Fig. 2. An *ORTEP* plot of 1-benzothiepin 1,1-dioxide.

stituent C atoms in thiepin 1,1-dioxide. The C(6)–C(7) bond takes part in the conjugation of the benzene group [C(6) to C(11)], and slightly distorts the C_s symmetry of the thiepin ring.

The thiepin ring takes the boat form, and the dihedral angle between 'bow' atoms [the plane through C(2), S and C(7)] and 'stern' atoms [the plane through C(3), C(4), C(5) and C(6)] is 70·4°. The SO_2 plane almost bisects the plane through C(2), C(3), C(6) and C(7), the angle being 88·9°.

The distances and angles for probable hydrogen

Table 3. *Distances and angles in probable hydrogen bonding*

Key for superscripts

	x	y	z
None			
(i)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
(ii)	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$

	$O\cdots C$	$O\cdots H$	$O\cdots H–C$
$O(2)\cdots H(2^i)–C(2^i)$	3·365 (4) Å	2·48 (4) Å	159 (3)°
$O(1)\cdots H(3^{ii})–C(3^{ii})$	3·343 (4)	2·44 (3)	145 (3)

bonding are listed in Table 3. They do not indicate strong bonding, but similar schemes are found in other sulphones (Ammon, Watts & Stewart, 1970; Boelema, Visser & Vos, 1967; Yasuoka, Kasai, Tanaka, Nagai & Tokura, 1972).

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Tris-(1-pyrazolyl)phosphine

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Abstract. $P(C_3H_3N_2)_3$, $M=232·19$, hexagonal, space group $P6_3$, $a=8·443$ (4), $c=8·946$ (5) Å, $V=552·3$ Å^3, $Z=2$, $D_c=1·396$ g cm^{-3}. The structure was determined from diffractometer intensity measurements (Mo $K\alpha$ radiation) and refined by full-matrix least-squares calculations to an R of 0·043 for 267 observed reflexions. The molecule is pyramidal with the P atom lying on a crystallographic threefold axis. The pyrazolyl ring is planar and coordinated asymmetrically with respect to the P–N bond [1·714 (4) Å], the P–N–C and P–N–N angles being 135·4 (4) and 115·0 (3)° respectively.

Introduction. The crystals are extremely sensitive to traces of water and were sealed in Lindemann glass capillaries in a dry box. Preliminary photographs (Cu $K\alpha$ radiation) showed the crystals to have Laue symmetry 6/m and systematic absences 00l, $l=2n+1$, indicating space groups $P6_3$ or $P6_3/m$.

A crystal, $0·3 \times 0·3 \times 0·3$ mm, cut from a large acicular crystal, was used in the measurement of cell dimensions and collection of intensities on a Picker FACS-I diffractometer. Nb-filtered Mo $K\alpha$ radiation ($\lambda K\alpha_1 = 0·70926$ Å) and a scintillation counter with

pulse-height discrimination were used. Cell dimensions were obtained by least squares from 11 reflexions with $2\theta > 30°$. Intensities were collected with a θ–2θ scan width of 1·5° and scan speed of 2° min⁻¹. Background measurements of 20 s were taken on each side of the scan. 351 intensities were recorded with $2\theta \le 50°$, of which 267 were regarded as observable $[I > 2\cdot3\sigma(I)$ where $\sigma(I)$ is the standard deviation of the intensity derived from counting statistics (Einstein & Jones, 1972)]. The intensities were corrected for Lorentz and polarization effects but not for absorption $[\mu(\text{Mo } K\alpha) = 2\cdot36$ cm⁻¹].

