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

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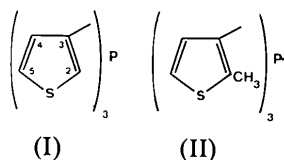
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Tri(3-thienyl)phosphine is monoclinic, space group $P2_1/c$, with $a = 9.84$ (1), $b = 16.02$ (2), $c = 10.42$ (1) Å, $\beta = 127.6$ (5)°, $Z = 4$. Conventional least-squares refinement gave $R = 0.097$ for 1880 reflexions and 181 parameters. The 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 $R = 0.075$ 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 C–P–C 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).



Crystal data

$C_{12}H_9PS_3$, $M_r = 280.2$; monoclinic, $a = 9.84$ (1), $b = 16.02$ (2), $c = 10.42$ (1) Å, $\beta = 127.6$ (5)°, $U = 1301$ Å³, $Z = 4$, $D_c = 1.426$ g cm⁻³; $F(000) = 576$, $\mu(\text{Mo } K\alpha) = 6.4$ 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

Arndt & Phillips (1961) linear diffractometer. Monochromatic Mo $K\alpha$ radiation was used with a scintillation counter and a pulse-height analyser. 3113 independent reflexions were measured, of which 1904 had $F^2 > 2\sigma(F^2)$, where $\sigma^2(F^2) = \sigma^2(F^2) + 0.0002F^2P$; $\sigma_c(F^2)$ being the standard deviation from counting statistics and P the inverse of the Lorentz-polarization factor. No correction was made for absorption.

Structure determination and refinement

The P atom was located from a Patterson function. The Fourier map calculated with the phases from this showed all the other atoms, though there was doubt as to the identity of the S atoms. When the most probable S positions had been chosen, the structure was refined by least squares, giving $R = 0.097$ for 1880 reflexions and 181 parameters.

Two of the S atoms had the largest temperature factors while the C(5) atoms had the smallest. This suggested that there might be disorder about the P-C bond which would bring S and C(5) close to each other in the average structure. Problems such as this cannot be successfully treated by conventional refinement procedures because of the high correlation between the parameters of atoms which are abnormally close. Such correlation can be avoided by the use of appropriate constraints (Pawley, 1971), which in the present case were as follows. Each thiophene ring was replaced by a

pair of rings, one related to the other by a rotation of approximately π about an axis close to the P-C bond. The members of each pair were given occupation factors constrained so that their sum was unity. All thiophene rings were kept identical and planar, although the positions of the atoms in the plane were variable. Each ring required six parameters [three to define the origin, chosen as C(3), and three Euler angles]. The anisotropic temperature factors for all the atoms were constrained to correspond to those of a

Table 1. *Fractional coordinates for the non-hydrogen atoms of the rings of highest occupancy*

C(32) means C(3) in ring 2, etc.

	<i>x</i>	<i>y</i>	<i>z</i>
P	0.0545 (1)	0.3903 (1)	0.8740 (1)
S(1)	0.4132	0.4339	0.7690
C(21)	0.3475	0.4153	0.8858
C(31)	0.1773	0.4042	0.7972
C(41)	0.0964	0.4111	0.6279
C(51)	0.2024	0.4266	0.5932
S(2)	0.4394	0.3925	1.3940
C(22)	0.2697	0.4247	1.2036
C(32)	0.2287	0.3697	1.0878
C(42)	0.3391	0.2984	1.1558
C(52)	0.4562	0.3009	1.3147
S(3)	-0.1145	0.1412	0.6720
C(23)	0.0121	0.2289	0.7416
C(33)	-0.0355	0.2863	0.8010
C(43)	-0.1804	0.2583	0.7898
C(53)	-0.2370	0.1836	0.7250

Table 2. *Final parameters*

Euler angles (in radians) (Goldstein, 1959), the centre of reference in the orthogonal system (Pawley, 1971), the occupation factor, and the oscillation parameter (degrees²) are given for each ring

Ring	ϕ	θ	ψ	X_o	Y_o	Z_o	Occupation factor	Oscillation parameter
1	3.506 (3)	1.611 (5)	-3.326 (6)	-3.328 (5)	6.475 (15)	6.579 (7)	0.807 (3)	98.5 (6.5)
2	-1.403 (1)	4.822 (1)	1.098 (2)	-4.671 (3)	5.922 (3)	8.977 (3)	0.939 (3)	18.7 (4.8)
3	5.132 (11)	0.434 (4)	-3.321 (12)	-5.445 (7)	4.586 (4)	6.610 (7)	0.742 (3)	13.2 (6.6)
4	-3.510 (11)	4.690 (18)	-3.398 (28)	-3.362 (20)	6.469 (62)	6.547 (26)	0.193	
5	1.403	1.680	1.098	-4.671	5.922	8.977	0.061	
6	-5.503 (20)	3.599 (17)	-3.639 (22)	-5.435 (17)	4.655 (12)	6.483 (22)	0.258	

