Crystal Structure and Rotameric Form of Bis(piperidinothiocarbonyl)hexasulfane

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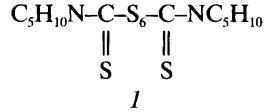
The title compound, $S_4(S_2CNC_5H_{10})_2$, crystallizes in the orthorhombic space group $Pna2_1$ (No. 33) with $a = 8.399(3)$, $b = 8.504(1)$, $c = 27.600(5)$ Å, and $Z = 4$. The crystal structure has been determined by X-ray methods and refined to $R = 0.039$ for 1464 observed reflections. The bond lengths along the C–S_6–C chain are C–S 1.803(8), S–S 2.016(3), 2.045(3), 2.040(2), 2.045(3) and 2.011(3), and S–C 1.822(8) Å; the bond angles at sulfur are 104.8(3), 107.3(1), 106.5(1), 106.6(1), 107.4(1) and 104.9(3)°. The torsion angles at the S–S bonds are 81.8, 93.4, −96.4, 92.3 and 82.4°. The rotameric form is *trans-cis–cis-trans*, corresponding to an opened S_6 ring with the terminal groups attached in outward positions.

The crystal structures of various acyclic tetrasulfanes have been reported.[1,2] A pentasulfane bridge occurs in $S_{19}(AsF_6)_2$,[3] where S_{19}^{2+} is X–S_5–X with X = cyclic S_7^+. We report here the structure of an acyclic hexasulfane, the bis(piperidinothiocarbonyl) derivative *1*. The structures of the mono-[4] and disulfane[5] are known.



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The hexasulfane was first prepared by Levi[6] in 1931, from S_2Cl_2 or SCl_2 and piperidinocarbodithioate salts. It is easily formed from the disulfane and sulfur,[7] or, together with the disulfane, from bis(piperidino)sulfane or -disulfane and CS_2.[8] We obtained it from bis(piperidino)tetrasulfane[9] and CS_2:

$$S_4(NC_5H_{10})_2 + 2\,CS_2 = S_4(S_2CNC_5H_{10})_2.$$

The analogous reaction with $Se_4(NC_5H_{10})_2$ gave Se_8 and $Se(S_2CNC_5H_{10})_2$.[10]

Experimental

The compound *1* crystallized from $CHCl_3$–EtOH as very thin, long prisms. Thicker, well-formed prisms were obtained on slow evaporation of a CS_2 solution over several d. The prisms were extended along the *a* axis and bounded by {001}, {00$\bar{1}$}, {011} and {01$\bar{1}$}. The crystal used measured 0.24×0.13×0.06 mm along the axes.

Unit cell dimensions were determined and intensity data recorded on a CAD4 diffractometer, using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71069 Å). Data collection parameters were: ω-scan mode; scan width 1.00+0.35 tanθ, plus 25 % on each side for background; scan rate 6.7–1.0° min^{-1}, θ_{max} = 28°. The intensities were corrected for Lorentz and polarization effects, decay (max 4 %) and absorption (transmission factors 0.90–0.95). Out of 2419 unique reflections, 1464 had $I > 2\sigma(I)$ and were used in the calculations. These were carried out using the Enraf-Nonius SDP programs. Atomic scattering factors, including anomalous dispersion terms, were from Ref. 11. Refinement was by full matrix least-squares, the sum minimized being $\Sigma w\Delta^2(F)$ with $w^{-1} = \sigma^2(F) = \sigma^2(I)/4LpI$, and $\sigma^2(I) = \sigma^2(I)_{count} + (0.02I)^2$.

