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Piperidinium Hydrogen Sulphide

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Abstract. $C_5H_{12}N^+HS^-$ is orthorhombic, space group *Pmab*, $a=9{\cdot}77$ (1), $b=7{\cdot}30$ (2), $c=9{\cdot}84$ (1) Å, $Z=4$, $D_x=1{\cdot}13$ g cm^{-3}. The structure consists of alternate $C_5H_{12}N^+$ and HS^- ions linked by short N-H···S hydrogen bonds to form infinite chains. The ring has a chair conformation with a crystallographic mirror plane through the S, N and C(3) atoms. Interatomic distances are: S···N 3·06; S···N′ 3·10; N–C(1) 1·49; C(1)–C(2) 1·49; C(2)–C(3) 1·49 Å.

Introduction. The crystals were obtained from the reaction of As_2S_3 with piperidine (in an attempt to prepare piperidinium thioarsenites); in order to compare the structure with that of $(C_5H_{12}N^+)_2As_4S_6^{2-}$ (Porter & Sheldrick, 1971) we have completed the structure determination.

Experimental. Intensities were determined with a Stoe Stadi-2 two-circle diffractometer, Mo *Kα* radiation, and two crystals of approximate dimensions 0·012 × 0·15 × 0·022 mm (layers *h*0*l* to *h*6*l*) and 0·013 × 0·16 × 0·024 mm (layers *hk*0 to *hk*5). The data from the second crystal were of poorer quality and were only used for the determination of inter-layer scale factors, not for structure refinement. 1302 reflexions were measured for the first crystal, of which 116 were rejected because the net count was less than 3*σ* based on counting statistics; averaging of equivalent reflexions led to 408 unique reflexions. The data were obtained in 'constant time' mode. Systematic absences were observed for *h*0*l* (*h* odd) and *hk*0 (*k* odd); thus possible space groups are *Pmab* and *P*2$_1$*ab*. The centrosymmetric *Pmab* was indicated by intensity statistics and confirmed by successful refinement of the structure. Consistent unit-cell dimensions were obtained from diffractometer measurements ($\lambda=0{\cdot}71069$ Å), and by least-squares analysis of $\sin^2\theta$ values from powder photographs taken with

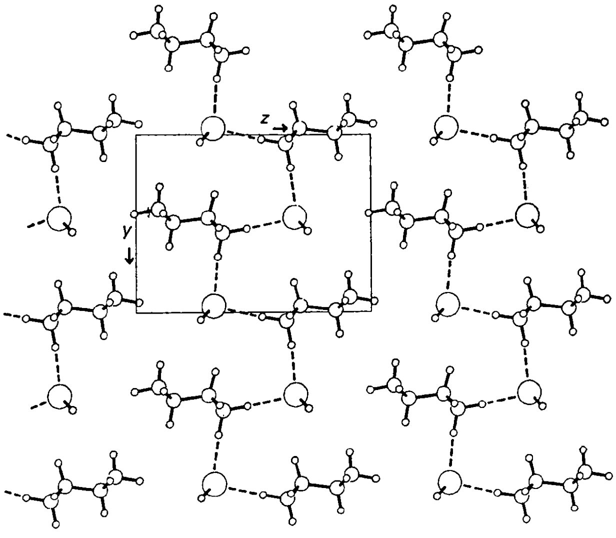

Fig. 1. Projection of one layer of the structure perpendicular to [100].

Table 1. *Fractional coordinates*

	10^4x	10^4y	10^4z
S	2500	9632 (3)	3269 (2)
N	2500	5472 (11)	3645 (7)
C(1)	3753 (7)	4641 (15)	3046 (7)
C(2)	3758 (10)	4901 (16)	1541 (9)
C(3)	2500	4140 (24)	905 (11)

Hydrogen coordinates and isotropic temperature factor:

	10^3x	10^3y	10^3z	10^2B
H(4)	250	685	345	6 (1) Å^2
H(4′)	250	528 (15)	467 (12)	6 (1)
H(1)	372 (7)	330 (15)	335 (7)	6 (1)
H(1′)	452 (9)	529 (12)	356 (8)	6 (1)
H(2)	459 (8)	438 (10)	107 (7)	6 (1)
H(2′)	383 (8)	623 (14)	135 (7)	6 (1)
H(3)	250	289 (19)	104 (11)	6 (1)
H(3′)	250	440	0	6 (1)

Table 2. *Anisotropic temperature factors* (Å^2 × 10^3)

The anisotropic temperature factor takes the form:

$$\exp\,[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*\\+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	55 (1)	54 (2)	45 (1)	1 (1)	0	0
N	54 (4)	72 (6)	44 (4)	−4 (3)	0	0
C(1)	49 (4)	104 (7)	73 (4)	17 (4)	7 (3)	9 (4)
C(2)	103 (7)	105 (8)	80 (5)	19 (5)	44 (5)	26 (6)
C(3)	194 (17)	101 (12)	42 (6)	−1 (6)	0	0

Table 3. *Bond lengths* (Å)

S——N′	3·098	C(1)–H(1′)	1·02 (9)
S——N	3·060	C(2)–H(2)	1·01 (8)
N——C(1)	1·488 (11)	C(2)–H(2′)	0·99 (10)
C(1)–C(2)	1·494 (14)	C(3)–H(3)	0·92 (14)
C(2)–C(3)	1·487 (16)		
		S——H(5)	1·37
S——H(4′)	2·08	S——H(4)	2·04
N——H(4′)	1·02 (12)	N——H(4)	1·02
C(1)–H(1)	1·03 (11)	C(3)–H(3′)	0·91

