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The Structure of Tris(2-methyl-3-thienyl)phosphine

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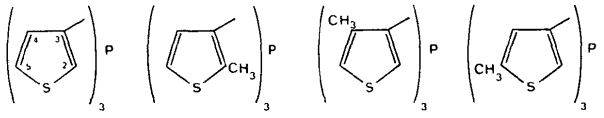
Tris(2-methyl-3-thienyl)phosphine is triclinic, space group $P\bar{1}$, with $a = 13{\cdot}095\,(10)$, $b = 8{\cdot}141\,(10)$, $c = 7{\cdot}598\,(5)$ Å, $\alpha = 97{\cdot}6\,(0{\cdot}5)$, $\beta = 94{\cdot}9\,(0{\cdot}5)$, $\gamma = 78{\cdot}8\,(0{\cdot}5)°$, $Z = 2$. Least-squares refinement with 3010 reflexions gave $R = 0{\cdot}060$ for 173 parameters. The configuration at the P atom is pyramidal with P–C 1·829 (2) Å and C$\hat{P}$C 100·9 (1)°. The thienyl rings are twisted so that the molecule does not have threefold symmetry; all the methyl groups are on the same side of the P atom as the lone pair. The NMR spectra of a series of tris(methyl-3-thienyl)phosphines can be qualitatively explained by the fact that for the *ortho* compounds the methyl groups are constrained to be on the same side of the P atom as the lone pair, whereas in the other compounds the thienyl rings can reorientate.

Introduction

The crystal structures of tri(3-thienyl)phosphine (I) (Hazell, Hazell & Pawley, 1977) and tris(2-methyl-3-thienyl)phosphine (II) have been studied in connexion with studies of NMR spectra of aromatic and heteroaromatic phosphine derivatives (Jakobsen & Nielsen, 1969; Jakobsen & Begtrup, 1971; Sørensen, Hansen & Jakobsen, 1972).



The exceptional values of the $^{31}P-^{1}H$ and the $^{31}P-^{13}C$ coupling constants for the *ortho* methyl-substituted trithienylphosphines (Table 5) were attributed to the steric interactions of the methyl groups twisting the rings into a conformation different from that in the unsubstituted and non-*ortho* substituted trithienylphosphines. X-ray analyses have been undertaken to compare the orientations of the thienyl groups in unsubstituted and *ortho* methyl-substituted compounds.

Crystal data

$C_{15}H_{15}PS_3$, $M_r = 322{\cdot}5$; triclinic, $a = 13{\cdot}095\,(10)$, $b = 8{\cdot}141\,(10)$, $c = 7{\cdot}598\,(5)$ Å, $\alpha = 97{\cdot}6\,(0{\cdot}5)$, $\beta = 94{\cdot}9\,(0{\cdot}5)$, $\gamma = 78{\cdot}8\,(0{\cdot}5)°$, $U = 786{\cdot}1$ Å^3; $Z = 2$, $D_c = 1{\cdot}36$ g cm^{-3}; $F(000) = 336$, μ(Mo $K\alpha$) = 5·41 cm^{-1}; space group $P\bar{1}$. The compound crystallizes from methanol as colourless needles elongated along [001] and bounded by {100} and {010}.

Experimental

A crystal 0·2 × 0·1 × 0·3 mm was mounted with c^* parallel to ϕ, and intensities were measured out to $\sin\theta/\lambda = 0{\cdot}65$ on a Picker FACS-1 diffractometer in the symmetrical A setting with an ω–2θ scan. Monochromatic Mo $K\alpha$ radiation was used with a scintillation counter in conjunction with a pulse-height analyser. 3616 independent reflexions were recorded, of which 3010 had $F^2 > 3\sigma(F^2)$ according to counting statistics. No correction was applied for absorption.