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Table 1. Atomic coordinates for $S_4(S_2CNC_5H_{10})_2$ with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
S(1)	0.41930(28)	0.29660(20)	0[a]	4.56(4)
S(2)	0.50437(25)	0.50774(23)	0.02079(7)	4.38(4)
S(3)	0.31814(24)	0.66249(20)	0.01936(6)	4.08(4)
S(4)	0.22495(24)	0.66553(19)	0.08762(6)	4.04(4)
S(5)	0.03670(23)	0.51308(23)	0.08739(7)	4.48(4)
S(6)	0.11915(29)	0.30176(20)	0.10830(6)	4.50(4)
S(7)	0.43877(26)	0.47316(22)	−0.09449(7)	4.54(4)
S(8)	0.10239(25)	0.47786(21)	0.20275(7)	4.39(4)
N(1)	0.3875(8)	0.1660(6)	−0.08550(18)	4.3(1)
N(2)	0.1520(8)	0.1723(6)	0.19343(19)	4.5(1)
C(1)	0.4159(9)	0.3046(7)	−0.06526(22)	3.7(1)
C(2)	0.3840(10)	0.0154(8)	−0.06017(25)	4.7(2)
C(3)	0.5074(10)	−0.0940(8)	−0.07980(27)	4.7(2)
C(4)	0.4894(12)	−0.1170(10)	−0.13292(28)	6.0(2)
C(5)	0.4926(11)	0.0410(10)	−0.15812(25)	5.1(2)
C(6)	0.3651(11)	0.1473(19)	−0.3778(25)	5.5(2)
C(7)	0.1235(9)	0.3107(7)	0.17426(22)	3.6(1)
C(8)	0.1612(10)	0.0189(8)	0.16757(24)	4.5(2)
C(9)	0.0374(11)	−0.0910(8)	0.18665(27)	5.0(2)
C(10)	0.0525(12)	−0.1125(9)	0.24101(29)	5.9(2)
C(11)	0.0527(11)	0.0447(9)	0.26689(26)	5.5(2)
C(12)	0.1720(11)	0.1523(8)	0.24631(23)	4.9(2)

[a]Fixed coordinate.

Crystal data. $S_4(S_2CNC_5H_{10})_2$, $C_{12}H_{20}N_2S_8$, M = 448.82; orthorhombic, a = 8.399(3), b = 8.504 (1), c = 27.600(5) Å; V = 1971.4(1.4) Å^3, Z = 4, D_x = 1.512 g cm^{-3}; $F(000)$ = 936, μ(Mo$K\alpha$) = 8.66 cm^{-1}, space group $Pna2_1$ (No. 33) from systematic absences and structure refinement.

The structure was solved by direct (MULTAN) and Fourier difference methods. The hydrogen atoms were placed geometrically such that C–H = 0.95 Å. They were assigned a common, fixed B_{iso} and were held fixed. With anisotropic thermal parameters for the other atoms, refinement converged at R = 0.039, R_w = 0.048, S = 1.255. Parameter shifts in the last cycle were less than one percent of the e.s.d.'s. The highest peak in the final difference Fourier map was 0.32 e Å^{-3}. Atomic coordinates for non-hydrogen atoms are listed in Table 1. Thermal parameters, complete bond distances and angles, hydrogen coordinates, torsion angles and planes have been deposited with the Cambridge Crystallographic Data Centre.

There is a pronounced pseudo-symmetry in the structure, approaching the symmetry of the centrosymmetric space group *Pnab* (alt. *Pbcn*, No. 60). There is a pseudo-molecular two-fold axis parallel to the *b* crystal axis at x = 0.27 (see Table 1). The intensity distribution was centrosymmetric, but out of 46 recorded $hk0$ reflections with k odd, 27 had $I > 2\sigma(I)$, although none were strong. The pseudo-symmetry led to correlations between the y coordinates and, particularly, the z coordinates of atoms in the two halves of the molecule, and between the associated β_{22}, β_{33}, and β_{23} thermal parameters; the highest correlation coefficients were 0.806, 0.840, and 0.809 for z of S(2) and S(5), S(3) and S(4), and S(7) and S(8), respectively.

The structure presented here gave slightly (although not significantly) better agreement indexes than the inverted structure.

Results and discussion

Dimensional data are given in Table 2, and a view of the molecule is shown in Fig. 1.