Coordinates of ring atoms, in Å, in the molecular systems defined by these Euler angles

S	2.461 (3)	0.690	0.000	C(5)	2.081 (5)	-1.009 (4)	0.000
C(2)	0.791 (4)	1.085 (4)	0.000	H(2)	0.538 (27)	2.022 (27)	0.000
C(3)	0.000	0.000	0.000	H(4)	0.306 (28)	-2.095 (27)	0.000
C(4)	0.776 (4)	-1.201 (4)	0.000	H(5)	2.792 (30)	-1.519 (32)	0.000

T, L and S tensors (in Å², degrees² and degree Å respectively). For S, two rows of numbers are given, the lower being S_{ji}.

	11	22	33	12	13	23
T	0.0530 (5)	0.0529 (5)	0.0704 (6)	0.0092 (5)	0.0020 (5)	0.0054 (5)
L	8.40 (27)	10.01 (29)	12.92 (38)	3.40 (29)	-2.52 (42)	0.54 (36)
S	0.014 (26)	0.032 (23)	0.0	0.066 (9)	0.296 (10)	0.301 (10)
				-0.163 (10)	-0.341 (12)	-0.226 (14)

The centre of reaction is at (-5.001, 6.311, 7.183).

Table 3. *Torsion angles LP-P-C-C*

LP(1) is a point on the lone pair, *i.e.* on the line joining the centre of gravity of C(31), C(32), C(33) with P; LP(2) is determined from C(34), C(35) and C(36). LP(1) is at (-0.0146, 0.4277, 0.8527) and LP(2) at (-0.0091, 0.4242, 0.8588).

LP(1)-P-C(31)-C(21)	114.4°	LP(2)-P-C(34)-C(24)	-64.1°
LP(1)-P-C(32)-C(22)	-16.2	LP(2)-P-C(35)-C(25)	163.0
LP(1)-P-C(33)-C(23)	142.4	LP(2)-P-C(36)-C(26)	-42.7
LP(1)-P-C(31)-C(41)	-60.5	LP(2)-P-C(34)-C(44)	107.3
LP(1)-P-C(32)-C(42)	165.1	LP(2)-P-C(35)-C(45)	-18.3
LP(1)-P-C(33)-C(43)	-32.8	LP(2)-P-C(36)-C(46)	142.7

Table 4. *Bond lengths (Å) compared with those in tris(2-methyl-3-thienyl)phosphine (II) and in thiophene*

C(32) means C(3) in ring 2; P-C(3) is the mean P-C distance.

	(I)	(II)	Thiophene
P-C(31)	1.824 (6)		
P-C(32)	1.830 (4)		
P-C(33)	1.821 (5)		
P-C(3)	1.825 (4)	1.829 (2)	
C(2)-S	1.716 (5)	1.722 (2)	1.718
S-C(5)	1.741 (5)	1.704 (2)	1.718
C(3)-C(2)	1.342 (4)	1.367 (2)	1.352
C(4)-C(5)	1.319 (6)	1.346 (3)	1.352
C(3)-C(4)	1.430 (4)	1.434 (3)	1.455
C(2)-H(2)	0.97 (3)		1.085
C(4)-H(4)	1.01 (3)	0.95 (4)	1.073
C(5)-H(5)	0.87 (3)	0.91 (4)	1.085

rigid body in the TLS approximation. This gave $R = 0.080$ and $R_w = 0.080$ for only 76 parameters.

The TLS approximation is based on the assumption that the thermal motion resembles that of a rigid molecule. In the present structure considerable libration about the P-C bonds could be expected and the program was modified so that an extra libration parameter could be introduced for each pair of rings. The extra parameters were found to correlate strongly with the disorder parameters as well as with the TLS parameters. The best results were obtained when ring 5, with

Table 5. *Angles (°) [the mean values are compared with those in tris(2-methyl-3-thienyl)phosphine (II)]*

	Ring 1	Ring 2	Ring 3
C(3)-P-C(3)*	101.4 (4)	102.2 (4)	100.2 (4)
P-C(3)-C(2)	126.7 (2)	121.3 (2)	127.0 (2)
P-C(3)-C(4)	122.2 (2)	127.7 (2)	121.8 (2)

	(I)	(II)	Thiophene
C(3)-P-C(3)	101.3 (3)	100.9 (1)	
C(2)-C(3)-C(4)	111.0 (2)	111.9 (2)	111.8
C(3)-C(4)-C(5)	114.5 (2)	112.8 (2)	111.8
C(3)-C(2)-S	112.8 (2)	111.2 (2)	112.6
C(4)-C(5)-S	111.0 (2)	112.1 (2)	112.6
C(2)-S-C(5)	90.7 (2)	92.1 (1)	91.3

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

Table 6. *P-C-C angles (°) in tri(3-thienyl)phosphines and related compounds*

θ_{trans} is the PCC angle furthest away from the lone pair.