Determination and refinement of the structure

The structure was solved by direct methods (*SYMBAD*, Danielsen, 1969). As insufficient signs could be determined, the additional information that the sign of 002 was −1 (the morphology suggests that the molecular centres are at $z = \frac{1}{4}$) was included. Only signs for reflexions with $h - k \equiv 0\,\{\text{mod } 5\}$ were determined; the resulting E map showed five molecules superimposed. The correct solution was chosen from packing considerations and the structure refined by least squares to give $R = 0{\cdot}060$ and $R_w = 0{\cdot}069$ for 3010 reflexions with 173 parameters.† The value of g (the isotropic extinction coefficient) was 7·9 (1·1) $\times 10^{-7}$ assuming $\bar{t}$ to be unity; the maximum value of $F_o/F_{o(\text{corr.})}$ was 0·72.

Atomic coordinates and thermal parameters are listed in Table 1. Attempts to analyse the thermal motion of the atoms assuming the molecule to be rigid

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32183 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and thermal parameters* ($Å^2 \times 10^{-3}$) (*for the hydrogen atoms: coordinates* $\times 10^3$ *and isotropic U values*)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	7639 (1)	3803 (1)	7630 (1)	53 (1)	45 (1)	35 (1)	−9 (1)	5 (1)	−11 (1)
C(2)	6333 (3)	2731 (4)	4780 (4)	59 (2)	38 (2)	54 (2)	−7 (1)	−4 (2)	6 (1)
C(3)	7310 (2)	3023 (3)	5330 (4)	50 (2)	33 (1)	44 (2)	−9 (1)	0 (1)	5 (1)
C(4)	7988 (3)	2678 (4)	3910 (4)	53 (2)	55 (2)	46 (2)	−8 (2)	2 (1)	3 (1)
C(5)	7520 (3)	2147 (5)	2335 (5)	78 (2)	62 (2)	46 (2)	−3 (2)	2 (2)	1 (2)
C(6)	5401 (3)	2915 (6)	5833 (6)	53 (2)	89 (3)	89 (3)	−11 (2)	7 (2)	12 (2)
S(1)	6251 (1)	2046 (1)	2535 (1)	74 (1)	69 (1)	60 (1)	−13 (1)	−20 (1)	−1 (1)
C(7)	9690 (3)	1986 (4)	7707 (4)	52 (2)	56 (2)	47 (2)	−11 (2)	−3 (2)	6 (1)
C(8)	9059 (2)	3537 (4)	7645 (4)	53 (2)	50 (2)	35 (2)	−11 (1)	1 (1)	3 (1)
C(9)	9658 (3)	4858 (4)	7734 (5)	68 (2)	57 (2)	50 (2)	−17 (2)	−2 (2)	8 (1)
C(10)	10697 (3)	4272 (5)	7846 (5)	68 (2)	76 (3)	65 (2)	−33 (2)	−2 (2)	11 (2)
C(11)	9383 (3)	306 (5)	7597 (6)	62 (2)	56 (2)	94 (3)	−10 (2)	−4 (2)	10 (2)
S(2)	10991 (1)	2141 (1)	7856 (1)	51 (1)	71 (1)	75 (1)	−10 (1)	−3 (1)	10 (1)
C(12)	6708 (3)	7147 (4)	8809 (4)	48 (2)	55 (2)	50 (2)	−8 (1)	−3 (1)	−6 (1)
C(13)	7234 (2)	6075 (4)	7519 (4)	51 (2)	47 (2)	46 (2)	−9 (1)	2 (1)	−1 (1)
C(14)	7418 (3)	6934 (4)	6069 (5)	73 (2)	44 (2)	53 (2)	−9 (2)	10 (2)	5 (1)
C(15)	7037 (3)	8583 (5)	6310 (5)	76 (3)	54 (2)	74 (2)	−19 (2)	−5 (2)	15 (2)
C(16)	6340 (3)	6775 (6)	10480 (5)	72 (3)	103 (3)	49 (2)	−3 (2)	15 (2)	−1 (2)
S(3)	6443 (1)	9175 (1)	8270 (1)	69 (1)	47 (1)	80 (1)	−2 (1)	1 (1)	−11 (1)

