

Fig. 2. Projection (100).

La caractéristique essentielle de la structure est l'empilement des molécules autour des axes hélicoïdaux d'ordre 4; les contacts de van der Waals s'effectuent

entre atomes d'azote et d'hydrogène (2,67 Å) (Fig. 2). Toutes les autres distances intermoléculaires sont supérieures à la somme des rayons de van der Waals. On peut donc prévoir, à plus basse température, une seconde phase plus compacte et de symétrie moins élevée. On note simplement la longueur de la liaison $C\equiv N$ [1,137 (14) Å] inférieure aux valeurs données pour l'état liquide par d'autres auteurs: 1,156 (1) Å (Casado *et al.*, 1971) et 1,159 (2) Å (Bak, Christensen, Dixon, Hansen-Nygaard & Rastrup-Andersen, 1962) et nettement supérieure à la moyenne des données bibliographiques pour des composés de coordination cristallisés: 1,11 (7) Å (Massaux & Le Bihan, 1976).

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Pyridinium 2,2,5,5-Tetrathio-cyclo-di(phosphadithianate), [(Pyridine)₂H]₂²⁺[P₂S₈]₂²⁻

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Abstract. $C_{20}H_{22}N_4P_2S_8$, monoclinic, $P2_1/n$, $a = 10.677$ (8), $b = 12.048$ (8), $c = 12.399$ (8) Å, $\beta = 114.76$ (6)°, $U = 1448$ Å³, $Z = 4$, $D_x = 1.461$ g cm⁻³, $\mu(\text{Cu } K\alpha) = 45.35$ cm⁻¹. The structure was solved by direct methods and refined to an R of 0.047 for 1641 unique diffractometer data. The cation consists of two pyridine moieties linked by an approximately linear hydrogen bond, with twofold disorder of the H atom position. The anion contains a (PSS)₂ six-membered ring in a chair conformation, and lies on a crystallographic centre of symmetry.

Introduction. The sample was isolated from the reaction of P₄S₁₀ with pyridine (possibly in the presence

of a trace of moisture), and an X-ray crystal structure determination was undertaken when spectroscopic methods proved uninformative. Both the cation and anion are found to have novel structures.

P₄S₁₀ (1 g) was refluxed for 3 h in pyridine (20 ml, dried over solid KOH) and the deep-orange solution allowed to cool slowly. After several days irregular yellow crystals had formed. Intensities were determined with a Syntex P2, four-circle diffractometer, Cu $K\alpha$ radiation, a graphite monochromator, and a crystal of approximate dimensions 0.5 × 0.06 × 0.06 mm sealed in a Lindemann-glass capillary tube. 2537 reflexions were measured; after application of Lp and empirical absorption corrections, equivalent reflexions were

averaged to give 1641 unique reflexions with $F > 5\sigma(F)$ based on counting statistics. Unit-cell dimensions were obtained from diffractometer measurements of 15 reflexions. The structure was solved by multisolution Σ_2 sign expansion and refined by full-matrix least squares, with an overall isotropic temperature factor for the H atoms and the remaining atoms anisotropic. Initially the hydrogen-bonded H atom was omitted, and a riding model was employed for the other H atoms: the C-H vectors were held constant in magnitude (1.00 Å) and direction, but the CH atom pairs were free to move. A difference electron density synthesis revealed a twofold disorder of the hydrogen-bonding H atom along the N-N vector. It was inserted as two atoms, each with a site-occupation factor fixed at 0.5 and U fixed at 0.05 Å², and subject to the same riding model as the H atoms attached to C. The scattering factors of Cromer & Mann (1968) were employed for C, N, S and P, and the bonded-atom scattering factor of Stewart, Davidson & Simpson (1965) was used for H. With the weighting scheme $w = 1/[\sigma^2(F) + 0.000083F^2]$ the refinement converged to $R' = \Sigma w^{1/2} \Delta / \Sigma w^{1/2} |F_o| = 0.048$ and a

corresponding unweighted R index of 0.047. The results of the final least-squares cycle are given in Tables 1 and 2, and the resulting interatomic distances and angles in Tables 3 and 4.†

