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References

- BIJVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). *Nature, Lond.* **168**, 271–272.
- CROMER, D. T. & MANN, G. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DREW, M. G. B. & KAY, A. (1971). *J. Chem. Soc. (A)*, pp. 1846–1850.
- EDSALL, J. T., FLORY, P. J., KENDREW, J. C., LIQUORI, A. M., NÉMETHY, G., RAMACHANDRAN, G. N. & SCHERAGA, H. A. (1966). *Biopolymers*, **4**, 121–129.
- HARDING, M. M. & LONG, H. A. (1968). *Acta Cryst.* **B24**, 1096–1102.
- HENDRICKSON, W. A. & KARLE, J. (1971). *Acta Cryst.* **B27**, 427–431.
- IMMIRZI, A. (1967). *Ric. Sci.* **34**, 743–749.
- IUPAC (1970). *Nomenclature of Inorganic Chemistry*. London: Butterworths.
- LENZ, G. R. & MARTELL, A. E. (1964). *Biochemistry*, **3**, 745–750.
- LI, N. C. & MANNING, R. A. (1955). *J. Amer. Chem. Soc.* **77**, 5225–5228.
- LIVINGSTONE, S. E. & NOLAN, J. D. (1968). *Inorg. Chem.* **7**, 1447–1451.
- MCAULIFFE, C. A., QUAGLIANO, J. V. & VALLARINO, L. M. (1966). *Inorg. Chem.* **5**, 1996–2003.
- RAMACHANDRA AYYAR, R. (1968). *Z. Kristallogr.* **126**, 227–239.
- SHINDO, H. & BROWN, T. L. (1965). *J. Amer. Chem. Soc.* **87**, 1904–1909.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WARREN, R. C., MCCONNELL, J. F. & STEPHENSON, N. C. (1970). *Acta Cryst.* **B26**, 1402–1407.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.

Acta Cryst. (1973). **B29**, 767

The Crystal and Molecular Structure of (3,7-Dimethyl-2,6-octadienyl)triphenylphosphonium bromide

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The title compound crystallizes in space group $P2_1/c$ with unit-cell constants $a = 12.614$ (4), $b = 13.845$ (5), $c = 15.838$ (6) Å and $\beta = 113.35$ (5)°. The structure was solved by the symbolic addition procedure and refined by full-matrix least-squares methods to an R value of 0.055 based on 2969 observed reflexions. The significantly planar phenyl groups are in a propeller configuration around the P atom. Rigid-body thermal analysis of the phenyl groups shows a libration of 8–9° around the P–C bond. The C–C bond lengths in the phenyl groups are 0.019 Å shorter for the bonds furthest away from the phosphorus atom compared with the bonds closest to this atom. The 3,7-dimethyl-2,6-octadienyl chain consists of two planar isoprene units joined head-to-tail at a dihedral angle of 75.8°. The bromine atom has eight hydrogen neighbours at distances of 2.70–3.26 Å.

Introduction

(3,7-Dimethyl-2,6-octadienyl)triphenylphosphonium bromide, $C_{28}H_{32}PBr$, is a Wittig salt (Wittig, 1956) commonly used as a reactant in the synthesis of alkenes. Examples of use are given by Kjøsén & Liaaen-Jensen (1970) and by Surmatis & Ofner (1963) who also describe the preparation of the compound. The cation is shown schematically in Fig. 1 which gives the numbering used for the carbon atoms. The 3,7-dimethyl-2,6-octadienyl chain is made up of two isoprene units as in geraniol. Later in this paper the compound will be called GTPPBR, short for geranyltriphenylphosphonium bromide.

It was of interest to study the configuration around the phosphorus atom since this is the primary reaction site. Furthermore the conformation around the C(20)–C(21)

bond might be either *cis* or *trans* and the orientation of the two isoprene units relative to each other was also unknown.

Experimental

Crystal data

The crystals were produced by crystallization from a 40–65°C chloroform–petroleum spirit solution by Siv. ing. H. Kjøsén at the Organic Chemistry Laboratories of NTH. They are colourless prismatic needles of good crystal quality and elongated in the [100] direction. The forms {011} and {100} are well developed.

Crystallographic data:

(3,7-Dimethyl-2,6-octadienyl)triphenylphosphonium bromide, $C_{28}H_{32}PBr$.
F.W. 479.46; monoclinic, $Z = 4$; $\lambda(\text{Cu } K\alpha) = 1.5418$ Å

Table 1. Observed and calculated structure factors. The columns are I, 10F_obs, 10F_calc. Asterisks indicate unobserved reflexions.

Table with multiple columns containing numerical data for structure factors. The columns are organized into groups, with the first column being the primary index and subsequent columns containing observed and calculated values. Asterisks are used to denote unobserved reflexions.

Table 1 (cont.)

A large table with multiple columns containing numerical data, organized in a grid-like structure. The table includes various numbers, some with signs, and is divided into sections by small headers like 'HE 7, KE 10' or 'HE 10, KE 10'. The data appears to be a continuation of a larger dataset from a previous page.

$$\begin{aligned}
 a &= 12.614 \pm 0.004 \text{ \AA} \\
 b &= 13.845 \pm 0.005 \\
 c &= 15.838 \pm 0.006 \\
 \beta &= 113.35 \pm 0.05^\circ \\
 V &= 2539.4 \text{ \AA}^3 \\
 D_x &= 1.254 \text{ g cm}^{-3} \text{ for } Z=4 \\
 \mu &= 30.9 \text{ cm}^{-1} \text{ for Cu } K\alpha
 \end{aligned}$$

Systematic absences: $h0l$ when l odd and $0k0$ when k odd. Space group: $P2_1/c$ (No. 14).

Intensity measurements

A prismatic crystal of dimensions $0.13 \times 0.13 \times 0.16$ mm was used for the intensity measurements. Its greatest length was in the direction of the a axis. The crystal was mounted on a Picker FACS-1 automatic diffractometer with this axis approximately parallel to the goniometer-head axis. Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) was used. The lattice parameters given above were obtained by least-squares refinement of the setting angles for 12 high-angle reflexions.