	x	y	z	U_{iso}		x	y	z	U_{iso}
H(4)	868 (2)	276 (3)	403 (4)	41 (8)	H(112)	931 (4)	−16 (6)	622 (7)	122 (17)
H(5)	781 (3)	189 (5)	123 (5)	86 (13)	H(113)	990 (4)	−37 (6)	811 (6)	98 (15)
H(61)	472 (4)	288 (6)	510 (7)	170 (18)	H(14)	778 (3)	634 (5)	513 (5)	59 (11)
H(62)	517 (4)	396 (6)	648 (6)	126 (16)	H(15)	707 (3)	928 (5)	561 (5)	69 (12)
H(63)	559 (6)	269 (10)	701 (10)	131 (13)	H(161)	657 (4)	570 (7)	1070 (7)	146 (23)
H(9)	934 (3)	609 (4)	768 (4)	49 (9)	H(162)	567 (5)	706 (7)	1059 (8)	172 (23)
H(10)	1126 (3)	486 (5)	795 (5)	72 (13)	H(163)	658 (4)	749 (7)	1157 (8)	144 (20)
H(111)	879 (3)	33 (5)	793 (5)	65 (13)					

Table 2. *Bond lengths* (Å)

The mean values of chemically equivalent bonds are compared with those for tri(3-thienyl)phosphine (I) and thiophene. The standard deviations for the C—H distances are 0·04–0·05 Å.

	Ring 1	Ring 2	Ring 3	Mean	(I)	Thiophene
P—C(3)	1·824 (3)	1·829 (3)	1·834 (3)	1·825 (4)	1·825 (4)	
C(2)—S(1)	1·723 (3)	1·726 (3)	1·717 (4)	1·722 (2)	1·716 (5)	1·718
S(1)—C(5)	1·700 (4)	1·703 (4)	1·709 (4)	1·704 (2)	1·741 (5)	1·718
C(3)—C(2)	1·367 (4)	1·372 (4)	1·361 (4)	1·367 (2)	1·342 (4)	1·352
C(4)—C(5)	1·355 (5)	1·351 (5)	1·332 (5)	1·346 (3)	1·319 (6)	1·352
C(3)—C(4)	1·420 (4)	1·440 (5)	1·441 (5)	1·434 (3)	1·430 (4)	1·455
C(2)—C(6)	1·489 (5)	1·489 (5)	1·483 (5)	1·487 (3)		
C(4)—H(4)	0·92	1·01	0·92			1·073
C(5)—H(5)	0·93	0·95	0·84			1·085
C(6)—H(61)	1·01	0·83	0·90	0·93 (1)		
C(6)—H(62)	0·93	1·07	0·87			
C(6)—H(63)	0·94	0·88	1·01			

Table 3. *Bond angles* (°)

The mean values of chemically equivalent angles are compared with those for tri(3-thienyl)phosphine (I) and thiophene.

	Ring 1	Ring 2	Ring 3	Mean	(I)	Thiophene
C—P—C*	101·8 (2)	99·5 (1)	101·5 (1)	100·9 (1)	101·3 (3)	
P—C(3)—C(2)	121·8 (2)	121·6 (3)	123·3 (3)	122·2 (2)		
P—C(3)—C(4)	126·3 (2)	126·6 (3)	124·7 (2)	125·9 (2)		
C(2)—C(3)—C(4)	111·9 (3)	111·6 (3)	112·1 (3)	111·9 (2)	111·0 (2)	111·8
C(3)—C(4)—C(5)	113·1 (3)	112·7 (3)	112·7 (3)	112·8 (2)	114·5 (2)	111·8
C(3)—C(2)—S(1)	111·2 (3)	111·3 (3)	111·0 (3)	111·2 (2)	112·8 (2)	112·6
C(4)—C(5)—S(1)	111·8 (3)	112·3 (3)	112·2 (3)	112·1 (2)	111·0 (2)	112·6
C(2)—S(1)—C(5)	92·0 (2)	92·1 (2)	92·1 (2)	92·1 (1)	90·7 (2)	91·3
C(3)—C(2)—C(6)	129·2 (3)	128·5 (3)	129·3 (3)	129·0 (2)		
S(1)—C(2)—C(6)	119·6 (3)	120·2 (3)	119·7 (3)	119·8 (2)		

* The CPC angle listed under ring *j* is the angle not involving that ring.