Table 4. *Bond angles* (°)

C(1)—N—C(1)	110·7 (10)	H(2′)–C(2)—H(2)	103 (7)
C(2)—C(1)–N	110·1 (7)	H(3)—C(3)—C(2)	108 (4)
C(3)—C(2)–C(1)	111·5 (9)	S—H(4″)–N′	175 (9)
C(2)—C(3)–C(2)	111·5 (14)		
H(4′)–N—C(1)	110 (3)	N—H(4)—S	174
H(1)–C(1)–N	104 (4)	H(4″)–S—H(5)	107
H(1′)–C(1)–N	103 (5)	H(4″)–S—H(4)	98
H(1)–C(1)–C(2)	114 (4)	H(4)—S—H(5)	117
H(1′)–C(1)–C(2)	115 (5)	H(3)′–C(3)–C(2)	109
H(1′)–C(1)–H(1)	109 (6)	H(5)—S—H(5′)	110
H(2)–C(2)–C(1)	114 (5)	H(4′)–N—H(4)	109
H(2′)–C(2)–C(1)	108 (5)	H(4)—N—C(1)	109
H(2)–C(2)–C(3)	109 (4)	H(3′)–C(3)—H(3)	110
H(2′)–C(2)–C(3)	110 (5)		

a Guinier focusing camera and silicon internal calibrant ($d = 5{\cdot}4306$ Å).

The structure was solved by multisolution application of the $\sum_2$ formula, and refined by full-matrix least-squares calculations with anisotropic temperature factors for the sulphur, nitrogen and carbon atoms. It was found possible to refine the coordinates of six of the hydrogen atoms; two further hydrogen atoms [H(4) and H(3′)] were fixed in geometrically calculated positions. An overall isotropic temperature factor was employed for the hydrogen atoms. It was not possible to locate the remaining hydrogen atom (bonded to sulphur) and it was omitted entirely. The final weighted residual $\bar{R}' = \sum w^{1/2}\Delta / \sum w^{1/2}F_o$ was 0·078, with a corresponding unweighted R of 0·075. The weighting scheme employed was $w = (4{\cdot}68 + |F_o| + 0{\cdot}0210|F_o|^2)^{-1}$. Neutral atom scattering factors were used (Cromer, 1965; Cromer & Waber, 1965). Final atomic coordinates are given in Table 1 and anisotropic temperature factors in Table 2. The full covariance matrix was used in estimating the standard deviations in the bond lengths (Table 3) and bond angles (Table 4).*

Discussion. The short N–H···S hydrogen bonds of 3·06 and 3·10 Å must be almost linear in order to preserve approximately tetrahedral angles at nitrogen. The angle N–H(4′)···S refined to 175 (9)°. Fig. 1 shows that the structure contains hydrogen-bonded chains similar to those in $(C_5H_{12}N^+)_2As_4S_6^{2-}$ (Porter & Sheldrick, 1971), where the N–H···S distances were found to be 3·18 and 3·24 Å. Most of the postulated N–H···S hydrogen bonds in molecular compounds fall in the range 3·35–3·5 Å, although shorter values have been found in 3-hydro-5-thiol-1,2,4-triazole (3·24 Å) and α-thiopyridone (3·26 Å) (Hossain & Carlisle, 1966).

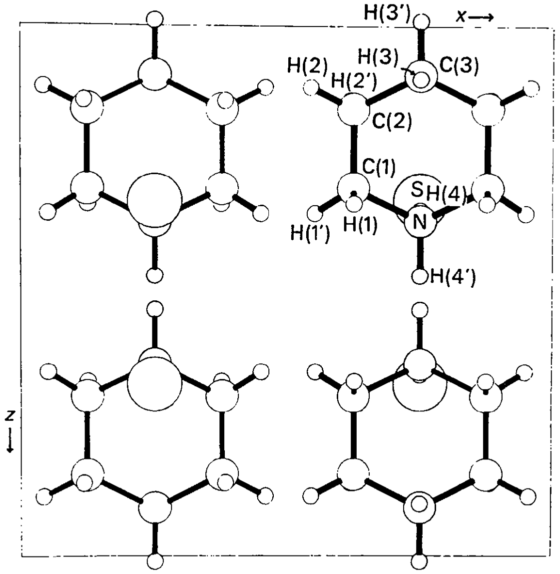

Fig. 2. Projection of the structure perpendicular to [010].

The ring has the expected chair conformation, but the thermal parameters and bond lengths involving the carbon and hydrogen atoms furthest from the nitrogen atom indicate that this end of the molecule is undergoing appreciable librational motion. There are few short intermolecular distances (Table 5). Fig. 2 shows a projection of the structure perpendicular to [010].

Table 5. *Non-bonded distances* (Å)

Within ring	
N—C(2)	2·44
N—C(3)	2·87
C(1)–C(1)	2·45
C(1)–C(2)	2·87
C(1)–C(3)	2·46
C(2)–C(2)	2·46

Intermolecular (less than 3·5 Å)

(*a*) related by a glide
S···H(1′) 2·93

(*b*) related by cell translation
S···H(1) 2·92

(*c*) related by **b** glide
S···H(3′) 3·22

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* A list of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30123. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.