Discussion. The anisotropic temperature factors were found to be in good agreement with the rigid-body-motion model of Schomaker & Trueblood (1968): $R_g = (\Sigma \Delta^2 / \Sigma U_{ij}^2)^{1/2}$ for the agreement between the observed and calculated U_{ij} was 0.052. Since the anion lies on a crystallographic centre of symmetry, the S tensor (relative to an origin at the centre) is zero, and the method is exactly equivalent to that of Cruickshank (1956). Librational tensors, with respect to axes parallel to x^* , y and z , were: L_{11} 13 (2), L_{12} 1 (1), L_{13} 7 (2), L_{22} 35 (2), L_{23} 35 (2), L_{33} 60 (4) ($\times 10^{-4}$ rad²); T_{11} 255 (11), T_{12} -25 (9), T_{13} 41 (7), T_{22} 342 (10), T_{23} 58 (7), T_{33} 409 (8) ($\times 10^{-4}$ Å²). These values were used in calculating the librational corrected bond lengths given in Fig. 1, but uncorrected values are used in the following discussion.

The six-membered (PSS)₂ ring adopts a chair conformation similar to that reported for S₆ by Donohue, Caron & Goldish (1961): S-S 2.059 (4) Å (2.06 Å in S₆), P-S-S 104.8 (2) and 104.6 (2)° (S-S-S 102.2°), and P-S-S-P torsion angle 72.8° (S-S-S-S 74.5°). The effectively isoelectronic

Table 1. Fractional coordinates ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
P(1)	-113 (1)	5701 (1)	6411 (1)
S(1)	266 (2)	3979 (1)	6299 (1)
S(2)	-1481 (1)	6089 (1)	4623 (1)
S(3)	-1375 (2)	5676 (1)	7198 (2)
S(4)	1552 (1)	6605 (1)	6997 (1)
N(1)	-2193 (5)	9310 (4)	5539 (4)
N(2)	-4134 (4)	7815 (4)	5256 (4)
C(1)	-2512 (7)	10307 (5)	5027 (6)
C(2)	-1497 (7)	11113 (5)	5289 (7)
C(3)	-172 (7)	10872 (5)	6049 (6)
C(4)	143 (6)	9852 (5)	6571 (5)
C(5)	-921 (6)	9078 (5)	6276 (6)
C(6)	-4716 (6)	7161 (5)	4317 (5)
C(7)	-5725 (6)	6406 (5)	4263 (6)
C(8)	-6096 (6)	6367 (5)	5179 (7)
C(9)	-5483 (7)	7045 (6)	6130 (6)
C(10)	-4481 (6)	7768 (5)	6148 (6)

Table 2. Hydrogen-atom coordinates ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	-3482	10455	4442
H(2)	-1753	11872	4938
H(3)	572	11438	6216
H(4)	1104	9663	7149
H(5)	-701	8320	6635
H(6)	-4434	7216	3645
H(7)	-6161	5899	3565
H(8)	-6827	5835	5154
H(9)	-5755	7071	6810
H(10)	-4014	8268	6848
H(11)	-2923	8731	5372
H(12)	-3409	8355	5285

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33246 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Bond lengths (not corrected for libration) (Å)

P(1)-S(1)	2.129 (4)	P(1)-S(4)	1.946 (4)
P(1)-S(2)	2.132 (4)	S(1)-S(2)	2.059 (4)
P(1)-S(3)	1.966 (4)		
N(1)-C(1)	1.334 (10)	N(2)-C(6)	1.324 (9)
N(1)-C(5)	1.309 (9)	N(2)-C(10)	1.306 (10)
C(1)-C(2)	1.388 (11)	C(6)-C(7)	1.389 (10)
C(5)-C(4)	1.395 (10)	C(10)-C(9)	1.372 (11)
C(2)-C(3)	1.361 (11)	C(7)-C(8)	1.351 (11)
C(4)-C(3)	1.362 (11)	C(9)-C(8)	1.355 (11)

Table 4. Bond angles (°)