Table 4. *Torsion angles LP—P—C—C, where LP is a point* (0·740992, 0·339359, 0·842911) *on the lone pair*

	τ		τ
LP—P—C(3)—C(2)	41·7°	*LP*—P—C(8)—C(9)	−123·3°
LP—P—C(3)—C(4)	−139·6	*LP*—P—C(13)—C(12)	9·6
LP—P—C(8)—C(7)	51·6	*LP*—P—C(13)—C(14)	−169·5

were not successful; the bond lengths have not therefore been corrected for thermal motion. Bond lengths are given in Table 2, bond angles in Table 3, and torsion angles in Table 4.

Computational details

Calculations were carried out on a CDC 6400 computer with the following programs: data reduction: *DATAP* and *DSORTH* (State University of New York at Buffalo); Fourier syntheses: *ZALKINS* (A. Zalkin, Lawrence Radiation Laboratory); least-squares refinement: *LINUS* (Coppens & Hamilton, 1970); distances and angles: *ORFFE* (Busing, Martin & Levy, 1964); drawings: *ORTEP* (Johnson, 1965).

The quantity minimized was $r = \Sigma\, w(|F_o| - |F_c|)^2 / \Sigma\, w|F_o|^2$, where $w = \{[\sigma(F_o^2) + 1{\cdot}02F_o^2]^{1/2} - |F_o|\}^{-2}$. The scattering factors of Cromer & Mann (1968) were used for P, S, and C and that of Stewart, Davidson & Simpson (1965) for H.

Table 5. ^{31}P—^{1}H *and* ^{31}P—^{13}C *coupling constants (in* Hz*) for tri(3-thienyl)phosphines*

	(I)	(II)	(III)	(IV)
^3J P—H(2)	4·23	—	1·93	4·65
^3J P—H(4)	2·52	1·09	—	2·43
^2J P—C(2)	23·09	33·88	0·25	—
^2J P—C(4)	17·50	1·09	27·38	—

Discussion

The molecule is shown in Fig. 1. The configuration at the P atom is pyramidal with C$\hat{P}$C 100·9 (1)° and P—C 1·829 (2) Å; triphenylphosphine (Daly, 1964) has C$\hat{P}$C 103·0 (1)° and P—C 1·828 (3) Å. The molecule does not have threefold symmetry, the rings being twisted by different amounts (Table 4). The rings are all arranged so that the methyl groups are on the same side of the P atom as the lone pair. The bond distances and angles in the thiophene ring are similar to those in tri(3-thienyl)phosphine and thiophene (Bak, Christensen, Rastrup-Andersen & Tannenbaum, 1956).

The conformation of a molecule in the solid state need not be the same as in solution. However, Brock & Ibers (1973) have shown that triphenylphosphine has almost the same energy in the free state (torsion angle $\tau = 38{\cdot}6°$ for all rings) as in the solid state ($\tau_1 = 24{\cdot}8°$, $\tau_2 = 61{\cdot}8°$, $\tau_3 = 28{\cdot}0°$). For (II) the rings must be free to oscillate but the bulky methyl groups prevent free rotation; (I), however, is disordered showing that the rings can reorientate. So it would seem that in solution (II) and (III) must have their methyl groups on the same side of the P atom as the lone pair, whereas the thiophene rings in (I) and (IV) can reorientate so that, for example, C(2$^{\rm I}$) [the superscript I means C(2) in compound I] is sometimes on the same side as the lone pair, sometimes on the other. Interaction with the lone pair will be greater for C(2$^{\rm II}$) and C(4$^{\rm III}$) than for C(2$^{\rm I}$) and C(4$^{\rm I}$), giving larger values of J[P—C(2$^{\rm II}$)] and J[P—C(4$^{\rm III}$)], whereas the interaction with C(4$^{\rm II}$) and C(2$^{\rm III}$) will be smaller giving smaller coupling constants. Similarly J[P—H(4$^{\rm II}$)]and J[P—H(2$^{\rm III}$)] should decrease, whereas J[P—H(2$^{\rm IV}$)] and J[P—H(4$^{\rm IV}$)] should be about the same as in the unsubstituted compound. Thus, by assuming (on the basis of crystal structure determinations) that the *ortho* methyl groups are constrained to be on the same side of the P atom as the lone pair, while the unsubstituted and the 5-methylthiophene rings can reorientate, it is possible to give a qualitative explanation for the variation of coupling constants for the tri(3-thienyl)phosphines.