Rotameric form. The torsion angles along the

Table 2. Distances (Å) and angles (°) in $S_4(S_2CNC_5H_{10})_2$ with e.s.d.'s in parentheses.

(*a*) Bond distances[a]			
S(1)–S(2)	2.016(3)	S(5)–S(6)	2.011(3)
S(2)–S(3)	2.045(3)	S(4)–S(5)	2.045(3)
	S(3)–S(4)	2.040(2)	
S(1)–C(1)	1.803(8)	S(6)–C(7)	1.822(8)
C(1)–S(7)	1.656(8)	C(7)–S(8)	1.634(8)
C(1)–N(1)	1.326(10)	C(7)–N(2)	1.312(9)
N(1)–C(2)	1.459(10)	N(2)–C(8)	1.489(10)
N(1)–C(6)	1.464(10)	N(2)–C(12)	1.479(10)
(*b*) Bond angles[a]			
C(1)–S(1)–S(2)	104.8(3)	C(7)–S(6)–S(5)	104.9(3)
S(1)–S(2)–S(3)	107.3(1)	S(4)–S(5)–S(6)	107.4(1)
S(2)–S(3)–S(4)	106.5(1)	S(3)–S(4)–S(5)	106.6(1)
S(1)–C(1)–S(7)	121.2(5)	S(6)–C(7)–S(8)	121.0(5)
S(1)–C(1)–N(1)	113.0(6)	S(6)–C(7)–N(2)	111.7(6)
S(7)–C(1)–N(1)	125.8(7)	S(8)–C(7)–N(2)	127.3(7)
C(1)–N(1)–C(2)	125.6(7)	C(7)–N(2)–C(8)	127.0(7)
C(1)–N(1)–C(6)	122.3(8)	C(7)–N(2)–C(12)	121.4(7)
C(2)–N(1)–C(6)	112.0(7)	C(8)–N(2)–C(12)	111.5(7)
(*c*) Torsion angles			
C(1)S(1)S(2)S(3)	81.8	S(4)S(5)S(6)C(7)	82.4
S(1)S(2)S(3)S(4)	93.4	S(3)S(4)S(5)S(6)	92.3
	S(2)S(3)S(4)S(5)	−96.4	
S(2)S(1)C(1)S(7)	−12.9	S(5)S(6)C(7)S(8)	−12.6
S(2)S(1)C(1)N(1)	169.6	S(5)S(6)C(7)N(2)	170.3
(*d*) Intramolecular non-bonded distances			
S(1)···C(2)	2.926(8)	S(6)···C(8)	2.930(8)
S(7)···C(6)	3.080(10)	S(8)···C(12)	3.074(9)
S(7)···S(2)	3.242(3)	S(8)···S(5)	3.245(3)

[a]In the piperidino groups: C–C 1.471(13)–1.517(13), mean 1.500(6) Å; N–C–C and C–C–C 109.5(8)–112.1(8), mean 110.8(3)°.

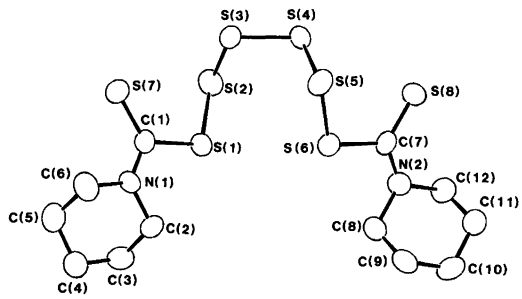

Fig. 1. The bis(piperidinothiocarbonyl)hexasulfane molecule, as seen normal to the *b* crystal axis.

eight-membered C–S_6–C chain are 81.8–96.4° and are in the normal range. The signs of the angles, ++−++, or −−+−− for the enantiomorph which is also present in the unit cell, are those of the *trans-cis–cis-trans* rotamer. This form may be regarded as arising from an opened S_6 ring, with terminal groups attached in outward, *trans* positions (Fig. 1). The S(1)···S(6) distance, 3.911(2) Å, is shorter than the S(2)···S(5) distance of 4.337(3) Å.