$P6_3/m$ with $Z = 2$ requires the molecule to have $3/m$ symmetry in an ordered structure. Chemically this was considered unreasonable and the space group was assumed to be $P6_3$ (subsequently confirmed by the structure refinement). For $P6_3$ with $Z = 2$, the asymmetric unit is one third of a molecule, which requires the P atom to lie on a crystallographic threefold axis. A Patterson map followed by a difference map located the non-hydrogen atoms. At this stage it was not possible to distinguish between the C and N atoms and refinement of the positional coordinates and isotropic temperature factors by full-matrix least-squares (minimizing $\sum w(|F_o| - |F_c|)^2)$ with C scattering factors for all the ring atoms reduced $R = \sum||F_o| - |F_c||/\sum|F_o|$ from 0·276 to 0·095. A difference synthesis located the three H atoms of the asymmetric unit and distinguished the N atoms, Two further cycles of least-squares refinement including the H atoms in the structure factor calculations but not refining their parameters reduced R to 0·065. Least-squares refinement with anisotropic temperature parameters for the P, C and N atoms converged with $R = 0\cdot047$. During the final two cycles, the H atoms were allowed to refine with isotropic temperature factors giving $R = 0\cdot043$ for the 267 observed reflexions and a maximum shift to error of 0·04 on the last cycle. A final difference map indicated 'ripples' in the neighbourhood of the P atom as the major feature. Weights derived from counting statistics $(w = 1/\sigma F^2)$ were used throughout. Scattering factors were those of Stewart, Davidson & Simpson (1965) for H and Cromer & Waber (1965) for C, N and P.

No anomalous dispersion correction was applied for the P atom. The programs used in the structure determination and refinement have been described (Einstein & Jones, 1972).

The final positional and thermal parameters are shown in Table 1.* The conformation of the molecule and the atom labelling are shown in Fig. 1 and bond lengths and angles in Table 2.

Discussion. The molecule is pyramidal and has crystallographic threefold symmetry with an N–P–N' angle

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* The list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31241 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
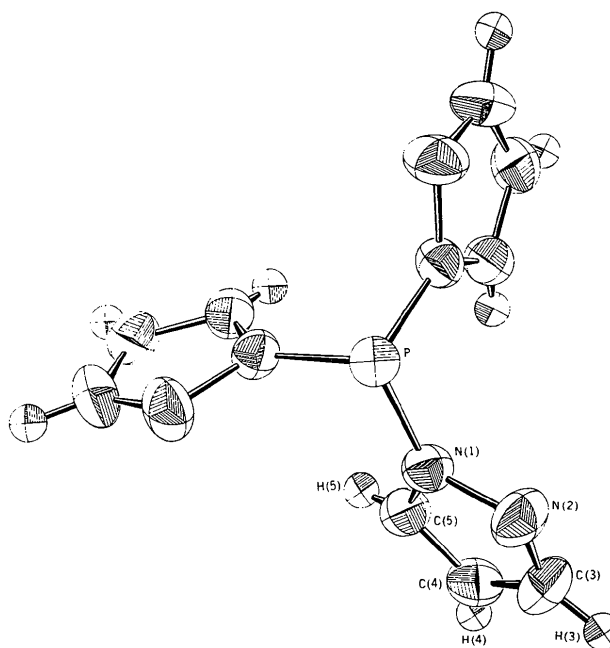

Fig. 1. Perspective view of tris-(1-pyrazolyl)phosphine, parallel to c, drawn by *ORTEP* (Johnson, 1965). Except for the H atoms, thermal ellipsoids are shown with 50 % probability.

Table 1. *Final atomic parameters*

The values of the atomic fractional coordinates and their estimated standard deviations (in parentheses) are multiplied by 10^4 for the heavy atoms and by 10^3 for the H atoms. The thermal parameters are anisotropic U_{ij} values (Å² × 10⁴) for the C, N and P atoms in the form exp $\{-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)\}$ and isotropic U values (Å² × 10³) for the H atoms.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	3333	6667	0	396 (8)	396	302 (11)	198	0	0
N(1)	1716 (6)	6926 (6)	−954 (5)	429 (26)	417 (26)	408 (25)	242 (22)	61 (23)	66 (23)
N(2)	15 (6)	6104 (6)	−301 (6)	435 (28)	673 (34)	570 (39)	279 (26)	163 (26)	96 (27)
C(3)	−994 (9)	6384 (10)	−1244 (9)	347 (37)	695 (47)	935 (61)	261 (37)	6 (42)	47 (43)
C(4)	−24 (8)	7379 (7)	−2467 (9)	573 (42)	501 (38)	656 (39)	343 (34)	−76 (38)	100 (36)
C(5)	1669 (9)	7700 (8)	−2242 (8)	450 (38)	461 (37)	561 (39)	247 (30)	76 (36)	95 (33)
				U					
H(3)	−220 (9)	601 (9)	−109 (8)	80 (23)					
H(4)	−35 (5)	773 (6)	−337 (4)	13 (12)					
H(5)	253 (7)	817 (7)	−283 (5)	23 (15)					