The intensities were measured in the $\theta-2\theta$ scan mode with a scan speed of 1° min^{-1} in 2θ and a scan width of 1.8° plus a dispersion correction. The background was recorded for 20 sec at each side of the reflexions. Two standard reflexions (400 and 040) were measured

each 30 reflexions. The sum of the net counts for the standards fell approximately 9% during the 251 hours of exposure. The two standards showed a parallel fall with no abrupt changes, and the decrease was probably due to some radiation damage as the crystal used got a slightly milky colour, as opposed to other non-irradiated crystals which retained their clear, colourless appearance.

The intensities of all 4227 reflexions with $2\theta < 128^\circ$ (space-group extinctions excluded) were measured. 2969 reflexions with net intensity I greater than $2\sigma(I)$ were regarded as observed, $\sigma(I)$ being defined as $\sqrt{\sigma_N^2 + (0.01 \cdot N)^2}$ where the last term accounts for a 1% instrumental instability. σ_N is the statistical counting error and N is the sum of peak and background counts. The reflexions were brought on a common scale by using the sum of the intensities of the two standard reflexions as a standard and interpolating linearly between the standard measurements.

The intensity were corrected for Lorentz and polarization effects. No absorption correction was made. Maximum μR is approximately 0.5. The program *SCALER* was used to determine the scale factor and a common temperature factor by a least-squares fit of a straight line to a Wilson plot. The program also calculates normalized structure factors, $|E_h|$'s, and their

Table 2. Fractional coordinates and thermal parameters

Thermal parameters, U_{ij} ($\times 10^4$) are of the form

$$U = \exp[-2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2klb^* c^* U_{23} + 2hla^* c^* U_{13} + 2hka^* b^* U_{12})]$$

Standard deviations from the least-squares refinement are given in parentheses.

The hydrogen atoms are numbered according to their bonded carbon atoms. The three phenyl rings have been denoted $\phi 1$, $\phi 2$ and $\phi 3$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0.13782 (4)	0.41672 (3)	0.42309 (3)	530 (3)	719 (3)	657 (3)	-21 (3)	286 (2)	-55 (3)
P	0.79272 (8)	0.30245 (7)	0.42931 (7)	383 (6)	438 (7)	474 (7)	-6 (5)	167 (5)	15 (6)
$\phi 1C(1)$	0.6558 (3)	0.3208 (2)	0.4360 (2)	348 (21)	429 (24)	561 (26)	-1 (20)	179 (20)	39 (22)
$\phi 1C(2)$	0.6511 (4)	0.3472 (4)	0.5178 (4)	462 (30)	985 (41)	700 (37)	-49 (30)	247 (29)	-219 (32)
$\phi 1C(3)$	0.5456 (5)	0.3678 (4)	0.5220 (4)	738 (40)	1307 (53)	946 (49)	18 (37)	509 (39)	-309 (41)
$\phi 1C(4)$	0.4466 (5)	0.3622 (4)	0.4450 (5)	528 (37)	717 (39)	1257 (61)	108 (31)	467 (43)	-25 (39)
$\phi 1C(5)$	0.4491 (4)	0.3369 (4)	0.3631 (4)	440 (31)	656 (36)	841 (43)	-19 (28)	113 (32)	141 (33)
$\phi 1C(6)$	0.5545 (4)	0.3168 (3)	0.3577 (3)	463 (29)	550 (31)	658 (34)	-7 (24)	232 (27)	55 (27)
$\phi 2C(1)$	0.9014 (3)	0.2761 (3)	0.5410 (3)	385 (23)	459 (30)	464 (26)	20 (21)	193 (21)	31 (22)
$\phi 2C(2)$	0.9922 (4)	0.3383 (4)	0.5838 (3)	545 (31)	631 (35)	598 (34)	-52 (27)	157 (27)	86 (29)
$\phi 2C(3)$	1.0762 (4)	0.3148 (4)	0.6691 (4)	563 (34)	934 (44)	599 (36)	-94 (34)	83 (28)	34 (34)
$\phi 2C(4)$	1.0694 (5)	0.2303 (4)	0.7115 (4)	557 (34)	922 (44)	550 (36)	130 (32)	144 (30)	174 (33)
$\phi 2C(5)$	0.9791 (4)	0.1684 (4)	0.6696 (3)	742 (36)	608 (37)	650 (35)	82 (30)	266 (29)	211 (30)
$\phi 2C(6)$	0.8951 (4)	0.1893 (4)	0.5837 (3)	614 (34)	507 (32)	567 (33)	-26 (28)	111 (28)	66 (28)
$\phi 3C(1)$	0.7825 (3)	0.2008 (3)	0.3567 (2)	451 (23)	468 (25)	417 (23)	20 (21)	173 (19)	10 (21)
$\phi 3C(2)$	0.7024 (4)	0.1281 (3)	0.3447 (3)	623 (32)	548 (30)	703 (34)	-34 (26)	349 (28)	-110 (26)
$\phi 3C(3)$	0.7003 (4)	0.0475 (4)	0.2919 (4)	732 (37)	617 (37)	897 (41)	-115 (31)	356 (32)	-190 (31)
$\phi 3C(4)$	0.7785 (5)	0.0396 (4)	0.2520 (3)	778 (39)	650 (38)	589 (34)	60 (32)	193 (30)	-133 (30)
$\phi 3C(5)$	0.8583 (4)	0.1104 (4)	0.2643 (3)	743 (37)	784 (42)	621 (33)	134 (32)	373 (30)	-31 (29)
$\phi 3C(6)$	0.8619 (4)	0.1911 (4)	0.3170 (3)	535 (30)	586 (34)	616 (32)	-22 (28)	241 (26)	2 (28)
C(19)	0.8310 (3)	0.4097 (3)	0.3830 (3)	396 (22)	489 (26)	636 (28)	-6 (22)	164 (21)	91 (25)
C(20)	0.7529 (3)	0.4263 (3)	0.2844 (3)	583 (26)	610 (29)	614 (28)	26 (26)	239 (23)	131 (26)
C(21)	0.6728 (3)	0.4928 (3)	0.2519 (3)	530 (28)	610 (31)	678 (33)	71 (25)	243 (26)	93 (27)
C(22)	0.6437 (3)	0.5629 (3)	0.3122 (3)	777 (34)	824 (39)	899 (37)	135 (30)	183 (29)	-4 (33)
C(23)	0.6010 (4)	0.5014 (4)	0.1492 (3)	1009 (42)	1178 (52)	785 (41)	199 (38)	196 (34)	363 (39)
C(24)	0.6317 (6)	0.5812 (5)	0.0989 (4)	1675 (66)	950 (49)	1301 (56)	191 (54)	358 (50)	144 (47)
C(25)	0.7325 (6)	0.5671 (5)	0.0812 (4)	1580 (60)	1414 (62)	1620 (61)	150 (53)	992 (54)	-180 (49)
C(26)	0.7523 (7)	0.6154 (5)	0.0130 (5)	1807 (79)	1002 (63)	1200 (63)	-555 (57)	922 (64)	-338 (47)
C(27)	0.6754 (6)	0.6790 (5)	-0.0615 (5)	2112 (77)	875 (52)	1387 (65)	39 (50)	543 (58)	173 (49)
C(28)	0.8668 (6)	0.6013 (6)	0.0128 (4)	1428 (61)	1940 (80)	1099 (53)	-572 (62)	233 (50)	203 (51)

Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(19a)	0.829 (2)	0.457 (2)	0.424 (2)	0.056 (10)
H(19b)	0.911 (2)	0.401 (2)	0.388 (2)	0.055 (9)
H(20)	0.767 (3)	0.385 (2)	0.237 (2)	0.087 (12)
H(22a)	0.700 (4)	0.566 (3)	0.378 (3)	0.156 (17)
H(22b)	0.571 (4)	0.549 (3)	0.309 (3)	0.162 (19)
H(22c)	0.629 (3)	0.623 (3)	0.290 (3)	0.126 (16)
H(23a)	0.518 (3)	0.495 (3)	0.141 (3)	0.148 (17)
H(23b)	0.612	0.439	0.118	0.150
H(24a)	0.557	0.596	0.038	0.150
H(24b)	0.635 (3)	0.637 (3)	0.140 (3)	0.153 (17)
H(25)	0.785 (4)	0.515 (4)	0.132 (3)	0.203 (23)
H(27a)	0.595 (6)	0.679 (6)	-0.066 (5)	0.285 (35)
H(27b)	0.649 (5)	0.655 (4)	-0.112 (4)	0.183 (24)
H(27c)	0.697 (4)	0.736 (4)	-0.072 (3)	0.179 (23)
H(28a)	0.917 (3)	0.563 (3)	0.055 (3)	0.105 (13)
H(28b)	0.886 (6)	0.676 (6)	0.033 (5)	0.314 (35)
H(28c)	0.864 (4)	0.574 (4)	-0.038 (4)	0.196 (22)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
φ1H(2)	0.720 (3)	0.351 (3)	0.572 (2)	0.057 (12)
φ1H(3)	0.550 (3)	0.383 (3)	0.581 (2)	0.075 (15)
φ1H(4)	0.382 (3)	0.377 (3)	0.451 (3)	0.081 (15)
φ1H(5)	0.382 (3)	0.332 (3)	0.307 (2)	0.067 (13)
φ1H(6)	0.555 (3)	0.302 (2)	0.296 (2)	0.066 (12)
φ2H(2)	0.997 (3)	0.395 (2)	0.556 (2)	0.060 (13)
φ2H(3)	1.136 (3)	0.361 (3)	0.701 (3)	0.103 (17)
φ2H(4)	1.123 (3)	0.215 (3)	0.771 (2)	0.080 (15)
φ2H(5)	0.973 (3)	0.111 (3)	0.699 (2)	0.071 (14)
φ2H(6)	0.834 (3)	0.145 (3)	0.557 (3)	0.108 (18)
φ3H(2)	0.649 (3)	0.131 (2)	0.372 (2)	0.046 (12)
φ3H(3)	0.643 (3)	-0.001 (3)	0.288 (3)	0.096 (18)
φ3H(4)	0.778 (3)	-0.017 (3)	0.217 (2)	0.080 (15)
φ3H(5)	0.910 (3)	0.105 (3)	0.236 (3)	0.089 (17)
φ3H(6)	0.916 (3)	0.240 (2)	0.323 (2)	0.054 (13)

statistical distribution. The values of $\langle |E_h| \rangle = 0.863$ and $\langle |E_h^2 - 1| \rangle = 0.941$ can be compared with theoretical values of 0.798 and 0.968 in the centrosymmetric case.

Determination and refinement of the structure

The structure was solved by the symbolic addition method (Karle & Karle, 1963). The program *SYMBOL* was used with a starting set of three origin-defining reflexions (45 $\bar{5}$, 75 $\bar{7}$ and 10 4 $\bar{5}$) and three symbolic signs (for 132, 392 and 749). There were strong indica-

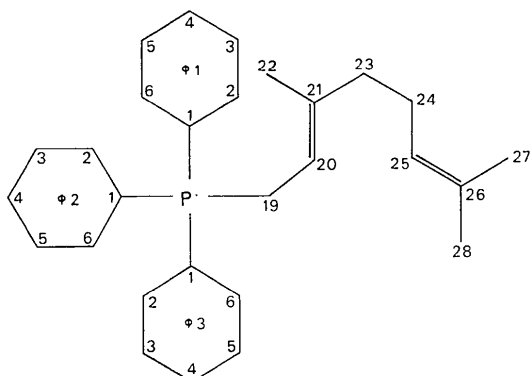


Fig. 1. Numbering of the atoms in a geranyltriphenylphosphonium ion as used in this paper.

tions for -, +, + as signs for the three symbols. An *E* map was calculated using this sign combination and the program *FOUFU1* (Borgen, Mestvedt & Finjord, 1969). The map showed two prominent maxima of relative strength 730 and 430. Assuming these maxima to be Br⁻ and P respectively, it was fairly easy to locate the phenyl rings and the first two atoms, C(19) and C(20), in the geranyl chain. A difference map using this information yielded the rest of the structure, *i.e.* C(21) to C(28).