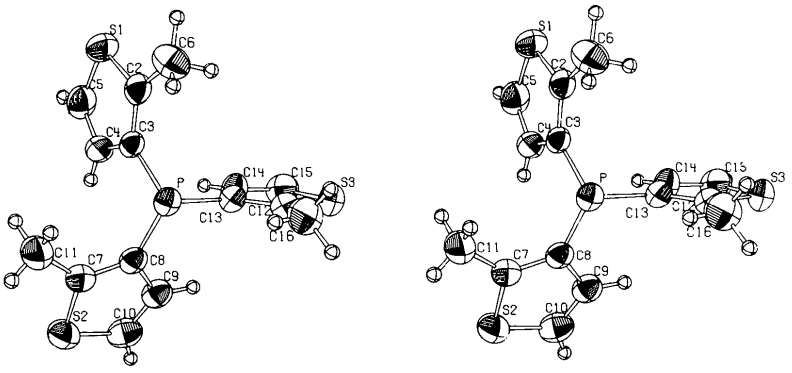


Fig. 1. The molecule viewed perpendicular to the plane through C(2), C(7) and C(12).

We are indebted to Hans Jørgen Jakobsen for providing the crystals and for helpful discussions.

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The Structure of a Rotationally Disordered Molecule: Tri(3-thienyl)phosphine

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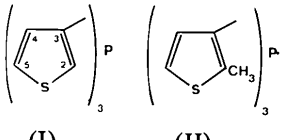
Tri(3-thienyl)phosphine is monoclinic, space group $P2_1/c$, with $a = 9\cdot84$ (1), $b = 16\cdot02$ (2), $c = 10\cdot42$ (1) Å, $\beta = 127\cdot6$ (5)°, $Z = 4$. Conventional least-squares refinement gave $R = 0\cdot097$ for 1880 reflexions and 181 parameters. The thienyl rings are disordered, so that for each ring there is another obtained by rotating *ca* 180° about the P–C bond. A constrained refinement assuming all thienyl rings to be identical gave $R = 0\cdot075$ for 74 parameters. The occupation factors were 0·807 (3), 0·939 (3) and 0·742 (3). Thermal motion was described by **T**, **L** and **S**, and by extra parameters to account for oscillations about the P–C bonds. The configuration at the P atom is pyramidal with P–C 1·825 (4) Å and CP̂C 101·3 (3)°. The thienyl rings are twisted so that the molecule does not have threefold symmetry. For the three rings with highest occupancy, two have their S atoms on the opposite side of the P atom to the lone pair.

Introduction

The crystal structures of tri(3-thienyl)phosphine (I) and tris(2-methyl-3-thienyl)phosphine (II) (Hazell & Hazell, 1977) have been determined in connexion with studies of NMR spectra of aromatic and heteroaromatic phosphine derivatives (Jakobsen & Nielsen, 1969; Jakobsen & Begtrup, 1971; Sørensen, Hansen & Jakobsen, 1972).



(I) (II)

Crystal data

$C_{12}H_9PS_3$, $M_r = 280\cdot2$; monoclinic, $a = 9\cdot84$ (1), $b = 16\cdot02$ (2), $c = 10\cdot42$ (1) Å, $\beta = 127\cdot6$ (5)°, $U = 1301$ Å^3, $Z = 4$, $D_c = 1\cdot426$ g cm^{-3}; $F(000) = 576$, μ(Mo $K\alpha$) = 6·4 cm^{-1}; space group $P2_1/c$. The compound crystallizes from CH_3CN as white needles elongated in the [001] direction and bounded by {100}, {010} and {110}.

Experimental

The crystals were kindly provided by H. J. Jakobsen. A crystal of cross-section 0·15 × 0·30 mm was mounted along **c** and intensities (l = 0 to 10) measured with an