

the following: the more stable molecular geometry could be developed in the low-melting *A*, while the less stable conformer is located in somewhat greater space per molecule in the high-melting stable *B*. Since the irreversible dimorphism could not be attributed to any hydrogen bonding, other types of close contacts were surveyed for both structures. *A* exhibits among the close contacts three H...H distances of 1.96, 1.98 and 2.12 Å (Figs. 4 and 5) which are considerably shorter than the sum of the van der Waals radii (2.4 Å). No such close contacts exist in *B*.

To summarize, we succeeded in determining the crystal structure of *A* and comparing it with that of *B*, but we found no marked difference which can account for the irreversible *A* → *B* phase transition. Nevertheless, our work may shed light on the strange realm of di- or polymorphism of crystals discussed by Woodard & McCrone (1975), e.g. D-mannitol (Kim, Jeffrey & Rosenstein, 1968).

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1,3-Diamino-4,7-methano-3a,4,5,6,7,7a-hexahydro-1 λ^4 ,3 λ^4 ,2-benzodithiazolium Chloride* [C₇H₁₄N₃S₂]Cl, a Derivative of a New C₂NS₂ Cationic Ring System

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Abstract

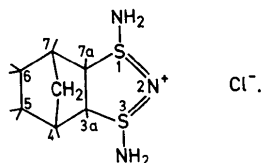
Trithiazyl trichloride [trichlorocyclotrithiazatriazene (NSCl)₃] reacts with norbornene to give a mixture of products, aqueous hydrolysis of which provides the

novel dithiazolium compound C₇H₁₄N₃S₂⁺.Cl⁻, *M_r* = 239.78, tetragonal, *P*4₂/*ncm*, *a* = 11.506 (1), *c* = 16.414 (2) Å, *V* = 2173 Å³, *Z* = 8, *D_c* = 1.47 Mg m⁻³. The final *R* = 0.030 for 96 parameters and 653 reflexions [*I* > 3σ(*I*)]. The S–N distances are all 1.662 (3) Å, and SNS = 115.7 (4) and NSN = 115.9 (3)°, indicating the presence of a delocalized NSNSN cation chain. The structure and mechanism of formation are discussed.

* Alternative name: 3,5-Diamino-3 λ^4 ,5 λ^4 -dithia-4-azoniatricyclo[5.2.1.0^{2,6}]deca-3,4-diene chloride.

Introduction

The discovery of the superconductivity (0.27 K) and other metallic properties of poly(sulphur nitride), (SN)_x (see review by Labes, Love & Nichols, 1979), has stimulated renewed interest in the structures and properties of delocalized sulphur–nitrogen compounds. The title compound is of such a type; one canonical form, from which it is named, is



A mixture of trithiazyl trichloride, (NSCl)₃ (Jolly & Maguire, 1967), and excess norbornene (1:6 molar ratio) in dioxane solution [100 ml solvent g⁻¹ (NSCl)₃] was stirred (2 h) at room temperature and filtered to give a waxy green-yellow solid and repulsive-smelling red filtrate: the latter was discarded. The solid was dissolved in water and the solution filtered (a small amount of oily residue was discarded). After evaporation of the filtrate to dryness, the white solid [yield ~10% based on (NSCl)₃] was recrystallized twice from chloroform; slow cooling gave white needles. The crystals rapidly lost chloroform of crystallization and became powders. Recrystallization from aqueous solution gave colourless plates.

Single crystals were obtained from aqueous solution. A crystal 0.52 × 0.29 × 0.07 mm was mounted on a Picker FACS-1 diffractometer. Cell dimensions were obtained from the setting angles of 15 reflexions

Table 1. Fractional atomic coordinates ($\times 10^4$, for H $\times 10^3$) relative to the origin at 2/m, and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{iso}^*
S	4348 (1)	8965 (1)	6872 (1)	38
Cl(1)	7500 (0)	7500 (0)	6127 (1)	45
Cl(2)	2500 (0)	7500 (0)	5000 (0)	38
N(1)	4699 (2)	10301 (0)	6675 (3)	44
N(2)	4711 (3)	8015 (3)	6187 (2)	48
C(1)	5416 (3)	8638 (3)	7669 (2)	30
C(2)	4887 (3)	8741 (3)	8521 (2)	38
C(3)	5779 (3)	8276 (3)	9123 (2)	51
C(4)	4955 (3)	10045 (0)	8680 (3)	38
H(1)	568 (2)	794 (2)	753 (2)	18 (7)
H(2)	419 (3)	841 (3)	860 (2)	52 (11)
H(31)	544 (3)	821 (3)	966 (2)	54 (10)
H(32)	608 (3)	756 (3)	894 (2)	50 (10)
H(41)	452 (3)	1048 (0)	835 (2)	18 (11)
H(42)	481 (2)	1019 (0)	924 (3)	26 (11)
H(5)	540 (3)	794 (4)	610 (3)	73 (15)
H(6)	419 (3)	797 (3)	582 (2)	62 (13)

* For atoms other than H $U_{\text{iso}} = (U_1 \cdot U_2 \cdot U_3)^{2/3}$ where U_1 , U_2 and U_3 are the r.m.s. amplitudes of vibration along the principal axes of the U_{ij} .