Refinement was started with programs from the *XRAY* system (Stewart, Kruger, Kundell & Baldwin, 1971). The full-matrix least-squares program *CRYLSQ* minimizes $\sum w(|F_o| - |F_c|)^2$ and $w = 1$ during the first part of the refinement. The scattering factors used are those of Doyle & Turner (1968) for Br⁻, P and C and from Stewart, Davidson & Simpson (1965) for H. The scattering factors were corrected for anomalous scattering from bromine and phosphorus using the following coefficients:

	$\Delta f'$	$\Delta f''$
Br	-0.95	1.40
P	0.20	0.50

Anisotropic refinement converged at $R_1 = 0.073$ where $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. A difference map gave the positions of most of the hydrogen atoms, although stereochemical knowledge was needed to locate some of those in the outer part of the geranyl chain. Owing to very high thermal vibrations all maxima in this part of the molecule were poorly defined. With all hydrogen atoms in place and given isotropic temperature factors equal to the temperature factors of the carbon atoms to which they are bonded, the R_1 index was 0.063. In the subsequent refinement the reflexions were given weight $w = 1/\sigma^2(I)$ where $\sigma(I)$ is defined earlier. Only about 100 parameters could be varied at a time in order to stay within restrictions on computing time. The positions of H(23b) and H(24a) were not refined in the last cycles as these two atoms showed a tendency to refine into stereochemically unacceptable positions 1.5 and 1.4 Å away from their bonded carbon atoms. The refinement converged at an R_1 index of 0.055 and all shifts were then well below the standard deviations. The final weighted reliability index $R_2 = \sum w(|F_o| - |F_c|)^2 / \sum w F_o^2$ is 0.033. All reliability indexes given are based on 2969 observed reflexions. A final difference map showed some spurious maxima with a largest height of 0.3 e Å⁻³, but they appeared to be randomly distributed and are probably due to the lack of an absorption correction or to radiation damage to the crystal.

Observed and calculated structure factors are listed in Table 1. Final positional and thermal parameters are given in Table 2.

Results and discussion

The phenyl groups have been analysed for rigid-body thermal motion using programs developed by Evensen

(1970). The program *TERMVIB1* which determines tensors of translation (*T*) and libration (*L*) according to the method of Cruickshank (1956) was first used, but did not give very convincing results. However, using the program *TERMVIB2* which introduces the tensor *S* for the screw motion according to the method of Shoemaker & Trueblood (1968) the fit was very good. Each phenyl group was analysed together with the phosphorus atom. This is the same method as used by Goldstein, Seff & Trueblood (later GST) (1968) for a tetraphenylphosphonium ion where one would expect the phenyl groups to show much the same behaviour as in *GTPPBR*. The discrepancy between observed U_{ij} 's from the least-squares refinement and calculated U_{ij} 's based on the rigid-body model was used as a measure of the rigidity of the analysed groups of atoms. Average $U_o - U_c$ was 0.0034 \AA^2 , to be compared with an average least-squares $\sigma(U_o)$ of 0.0029 \AA^2 .

The results of the rigid-body analysis are given in Table 3. The rigid-body parameters for each phenyl group + P are referred to a new orthogonal coordinate system (x_0, y_0, z_0) with the origin in the centre of gravity of the seven atoms (hydrogen atoms have been ignored) and the z_0 axis normal to the best plane through the atoms. The y_0 axis is defined parallel to the crystallographic (001) plane. P- ϕ 1C(1) is approximately parallel to the local y_0 axis, P- ϕ 2C(1) is approximately parallel to the local $-x_0$ axis and P- ϕ 3C(1) makes an angle of 18° with the local x_0 axis. The diagonal components of *T*

have magnitudes from 0.042 to 0.057 \AA^2 indicating a fairly isotropic translational motion of 0.20 – 0.24 \AA . The only components of *L* that are significantly greater than zero are those corresponding to a libration around the P-C(1) axes. The magnitude of this libration is approximately 8 – 9° . These results are in good agreement with the results of GST who found an isotropic translational motion of about 0.2 \AA and a librational amplitude of about 6° around the P-C(1) bonds. The triphenylphosphonium (*TPP*⁺) group as a whole and the two isoprene parts of the geranyl chain have also

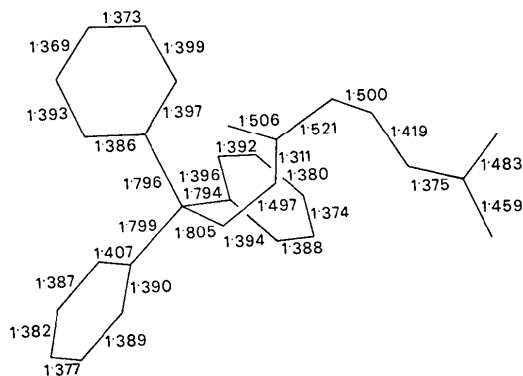


Fig. 2. Bond lengths (\AA).

Table 3. *Tensors of translation (T) and libration (L)*
Average standard deviations are 0.003 \AA in T_{ij} and 6 deg^2 in L_{ij} .

	$T_{ij} (\text{\AA}^2)$			$L_{ij} (\text{deg}^2)$		
$\phi 1 + P$:	0.057	-0.004	0.005	10.7	10.1	0.5
		0.042	0.000		83.3	-13.9
			0.042			17.2
$\phi 2 + P$:	0.046	-0.002	0.004	65.1	9.3	1.4
		0.047	-0.001		7.8	4.4
			0.045			11.6
$\phi 3 + P$:	0.048	0.002	0.001	56.0	10.0	9.2
		0.049	0.001		9.6	0.8
			0.043			11.5

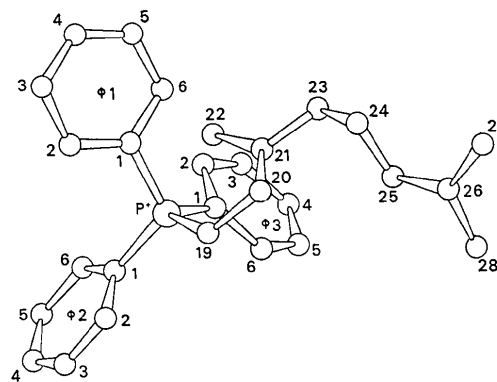


Fig. 3. A *GTPP*⁺ ion as seen along the y axis.