S(2)-P(1)-S(1)	102.2 (2)	P(1)-S(1)-S(2')	104.8 (2)
S(3)-P(1)-S(1)	101.9 (2)	P(1)-S(2)-S(1')	104.6 (2)
S(3)-P(1)-S(2)	101.9 (2)	S(4)-P(1)-S(1)	113.6 (2)
S(4)-P(1)-S(2)	112.6 (2)	S(4)-P(1)-S(3)	122.1 (2)
C(1)-N(1)-C(5)	120.5 (6)	C(6)-N(2)-C(10)	121.5 (6)
N(1)-C(1)-C(2)	120.0 (7)	N(2)-C(6)-C(7)	120.0 (7)
N(1)-C(5)-C(4)	122.2 (7)	N(2)-C(10)-C(9)	120.6 (7)
C(1)-C(2)-C(3)	119.6 (7)	C(6)-C(7)-C(8)	118.5 (7)
C(5)-C(4)-C(3)	117.8 (7)	C(10)-C(9)-C(8)	119.0 (7)
C(2)-C(3)-C(4)	119.9 (7)	C(7)-C(8)-C(9)	120.4 (7)

$P_2S_6Br_2$ (Einstein, Penfold & Tapsell, 1965) adopts a skew-boat conformation with S—S 2.03 Å, P—S—S 99.5 and 99.8°, and P—S—S—P 86°. Einstein *et al.* suggest that $P_2S_6Br_2$ does not adopt the chair conformation because this would lead to serious repulsions between ring and terminal atoms, or unacceptably small P—S—S—P and large P—S—S angles. In $[P_2S_8]^{2-}$ the shortest such S...S contacts are 3.78 and 3.80 Å although the ring geometry is close to that in S_6 .

The P(1)—S(4) bond [1.946 (4) Å] is significantly shorter than P(1)—S(3) [1.966 (4) Å], and the angles it subtends [113.6 (2), 112.6 (2) and 122.1 (2)°] are much larger than the other three valence angles at P

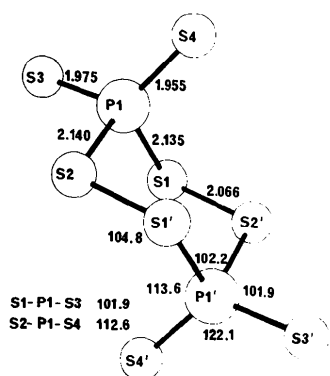


Fig. 1. The $[P_2S_8]^{2-}$ anion, showing angles (°) and librationaly corrected bond lengths (Å).

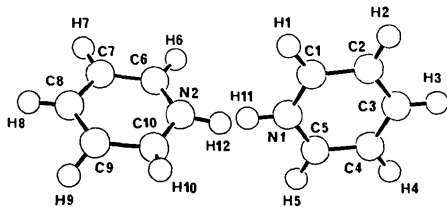


Fig. 2. The $[py_2H]^+$ cation, showing both positions for the disordered H atom.

[102.2 (2), 101.9 (2) and 101.9 (2)°]. This indicates that P(1)—S(4) has more double-bond character, and hence S(3) carries more of the negative charge than S(4). Since S(3) and S(3') are equatorial, this minimizes the repulsion between negatively charged atoms. The shortest H...S distances are clustered around 3.0–3.1 Å for all the S atoms, providing little evidence for C—H...S hydrogen bonding.

Although the overall cation geometry (Fig. 2), N...N distance [2.655 (7) Å] and difference electron density synthesis provide good evidence for an approximately linear but twofold-disordered hydrogen bond, the H coordinates should be regarded as tentative since a constrained refinement was necessary. The angle between the vectors C(8)...N(2) and C(3)...N(1) is 168.8°, and the angle between the planes of the two pyridine rings is 101.5°. Although several N—H...N hydrogen bonds have been reported, the only other cationic example appears to be a symmetrical but bent bond [N...N 2.63 Å, N—H—N 141 (12)°] bridging two dimethylamino groups in a substituted naphthalene (Truter & Vickery, 1972).

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