Octaatomic sequences with this rotameric form occur in the α-S_{18} and S_{20} rings of elemental sulfur;[12] there are four such sequences in each ring.

The *trans-cis–cis-trans* conformation in the crystalline state renders the hexasulfane molecule

more compact, although the largest intramolecular distance between non-hydrogen atoms, C(5)···C(11), is still 12.30(1) Å. It may be noted that transformation of this form to the extended all-*trans* form, or vice versa, involves only a rotation of ca. 180° around the central S(3)–S(4) bond.

The sulfur-sulfur bonds. The terminal bonds, S(1)–S(2) 2.016(3) and S(5)–S(6) 2.011(3) Å, are relatively short. In the disulfane, $(S_2CNC_5H_{10})_2$, the S–S distance is 1.995(1) Å;[5] in the latter, both disulfane sulfur atoms are bonded to a planar sp^2 carbon atom and the conformation is equatorial: The carbon plane makes an angle close to zero with the C–S–S plane, so that the carbon $p\pi$ orbital and the sulfur p lone-pair are parallel or nearly so; this leads to short S–S bonds.[13] In the hexasulfane, the conformation at the terminal groups is also equatorial: The interplanar angles (Table 3) are 11.7° at C(1) and 11.2° at C(7); however, only one of the sulfur atoms of each terminal S–S bond is attached to equatorial sp^2 carbon, and so the bonds are a little longer.

The three middle S–S distances, 2.045(3), 2.040(2) and 2.045(3) Å, are close to the distance, 2.057(11) Å, given by Donohue[14] as the "natural" value for the S–S bond in chains of sulfur atoms.

The terminal groups. The small deviations from planarity of the thiocarbonyl carbon atoms and the amino nitrogen atoms [see planes (2), (5) and (3), (6) of Table 3] may not be significant. However, the twists of the nitrogen planes relative to the carbon planes, ca. 5°, appear to be real.

The piperidino groups adopt the chair conformation. The magnitudes of the torsion angles at the N–C and C–C bonds of the rings (excluding hydrogen) are in the range 52.2–58.1°, with a mean of 56.0°.

Table 3. Some least-squares planes. The equation of the plane is $PX + QY + RZ = S$ where X, Y, Z are the coordinates in Å. Deviations (Å) of atoms from the plane are given in square brackets.

Plane (1): C(1), S(1), S(2)			
P	*Q*	*R*	*S*
0.9319	−0.3617	−0.0284	2.3694
Plane (2): S(1), C(1), S(7), N(1)			
0.9857	−0.1652	−0.0329	3.0591
[S(1) −0.004(2), C(1)		0.016(7), S(7)	−0.005(2),
N(1) −0.006(6), C(2)		0.153(8), C(6)	−0.118(9)]
Plane (3): C(1), N(1), C(2), C(6)			
0.9845	−0.1144	−0.1327	3.3749
[C(1) 0.007(7), N(1)		−0.019(6), C(2)	0.006(8),
C(6) 0.006(9), S(1)		−0.196(2), S(7)	0.139(2)]
Plane (4): S(5), S(6), C(7)			
0.9361	0.3500	−0.0334	1.7353
Plane (5): S(6), C(7), S(8), N(2)			
0.9861	0.1618	−0.0391	1.2803
[S(6) 0.005(2), C(7)		−0.018(7), S(8)	0.006(2),
N(2) 0.007(7), C(8)		−0.100(8), C(12)	0.087(9)]
Plane (6): C(7), N(2), C(8), C(12)			
0.9849	0.1336	−0.1104	0.8493
[C(7) −0.006(7), N(2)		0.015(7), C(8)	−0.005(8),
C(12) −0.004(9), S(6)		0.149(2), S(8)	−0.077(2)]
Angles (°) between planes:			
(1)–(2)	11.7	(4)–(5)	11.2
(2)–(3)	6.4	(5)–(6)	4.4

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