Table 2. *Interatomic distances* (Å) *and angles* (°)
and bond indices

		Bond index				Bond index
P——N(1)	1·714 (4)	1·04	C(5)–N(1)	1·335 (7)		1·18
N(1)–N(2)	1·374 (6)	1·13	C(3)–H(3)	0·91 (7)		0·97
N(2)–C(3)	1·303 (8)	1·60	C(4)–H(4)	0·95 (4)		0·97
C(3)–C(4)	1·372 (10)	1·28	C(5)–H(5)	0·82 (5)		0·96
C(4)–C(5)	1·331 (8)	1·58				
N(1)–P——N(1')	97·4 (2)		C(4)–C(5)–N(1)	108·8 (6)		
C(5)–N(1)–N(2)	109·6 (5)		N(2)–C(3)–H(3)	124 (5)		
P——N(1)–C(5)	135·4 (4)		C(4)–C(3)–H(3)	124 (5)		
P——N(1)–N(2)	115·0 (3)		C(3)–C(4)–H(4)	134 (2)		
N(1)–N(2)–C(3)	104·3 (4)		C(5)–C(4)–H(4)	121 (2)		
N(2)–C(3)–C(4)	112·5 (5)		C(4)–C(5)–H(5)	127 (3)		
C(3)–C(4)–C(5)	104·8 (6)		N(1)–C(5)–H(5)	124 (3)		

of 97·4 (2)°. The P–N length of 1·714 (4) Å (increased to 1·717 (4) Å if the N is assumed to 'ride' on the P atom) is slightly shorter than the value of 1·769 (19) Å given by Cruickshank (1964) for a P–N single bond in monosodium phosphoramidate, indicating that the $3d$ orbitals on the P atom may interact to a small extent with the π system of the pyrazolyl ring. The small but significant differences between the two C–C bonds (0·042 ± 0·013 Å) and the two C–N bonds (0·033 ± 0·010 Å) support this view. In pyrazole (Berthou, Elguero & Rérat, 1970; Larsen, Lehmann, Søtofte & Rasmussen, 1970) the C–C and C–N bonds are identical within the limits of experimental error. Molecular orbital calculations with the CNDO program of Pro-

Table 3. *Deviations of atoms from the least-squares plane* (Å) *through* N(1), N(2), C(3), C(4) *and* C(5)

The equation of the plane referred to orthogonal axes a, b^*, c is

$$0·2222x - 0·8499y - 0·4778z + 4·2286 = 0$$

N(1)	0·005	P	0·086
N(2)	−0·005	H(3)	−0·017
C(3)	0·008	H(4)	0·070
C(4)	0·001	H(5)	0·071
C(5)	−0·007		

χ^2 for the plane is 4·83.

fessor P. G. Perkins gave a bond index (Armstrong, Perkins & Stewart, 1973) of 1·04 for the P–N bond and 0·11 for the non-bonded P···N contact. Bond indices calculated by the program are listed in Table 2.

The atoms of the pyrazolyl ring are coplanar and the deviations are shown in Table 3. The angle between planes defined by adjacent pyrazolyl rings is 98·7 (5)°. The five-membered ring is linked asymmetrically to the P atom. The P–N–N and P–N–C angles are 115·0 (3) and 135·4 (4)°. We attribute this distinctive distortion to (1) the attraction between the N atom lone pair and the empty d orbitals of the P atom and (2) the repulsion of the P···H–C contact. (If symmetrical coordination was assumed, a value of approximately 2·8 Å would be expected for the P···H contact.) The P···H(5) distance is 3·05 Å. There are no particularly short intermolecular contacts, examples of the shortest being P···C = 3·71, P···H = 3·59, N···C = 3·35 and N···H = 2·62 Å.

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