Table 4. *Bond lengths (\AA) in the *TPP*⁺ ion*

The C-C and P-C distances have been corrected for rigid-body thermal motion (see text). Standard deviations are given in parentheses.

	Uncorrected $\phi 1$	Corrected	Uncorrected $\phi 2$	Corrected	Uncorrected $\phi 3$	Corrected
C(1)-C(2)	1.370 (7)	1.386	1.378 (7)	1.390	1.385 (7)	1.396
C(1)-C(6)	1.385 (7)	1.397	1.397 (7)	1.407	1.384 (7)	1.394
C(2)-C(3)	1.388 (8)	1.393	1.385 (8)	1.389	1.389 (8)	1.392
C(5)-C(6)	1.394 (8)	1.399	1.384 (8)	1.387	1.385 (8)	1.388
C(3)-C(4)	1.359 (9)	1.369	1.369 (9)	1.377	1.371 (9)	1.380
C(4)-C(5)	1.356 (9)	1.373	1.369 (9)	1.382	1.363 (9)	1.374
C(1)-P	1.790 (4)	1.796	1.794 (4)	1.799	1.790 (4)	1.794
C(2)-H(2)	0.95 (4)		0.91 (4)		0.94 (4)	
C(3)-H(3)	0.94 (4)		0.97 (4)		0.98 (4)	
C(4)-H(4)	0.88 (5)		0.94 (5)		0.96 (5)	
C(5)-H(5)	0.96 (4)		0.94 (4)		0.93 (4)	
C(6)-H(6)	1.01 (4)		0.94 (4)		0.93 (4)	

been analysed but they do not fit a rigid-body model.

Bond lengths in the TPP⁺ group are given in Table 4 and can also be found in Fig. 2 for the heavier atoms. The C–C and C–P⁺ distances of TPP⁺ have been corrected for rigid-body thermal motion using the L_{ij} values of Table 3 and the program *KORREKS* (Evensen, 1970) which is based on the method of Cruickshank (1956, 1961). There seem to be variations in the C–C bond lengths depending on their position in the phenyl rings. Average corrected bond length for the C(1)–C(2) type of bond is 1.395 ± 0.003 Å, for the C(2)–C(3) type 1.391 ± 0.002 Å, and for the C(3)–C(4) type 1.376 ± 0.002 Å. The shortening of the C(3)–C(4) type of bond compared with the C(1)–C(2) and C(2)–C(3) types is on the limits on significance, but is in agreement with the results of GST. They found that the ring bonds furthest away from the phosphorus atom are shorter than those nearest by an average of 0.019 Å which is exactly the same as in this work, and suggested non-rigid thermal motion as a possible explanation of the discrepancy. It may also be due to a resonance effect with the C(1)–P⁺ bond which is partly ionic in character owing to the deficiency of electrons at the phosphorus atom. The average C–H bond length in the phenyl rings is 0.95 Å, which must be regarded as normal in X-ray work (Stewart, Davidson & Simpson, 1965). An extra shortening of the

C–H bonds due to the rigid-body thermal vibration can be expected.

The configuration of a GTPP⁺ ion is shown in a projection along the y axis in Fig. 3. Fig. 4 shows the molecular packing in the x -axis projection. The three phenyl groups are in a 'propeller' configuration around the P⁺–C(19) 'shaft'. Best planes have been calculated through the phenyl groups and the isoprene groups using the program *LSQPL* from the *XRAY* system. The angles between the planes are given in Table 6 which shows that the angles between phenyl planes vary in the range 57.1 – 83.4° . The two isoprene planes make an angle of 54.8° and the dihedral angle at C(21)–C(23)–C(24)–C(25) is 75.8° . The least-squares planes are all significantly planar as can be seen from Table 5. The phosphorus atom deviates 0.03 – 0.11 Å from the phenyl ring planes. Table 7 shows some short non-bonded intramolecular distances. It can be seen that the distance between a phenyl C(1) and an *ortho* carbon atom in a neighbouring phenyl ring is rather short at 3.19 – 3.30 Å. A hydrogen atom of one phenyl ring is placed above C(1) of a neighbouring ring at a distance of 2.73 – 2.98 Å which is short compared with a sum of van der Waals radii of 2.97 Å. Since all the phenyl groups and the C(19) and C(20) atoms are involved in short contacts around the phosphorus atom the configuration must be

