C(1)-P-C(101)	92.6	C(1)-P-C(201)	86.6
C(1)-P-C(107)	123.7	C(1)-P-C(207)	121.6
C(101)-P-C(107)	83.6(4)	C(201)-P-C(207)	88.4(5)
C(101)-P-C(201)	178.3(4)	C(101)-P-C(207)	93.3(4)
C(107)-P-C(201)	95.6(5)	C(107)-P-C(207)	114.7(5)
P-C(101)-C(102)	114.2(8)	P-C(201)-C(202)	113.3(9)
P-C(101)-C(106)	126.0(8)	P-C(201)-C(206)	132.0(8)
P-C(107)-C(108)	113.1(8)	P-C(207)-C(208)	114.9(8)
P-C(107)-C(112)	124.5(8)	P-C(207)-C(212)	129.9(7)
P-C(1)-S(A)	123.2	P-C(1)-S(B)	123.2
P-C(1)-C(5A)	124.4	P-C(1)-C(5B)	124.4
S(A)-C(1)-C(5A)	112.3	S(B)-C(1)-C(5B)	112.3
C(1)-S(A)-C(3A)	93.4	C(1)-S(B)-C(3B)	93.6
S(A)-C(3A)-C(4A)	112.1	S(B)-C(3B)-C(4B)	112.6
C(3A)-C(4A)-C(5A)	109.4	C(3B)-C(4B)-C(5B)	110.6
C(1)-C(5A)-C(4A)	109.9	C(1)-C(5B)-C(4B)	110.1

Table II. Selected bond distances (Å) and angles (°), with standard deviations in parentheses.

Table III. Comparison of bond angles (°) about phosphorus in the bis(2,2'-biphenylene)spirophosphoranes (I)-(V), with estimated standard deviations in parentheses.

	(I)	(II)	(III)	(IV)	(V)
C _{axial} -P-C _{axial}	175.5(1)	177.4(2)	178.3(1)	179.3(1)	178.3(4)
Range of C _{axial} -P-C _{equat}	85.8-97.1(1)	86.2-95.9(2)	86.0-95.5(1)	86.1-94.3(1)	83.6-95.6(5)
Angles in equatorial plane*:					
C(1)-P-C(107)	151.9(1)	132.6(2)	125.6(1)	124.3(1)	123.7
C(1)-P-C(207)	106.1(1)	116.4(2)	123.5(1)	124.3(1)	121.6
C(107)-P-C(207)	101.8(1)	110.9(2)	111.0(1)	111.5(1)	114.7(5)

* C(1) corresponds to the carbon atom attached to phosphorus from the following groups: (I), 8-dimethylamino-1-naphthyl; (II), 1-naphthyl; (III), methyl; (IV), phenyl; (V), 2-thienyl.

angular distortion in (I) and (II) has been attributed [3, 4] to steric crowding between the naphthyl groups and the bis(biphenylene) rings. The presence of the less sterically demanding methyl, phenyl, or 2-thienyl groups does not appear to cause significant distortion towards the reactangular pyramidal arrangement.

Holmes *et al.* have used dihedral angles procedures to quantify the extent of distortion from idealised geometries in cyclic phosphoranes [1, 15] and in (I)-(IV) [3, 4]. Using this approach, (I) and (II) are found to have molecular structures displaced 64.0% and 24.8% respectively along a coordinate connecting trigonal bipyramidal to rectangular pyramidal geometries. In contrast, the methyl and phenyl

phosphoranes (III), (IV) are displaced in the opposite direction to this coordinate, to the extent of -16.9% and -15.0% respectively. While the rather higher errors in the present structure (attributable to the disorder present) reduces the significance [16] of results obtained using the dihedral procedure it is, nevertheless, of interest to examine the results (Table IV). Taking the 2-thienyl group as the pivotal ligand, the direction of displacement from idealised trigonal bipyramidal geometry is the same as that found for the methyl and phenyl derivatives. The smaller displacement, -11.8% compared to -16.9% and -15.0%, appears to be in keeping with the low distortion of equatorial angles noted in Table III.

Table IV. Calculation of percent displacement from the idealised trigonal bipyramid (TP) toward the idealised reactangular pyramid (RP)^{a,b,c}.

$A = \sum_i \delta_i(C) - \delta_i(RP) $	238.9°
$B = \sum_i \delta_i(C) - \delta_i(TP) $	30.2°
$C = 217.7 - A$	— 21.2°
$D = \% (TP \rightarrow RP)$	— 11.8%

^a A, B – sum of the dihedral angles calculated from the position of the atoms attached to phosphorus relative to those for an idealised RP and TP respectively.

D – percent displacement, $= 100 (-B + C)/2(217.7)$.

^b 217.7° is the difference in the dihedral angle summation between the idealised geometries, RP and TP.

^c The percent displacements quoted in the text for (I)–(IV) refer to the use of unit bond distances rather than observed distances. Values using the observed bond distances are (I), 64.5%; (II), 24.8%; (III), — 17.3%; (IV), — 15.6%; (the values for (III) and (IV) have been calculated using final positional parameters given in ref. [4]).

While the axial P–C distance is significantly longer (by 0.056, 0.059 Å) than the equatorial distance for each biphenylene ligand, in keeping with a high degree of trigonal bipyramidal character, the shortness of both the P–C(201) and the P–C(207) bonds is somewhat surprising. The two six-membered rings within each biphenylene unit are almost co-planar, the dihedral angles for the two ligands being 1.4 and 5.3°.

The disordered 2-thienyl ligand shows almost equal preference for the two possible sites, with population parameters of 48% and 52%. There is little evidence of π -bonding in the P–C(thienyl) bond for not only is the heterocyclic ring orientated significantly out of the equatorial plane (34.9, 39.9°), but the P–C(1) distance of 1.858 Å is almost identical to that found in the methyl derivative (III), 1.859(2) Å. The orientation of the 2-thienyl group with respect to the P, C(1), C(107), C(207) equatorial plane appears to be dominated by steric factors. The value for this dihedral angle varies considerably within the group of phosphoranes [(I), 21.1°; (II), 5.8°; (IV), 28.3°] and reflects the differing spatial requirements of the monodentate ligands rather than the presence of significant π -interactions.

The possible apicophilicity of the 2-thienyl group appears to extend little influence upon the coordination polyhedron about phosphorus in the present structure. Rather, the almost regular trigonal bipyramidal arrangement adopted is a reflection of the strong preference of the biphenylene groups for occupying axial-equatorial positions and the small steric requirement of the equatorial heterocyclic ring.

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- [16] For example, distortion along the Berry coordinate, which imposes a C_{2v} constraint, requires terms B and C given in Table IV to be equal.