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Numbering is as in Fig. 1. Atoms with superscript i are related to those at x,y,z by 1.5 - y, 1.5 - x, z.

S-N(1)	1.622 (2)	C(1)-H(1)	0.89 (3)
S-N(2)	1.622 (4)	C(2)-H(2)	0.89 (4)
S-C(1)	1.834 (3)	C(3)-H(31)	0.97 (3)
C(1 ¹)-C(1)	1.540 (6)	C(3)-H(32)	0.94 (3)
C(1)-C(2)	1.530 (5)	C(4)-H(41)	0.89 (4)
C(2)-C(3)	1.522 (5)	C(4)-H(42)	0.95 (4)
C(2)-C(4)	1.525 (5)	N(2)-H(5)	0.81 (4)
C(3 ¹)-C(3)	1.538 (8)	N(2)-H(6)	0.85 (3)
Cl(1)-N(2)	3.265 (4)	Cl(1)-H(5)	2.47 (4)
Cl(1)-N(2)	3.259 (4)	Cl(2)-H(6)	2.43 (3)
N(1)-S-N(2)	115.9 (2)	C(1)-C(2)-H(2)	117 (2)
N(1)-S-C(1)	99.7 (2)	C(3)-C(2)-H(2)	112 (2)
N(2)-S-C(1)	100.6 (2)	C(4)-C(2)-H(2)	116 (2)
S-N(1)-S ¹	115.7 (2)	C(2)-C(3)-H(31)	111 (2)
S-C(1)-C(1 ¹)	109.2 (1)	C(2)-C(3)-H(32)	110 (2)
S-C(1)-C(2)	111.7 (2)	C(3 ¹)-C(3)-H(31)	110 (2)
C(1 ¹)-C(1)-C(2)	103.1 (2)	C(3 ¹)-C(3)-H(32)	111 (2)
C(1)-C(2)-C(3)	107.4 (3)	H(21)-C(3)-H(32)	112 (3)
C(1)-C(2)-C(4)	102.2 (3)	C(2)-C(4)-H(41)	115 (2)
C(3)-C(2)-C(4)	101.6 (4)	C(2)-C(4)-H(42)	109 (2)
C(2)-C(3)-C(3 ¹)	103.2 (2)	H(41)-C(4)-H(42)	113 (4)
C(2)-C(4)-C(2 ¹)	94.1 (4)	S-N(2)-H(5)	117 (3)
S-C(1)-H(1)	104 (2)	S-N(2)-H(6)	110 (3)
C(1 ¹)-C(1)-H(1)	113 (2)	H(5)-N(2)-H(6)	124 (4)
C(2)-C(1)-H(1)	116 (2)	Cl(1)-H(5)-N(2)	167 (4)
		Cl(2)-H(6)-N(2)	167 (3)

measured with Cu $K\alpha$ radiation. Intensities were measured out to $2\theta = 48^\circ$ with monochromated Mo $K\alpha$ radiation. Data were collected with the ω - 2θ step-scanning technique. The step length was 0.04° and the scan width $(3.0 + 0.0692 \tan \theta)^\circ$. Each step was counted for 1 s. 927 independent reflexions were measured, of which 653 had $I > 3\sigma(I)$ according to counting statistics. No absorption correction was made.

The structure was determined with MULTAN (Germain, Main & Woolfson, 1971). Least-squares refinement (LINUS, Coppens & Hamilton, 1970) of a scale factor, atomic coordinates, and anisotropic thermal parameters for the non-hydrogen atoms, isotropic for H, gave $R = 0.030$ and $R_w = 0.036$. Positions of the H atoms were obtained from a difference map. An isotropic extinction parameter, g , was also refined assuming t to be unity. The value for g was 2.2×10^{-6} , giving a minimum value for $F_o/F_o(\text{corrected})$ of 0.70. The weighting scheme was $w = \{[\sigma(F_o^2) + 1.02F_o^2]^{1/2} - F_o\}^{-2}$. Scattering factors were those of Cromer & Mann (1968) for S, N, and C, and of Stewart, Davidson & Simpson (1965) for H.

Atomic coordinates are given in Table 1,* bond lengths and angles in Table 2.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35647 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