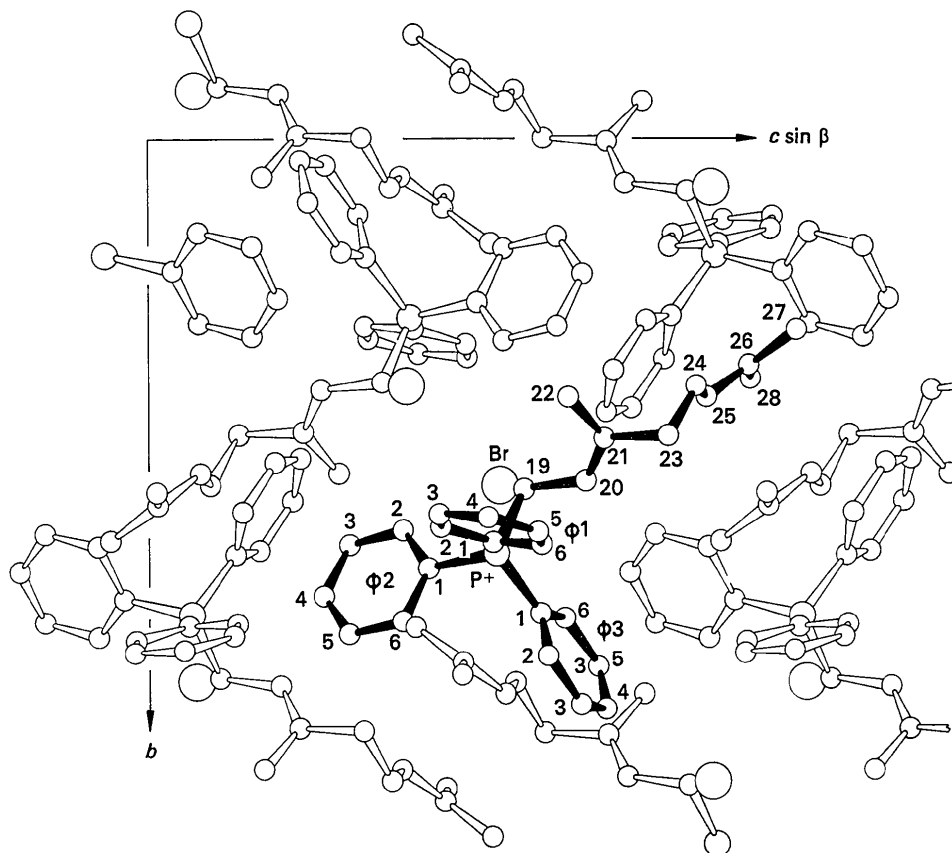


Fig. 4. Molecular packing in GTPPBR as seen along the x axis.

a result of minimization of steric hindrance within the molecule as a whole.

Table 5. Deviations (\AA) from least-squares planes

Phosphorus is given zero weight.

	$D(\varphi 1)$	$D(\varphi 2)$	$D(\varphi 3)$
C(1)	-0.008	0.004	-0.009
C(2)	0.003	0.003	0.005
C(3)	0.002	-0.004	0.000
C(4)	-0.002	-0.001	-0.001
C(5)	-0.003	0.008	-0.003
C(6)	0.008	-0.010	0.008
P	0.109	-0.029	0.085

	D		D
C(19)	0.002	C(24)	0.045
C(20)	-0.007	C(25)	-0.061
C(21)	0.010	C(26)	-0.011
C(22)	-0.004	C(27)	-0.008
C(23)	-0.002	C(28)	0.034

Table 6. Angles between planar groups

(a) Equations for best planes

Plane $\varphi 1$: C(1) \rightarrow C(6)
 $2.441x + 13.315y - 4.037z = 4.120$
 Plane $\varphi 2$: C(1) \rightarrow C(6)
 $-9.698x + 6.407y + 11.244z = -0.893$
 Plane $\varphi 3$: C(1) \rightarrow C(6)
 $4.258x - 6.475y + 9.759z = 5.521$
 Plane I1: C(19), C(20), C(21), C(22), C(23)
 $9.587x + 8.925y - 5.976z = 9.332$
 Plane I2: C(24), C(25), C(26), C(27), C(28)
 $1.792x + 11.083y + 7.574z = 8.277$

(b) Angles ($^\circ$) between planes defined above

Planes	$\varphi 2$	$\varphi 3$	I1
$\varphi 1$	77.8	57.1	38.5
$\varphi 2$		83.4	71.2
$\varphi 3$			83.6
I2			54.8

Table 7. Some short non-bonded intramolecular distances (\AA)

	Type of contact:	
$\varphi 2C(1)-\varphi 1C(2)$	P-bonded C to <i>ortho</i> -C in neighbouring phenyl group	3.19
$\varphi 1C(1)-\varphi 3C(2)$		3.20
$\varphi 3C(1)-\varphi 2C(6)$		3.30
$\varphi 3C(1)-\varphi 1C(6)$		3.30
C(19)- $\varphi 3C(6)$	Phenyl to geranyl	3.28
C(19)- $\varphi 2C(2)$		3.18
C(20)- $\varphi 1C(1)$		3.42
C(20)- $\varphi 1C(6)$		3.49
C(20)- $\varphi 3C(1)$		3.30
C(20)- $\varphi 3C(6)$		3.49
C(19)-C(22)	Intra-geranyl	3.04
C(20)-C(24)		3.47
C(21)-C(25)		3.25
C(24)-C(27)		3.11
$\varphi 1C(1)-\varphi 3H(2)$	C(1) to H in neighbouring phenyl group	2.80
$\varphi 2C(1)-\varphi 1H(2)$		2.73
$\varphi 3C(1)-\varphi 1H(6)$		2.98

The average $P^+-C(sp^2)$ bond length of 1.796 ± 0.002 \AA is quite normal for this type of bond and agrees well with the 1.796 ± 0.003 \AA bond length found by GST. The $P^+-C(sp^2)$ bond to C(19) is slightly longer at 1.805 ± 0.004 \AA (not corrected for thermal motion), which is to be expected owing to the larger (by 0.03 \AA according to Bastiansen & Trætterberg, 1962) covalent radii of the sp^3 hybridization. The P^+-C is appreciably shorter than the phosphine $P-C$ bond of 1.841 ± 0.003 \AA in $(CH_3)_3P$ found by Lide & Mann (1958) from microwave measurements. The phosphonium ion can be described as a resonance structure involving one completely covalent structure, four structures with one ionic $P-C$ bond, six with two bonds ionic, four with three bonds ionic and one completely ionic. The shortening in the phosphonium case compared with the phosphine may then be explained as resulting from the partly ionic character of the P^+-C bond.

Bond lengths in the geranyl chain are given in Table 8. The six $C(sp^2)-C(sp^3)$ bond lengths vary widely. In particular the C(24)-C(25) distance of 1.419 ± 0.011 \AA is very short compared with the normal $C(sp^2)-C(sp^3)$ bond of 1.493 \AA given by Bastiansen & Trætterberg (1962). On the other hand the neighbouring C(25)-C(26) double bond at 1.375 ± 0.011 \AA is longer than the normal value of 1.338 \AA cited by Bastiansen & Trætter-

Table 8. Bond lengths (\AA) in the geranyl part of GTPPBR

Standard deviations are given in parentheses.