	θ_{cis}	θ_{trans}
Tri(3-thienyl)phosphine	121.8	127.1
Tris(2-methyl-3-thienyl)phosphine	122.2	125.9
Triphenylphosphine	116.1	124.0
Tri- <i>o</i> -tolylphosphine	118.6	122.3
Tri- <i>m</i> -tolylphosphine	117.2	124.2

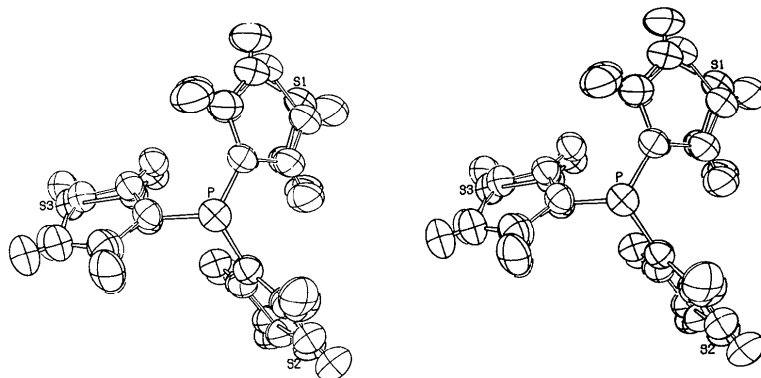


Fig. 1. The molecule viewed perpendicular to the plane through C(31), C(32) and C(33). The thienyl groups with the highest occupation factors are drawn with slightly thicker lines.

occupancy 0.06, was constrained to be coplanar with ring 2. The final R was 0.075 and R_w was 0.074 for 74 parameters.*

The fractional coordinates for P and for the rings of highest occupancy are given in Table 1. The final values for the parameters are given in Table 2.

The fact that ring 1 seems to have a much larger amplitude of libration around the P—C bond than the others is probably only another indication of the correlations. As has been pointed out (Pawley & Rinaldi, 1972), a good fit to a TLS model does not necessarily mean that the molecule moves as a rigid body, and similarly we should not attach too much physical significance to the oscillation parameters. Even for a system without disorder, it would not be possible to separate the internal oscillations from the rigid-body motion, but the model gives a good description of the thermal parameters of the atoms.

Computational details

Calculations were carried out on a CDC 6400 computer with the following programs: constrained refinements, *KONSLS* (Pawley, 1971); drawings, *ORTEP-II* (Johnson, 1971). The quantity minimized was $\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$, where $w = \{[\sigma(F_o^2) + 1.03F_o^2]^{1/2} - |F_o|\}^{-2}$. The scattering factors of Cromer & Mann (1968) were used for P, S and C, and that of Stewart, Davidson & Simpson (1965) for H.

Discussion

The molecule (Fig. 1) is disordered. Only bond lengths and angles corresponding to the three most probable orientations of the rings will be discussed as these are more accurately determined. The configuration at the P atom is pyramidal with $\text{C}\hat{\text{P}}\text{C}$ $101.3(3)^\circ$ and P—C $1.825(4) \text{ \AA}$ [*cf.* triphenylphosphine (Daly, 1964) which has $\text{C}\hat{\text{P}}\text{C}$ $103.0(1)^\circ$ and P—C $1.828(3) \text{ \AA}$, and (II) which has $\text{C}\hat{\text{P}}\text{C}$ $100.9(1)^\circ$ and P—C $1.829(2) \text{ \AA}$]. Unlike (II), for which C(2) in each ring is on the same side of the P atom as the lone pair, rings 1 and 3 have C(2) on the opposite side to the lone pair. The molecule does

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32216 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

not have threefold symmetry, the rings being twisted by different amounts (Table 3). Bond distances and angles are similar to those in (II) and thiophene (Bak, Christensen, Rastrup-Andersen & Tannenbaum, 1956), with which they are compared in Tables 4 and 5. P—C(3)—C(2) and P—C(3)—C(4) are not equal, the PCC angle opposite to the lone pair being the larger, the angles presumably being distorted to reduce the overcrowding of the bulky thiophene groups. A similar effect is found (Table 6) for (II) and also for triphenylphosphine, tri-*o*-tolylphosphine (Cameron & Dahlén, 1975) and tri-*m*-tolylphosphine (Cameron & Millar, 1974).

From our data it is not possible to distinguish between static and dynamic disorder. That the rings can be found in different orientations in the crystal suggests that they are free to reorientate in solution, thus accounting for the differences between the NMR spectra of (I) and (II) (Hazell & Hazell, 1977).

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