P—C(19)	1.805 (4)	C(22)—H(22b)	0.92 (5)
C(19)—C(20)	1.497 (6)	C(22)—H(22c)	0.90 (5)
C(20)—C(21)	1.311 (7)	C(23)—H(23a)	1.01 (5)
C(21)—C(22)	1.506 (7)	C(23)—H(23b)	1.03 (5)
C(21)—C(23)	1.521 (6)	C(24)—H(24a)	1.07 (5)
C(23)—C(24)	1.500 (10)	C(24)—H(24b)	0.96 (5)
C(24)—C(25)	1.419 (11)	C(25)—H(25)	1.09 (5)
C(25)—C(26)	1.375 (11)	C(27)—H(27a)	0.95 (5)
C(26)—C(27)	1.483 (10)	C(27)—H(27b)	0.83 (5)
C(26)—C(28)	1.459 (10)	C(27)—H(27c)	0.90 (5)
C(19)—H(19a)	0.93 (4)	C(28)—H(28a)	0.89 (5)
C(19)—H(19b)	0.99 (4)	C(28)—H(28b)	1.04 (5)
C(20)—H(20)	1.01 (4)	C(28)—H(28c)	0.87 (5)
C(22)—H(22a)	1.00 (5)		

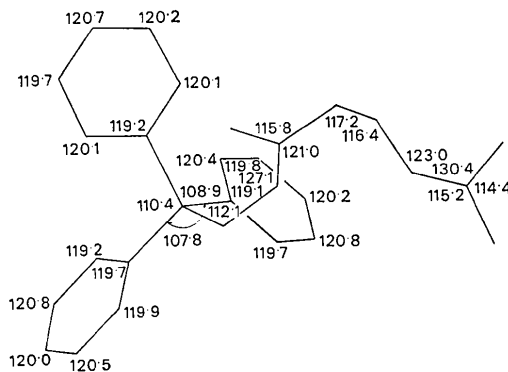


Fig. 5. Bond angles ($^\circ$).

berg. Since the thermal vibration is unusually high in this part of the molecule these discrepancies may be a result of non-rigid thermal motion.

The bond angles are given in Table 9 and Fig. 5. The C-C-C angles in the phenyl groups are all very close to the expected 120° and the C-P-C angles are only 1-2° from the ideal tetrahedral angle of 109.5°. Some deviations from expected values can be found in the geranyl chain and they have the effect of 'straightening out' the chain. The reason is probably close third-neighbour contacts. It can be seen from Table 7 that *inter alia* the C(19)···C(22) distance of 3.04 Å and the C(27)···C(24) distance of 3.11 Å are short compared with the sum of van der Waals radii.

Table 10 lists the shortest intermolecular distances. None of them is particularly short compared with the normal range of van der Waals contacts. Table 10 also gives the distances from the bromine anion to the nearest hydrogen atoms. There are eight hydrogen atoms around the bromine atom at distances of 2.70-3.26 Å. The closest approach is to the H(19*a*) and H(19*b*) atoms, which is to be expected owing to the attraction from the assumed localized positive charge on the phosphorus atom which is close to the H(19) atoms. The shortest Br···P distances is 4.44 Å.

I wish to thank Professor H. Sørum for kind and patient supervision of the work for a lic. techn. degree,

Table 9. Bond angles in GTPPBR

The standard deviations are given in parentheses.

$\phi 1$: C(1)-P- $\phi 2$ C(1)	110.4 (4)°	$\phi 3$: C(1)-C(2)-C(3)	120.4 (4)°
$\phi 1$ C(1)-P- $\phi 3$ C(1)	108.9 (4)	C(2)-C(3)-C(4)	119.8 (4)
$\phi 2$ C(1)-P- $\phi 3$ C(1)	107.8 (4)	C(3)-C(4)-C(5)	120.2 (5)
$\phi 3$ C(1)-P-C(19)	110.0 (4)	C(4)-C(5)-C(6)	120.8 (5)
$\phi 1$ C(1)-P-C(19)	109.7 (4)	C(5)-C(6)-C(1)	119.7 (4)
$\phi 1$: C(1)-C(2)-C(3)	120.1 (4)	C(6)-C(1)-C(2)	119.1 (4)
C(2)-C(3)-C(4)	120.2 (4)	P-C(19)-C(20)	112.1 (4)
C(3)-C(4)-C(5)	120.7 (5)	C(19)-C(20)-C(21)	127.1 (4)
C(4)-C(5)-C(6)	119.7 (5)	C(20)-C(21)-C(22)	123.2 (4)
C(5)-C(6)-C(1)	120.1 (4)	C(20)-C(21)-C(23)	121.0 (4)
C(6)-C(1)-C(2)	119.2 (4)	C(22)-C(21)-C(23)	115.8 (4)
$\phi 2$: C(1)-C(2)-C(3)	119.9 (4)	C(21)-C(23)-C(24)	117.2 (4)
C(2)-C(3)-C(4)	120.5 (4)	C(23)-C(24)-C(25)	116.4 (6)
C(3)-C(4)-C(5)	120.0 (4)	C(24)-C(25)-C(26)	123.0 (6)
C(4)-C(5)-C(6)	120.8 (5)	C(25)-C(26)-C(27)	130.4 (7)
C(5)-C(6)-C(1)	119.2 (4)	C(25)-C(26)-C(28)	115.2 (7)
C(6)-C(1)-C(2)	119.7 (4)	C(27)-C(26)-C(28)	114.4 (7)

Table 10. Intermolecular and bromine distances

Distances are included within a limit 0.2 Å greater than the sum of van der Waals radii of the participants.

$$R_C = 1.80 \text{ \AA}, \quad R_O = 1.36 \text{ \AA}, \quad R_H = 1.17 \text{ \AA}, \quad R_{Br} = 1.95 \text{ \AA}$$

Symmetry operations:

1: $x+1, y, z$	9: $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$
2: x, y, z	12: $x, -y+\frac{1}{2}, z+\frac{1}{2}$
4: $-x+2, -y+1, -z+1$	15: $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$
7: $-x+1, -y+1, -z+1$	17: $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$
8: $-x+1, -y+1, -z$	

		Symmetry operation		Symmetry operation
Br—H(19 <i>b</i>)	2.70 Å	1	$\phi 1$ H(2)- $\phi 3$ C(4)	3.05 Å 12
Br—H(19 <i>a</i>)	2.88	7	$\phi 1$ H(2)- $\phi 3$ C(5)	2.90 12
Br— $\phi 1$ H(4)	2.98	2	$\phi 1$ C(5)- $\phi 3$ H(3)	3.15 17
Br— $\phi 2$ H(4)	2.96	9	$\phi 1$ C(5)-H(24 <i>b</i>)	2.97 17
Br— $\phi 3$ H(4)	2.96	17	$\phi 2$ C(4)- $\phi 3$ H(5)	3.16 12
Br— $\phi 2$ H(2)	3.26	1	$\phi 2$ C(2)- $\phi 3$ H(5)	3.08 12
Br— $\phi 2$ H(2)	3.20	7	$\phi 2$ C(3)- $\phi 3$ H(5)	2.92 12
Br—H(22 <i>a</i>)	3.01	7	$\phi 2$ C(4)- $\phi 3$ H(6)	3.13 12
$\phi 1$ C(3)- $\phi 1$ C(4)	3.77	7	$\phi 2$ C(5)- $\phi 3$ H(6)	3.12 12
$\phi 1$ C(2)- $\phi 3$ C(4)	3.75	12	$\phi 2$ H(3)-C(21)	3.01 4
$\phi 1$ C(2)- $\phi 3$ C(5)	3.78	12	$\phi 2$ H(3)-C(22)	3.06 4
$\phi 1$ C(5)- $\phi 3$ C(3)	3.80	17	$\phi 3$ C(3)-H(28 <i>c</i>)	3.15 12
$\phi 1$ C(5)-C(24)	3.80	17	$\phi 3$ C(6)-H(28 <i>b</i>)	3.15 15
$\phi 2$ C(3)- $\phi 3$ C(5)	3.77	12	$\phi 3$ C(3)-H(22 <i>b</i>)	3.15 17
$\phi 2$ C(4)- $\phi 3$ C(5)	3.80	12	C(23)—H(24 <i>a</i>)	3.15 8
$\phi 2$ C(4)- $\phi 3$ C(6)	3.78	12		
$\phi 2$ C(5)- $\phi 3$ C(6)	3.76	12		
$\phi 3$ C(6)-C(28)	3.63	15		

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References

- BASTIANSEN, O. & TRÆTTEBERG, M. (1962). *Tetrahedron*, **17**, 147–154.
- BORGEN, O., MESTVEDT, B. & FINJORD, J. (1969). Techn. Report 52, Institutt for Fysikalsk Kjemi, NTH.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757–758.
- CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896–897.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- EVENSEN, A. M. (1970). Thesis. Institutt for Røntgenteknikk, NTH.
- GOLDSTEIN, P., SEFF, K. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 778–791.
- KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969–975.
- KJØSEN, H. & LIAAEN-JENSEN, S. (1970). *Acta Chem. Scand.* **24**, 2259–2260.
- LIDE, D. R. JR & MANN, D. E. (1958). *J. Chem. Phys.* **29**, 914–920.
- SHOEMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- STEWART, J. M., KRUGER, G. J., KUNDELL, F. A. & BALDWIN, J. C. (1971). The XRAY System, Version of Oct. 1971. Computer Science Center, Univ. of Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- SURMATHIS, J. D. & OFNER, A. (1963). *J. Chem. Soc.* **28**, 2735–2739.
- WITTIG, G. (1956). *Angew. Chem.* **68**, 505–508.

Acta Cryst. (1973). **B29**, 776

The Crystal and Molecular Structure of 3-Thioamidopyridine

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Crystals of 3-thioamidopyridine, $C_6H_6N_2S$, are monoclinic, space group $P2_1/n$ with four molecules in a unit cell of dimensions $a=4.004$, $b=10.572$ and $c=15.400$ Å, $\beta=96.42^\circ$. The crystal structure was solved by three-dimensional Patterson and Fourier syntheses using the heavy-atom technique. The atomic coordinates of all the atoms in the structure were initially refined by block-diagonal, least-squares calculations and completed by two cycles of full-matrix refinement. The final R index was 0.035 for 712 reflexions obtained from a Hilger-Watts four-circle automatic diffractometer using Mo $K\alpha$ radiation. The mean bond lengths in the pyridine ring are C–C = 1.378, C–N = 1.330 Å, with r.m.s. deviations of 0.005 and 0.006 Å respectively. The thioamido group has the dimensions C–C = 1.488, C–N = 1.307 and C–S = 1.666 Å with a mean e.s.d. of 0.005 Å. The locations of the amido hydrogen positions, together with the bond lengths and angles within the thioamido group, suggest a significant contribution from the ionic canonical form, as well as the amide form, to the overall electron arrangement within the thioamido group. The angle between the plane of the pyridine molecule and that of the thioamido group is 33.8° . Non-bonded contact radii of some atoms are proposed to interpret this interplanar angle. Two types of hydrogen bond have been found, one is of the type N–H...S (3.423 Å) and connects pairs of molecules across centres of symmetry and the other is of type N–H...N (2.955 Å) and connects pairs of molecules through the screw axis.

Introduction

The crystal and molecular structure of 3-thioamidopyridine is the third in a series of three isomeric thioamidopyridines of general formula $C_6H_6N_2S$, to be reported. In a previous article (Downie, Harrison, Raper & Hepworth, 1972) the structure of 2-thioamidopyridine was described and the results compared with the previously reported data for 4-thioamidopyridine (Colleter & Gadret, 1967). The structure of the 2-propyl derivative of 4-thioamidopyridine has also been re-

ported (Colleter, Gadret & Gourselle, 1970). The structural interest in these compounds has centred on the parameters of the thioamide group and the consequent electron arrangement within the group. Additional features of interest have been the non-coplanarity of the pyridine ring with the thioamide group and the hydrogen-bonding schemes. These features of interest are reviewed in this article.

In addition to these items of structural interest the thioamidopyridines have wide-ranging chemical, biochemical and industrial applications. The anti-tuber-