SHORT STRUCTURAL PAPERS

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Acta Cryst. (1977). B**33**, 2264–2266

A Refinement of Dicyanotrisulfane at 100 K

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(*Received* 22 *November* 1976; *accepted* 17 *January* 1977)

Abstract. NCS_3CN, orthorhombic, $Pnma$, $Z = 4$, $a =$ 10·060 (2), $b =$ 12·715 (2), $c =$ 4·240 (1) Å, $V =$ 542·3 (2) Å^3 at 100 K. Single-crystal diffractometer data up to $\sin\theta/\lambda =$ 0·87 Å^{-1}, Nb-filtered Mo $K\alpha$ radiation, $\lambda =$ 0·71069 Å, $\mu =$ 11·67 cm^{-1}. The structure has been refined separately for all reflections and for high-order reflections only. The geometry of the bonded thiocyanate group differs considerably from that of a thiocyanate ion. The intermolecular bonding consists of three S···N van der Waals interactions.

Introduction. The title compound was prepared as described by Féher & Weber (1958). Yellow plates were formed on cooling a solution in hot chloroform. A crystal with dimensions 0·21 × 0·36 × 0·57 mm was sealed in a glass capillary and kept at 100 K in a flow of cold nitrogen gas.

Data in one octant of reciprocal space were collected on a Picker FACS-I diffractometer up to $\sin\theta/\lambda =$ 0·87 Å^{-1}, yielding 1238 independent reflections with $F_o^2 > 0$. At this point the data collection had to be terminated as the crystal broke. The step-scan data were analysed with the profile analysis of Blessing, Coppens & Becker (1974). Three standard reflections, recorded every 40 reflections, showed a maximum fluctuation of about 3%, mainly as a result of ice forming. The data were rescaled with respect to these standards and corrected for absorption. The linear absorption coefficient $\mu =$ 11·67 cm^{-1}; the transmission factor ranged from 0·64 to 0·79.

A weighting scheme, $w(F^2) = [\sigma(F^2)_{\text{counting}} + 0{\cdot}03F^2]^{-2}$, was used in the structure refinement.

Initial positional parameters for the atoms were taken from the room-temperature study of Féher & Linke (1964). Atomic scattering factors were as listed in *International Tables for X-ray Crystallography* (1974). For the S atoms the anomalous-dispersion factors of Cromer & Liberman (1970) were applied. Extinction was found to be negligible. A refinement for all reflections (conventional refinement) resulted in $R(F) =$ 3·4%, $R_w(F) =$ 4·0%, and a goodness-of-fit S† = 1·46.

A refinement for the 757 reflections with $\sin\theta/\lambda >$ 0·60 Å^{-1} (high-order refinement) resulted in $R(F) =$ 4·4%, $R_w(F) =$ 4·2% and a goodness-of-fit $S =$ 1·19.‡

Table 1. *Positional parameters*

Conventional refinement

	x	y	z
S(1)	0·52003 (4)	0·25	0·48647 (10)
S(2)	0·43631 (3)	0·12073 (2)	0·26715 (7)
C	0·29410 (13)	0·11045 (9)	0·48149 (29)
N	0·19564 (11)	0·10122 (10)	0·61884 (30)

High-order refinement

	x	y	z
S(1)	0·52000 (5)	0·25	0·48633 (12)
S(2)	0·43630 (4)	0·12072 (3)	0·26727 (9)
C	0·29433 (15)	0·11028 (11)	0·48156 (37)
N	0·19532 (17)	0·10133 (14)	0·61957 (43)

Table 2. *Bond lengths* (Å) *and angles* (°)

	Conventional refinement	High-order refinement	High-order refinement corrected for libration
S(1)–S(2)	2·068 (1)	2·067 (1)	2·071 (1)
S(2)–C	1·700 (1)	1·698 (2)	1·701 (2)
C–N	1·155 (2)	1·161 (2)	1·163 (2)
S(2)–S(1)–S(2)′	105·30 (3)	105·34 (3)	
S(1)–S(2)–C	99·42 (4)	99·47 (6)	
S(2)–C–N	177·62 (12)	177·69 (16)	

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† Defined as $S = [\Sigma\, w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$, with NO the number of observations and NV the number of variables.

‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32439 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

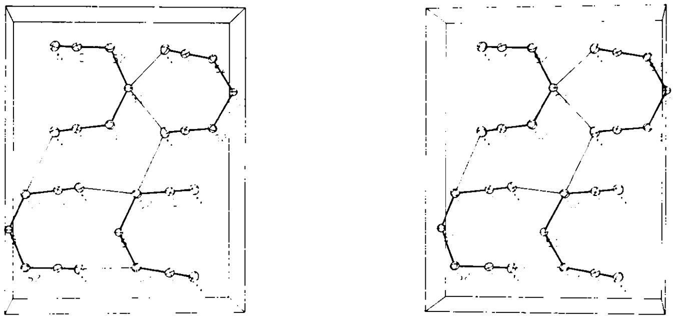

Fig. 1. Stereoscopic view of the structure. The thermal ellipsoids are the 50% probability surfaces.

The atomic coordinates are reported in Table 1, the bond lengths and angles in Table 2. The bond lengths in the last column of Table 2 have been corrected for librational shortening, wth the **TLS** method of Schomaker & Trueblood (1968).

Discussion. The structure of dicyanotrisulfane has been determined at room temperature from two-dimensional data by Fèher & Linke (1964). The accuracy of that work was limited. An accurate knowledge of the geometry of the $S_3(CN)_2$ molecule would be of interest in the framework of a study of sulfur-containing compounds. Therefore, the present refinement at low-temperature was undertaken.

The geometry of the thiocyanate group in the $S_3(CN)_2$ molecule [r_{CN} = 1·163 (2) Å, r_{CS} = 1·701 (2) Å] differs considerably from that of the thiocyanate ion in NaSCN and NH_4SCN [r_{CN} = 1·177 (1) Å, r_{CS} = 1·648 (1) Å], reported by Bats, Coppens & Kvick (1977) and Bats & Coppens (1977). The amount of π bonding in the CS bond is obviously smaller in the S-bonded thiocyanate group than in the thiocyanate ion. The S—S bond length in the title compound [2·071 (1) Å] is somewhat longer than that of 2·050 (2) Å observed in *cyclo*-octasulfur (Coppens, Yang, Blessing, Cooper & Larsen, 1977), which may be because of a different amount of double-bond character.

Table 3. *Non-bonded interactions*

$S(1)\cdots N^{i,ii}$	3·078 (2)	$S(2)–S(1)–N^{i}$	89·4 (1)
		$S(2)–S(1)–N^{ii}$	164·9 (1)
		$N^{i}–S(1)–N^{ii}$	75·8 (2)
$S(2)\cdots N^{iii}$	3·089 (2)	$S(1)–S(2)–N^{iii}$	87·6 (1)
$S(2)\cdots N^{iv}$	3·181 (2)	$S(1)–S(2)–N^{iv}$	164·5 (1)
		$C–S(2)–N^{iii}$	170·9 (2)
		$C–S(2)–N^{iv}$	71·7 (2)
		$N^{iii}–S(2)–N^{iv}$	100·1 (2)

Symmetry code

(i)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$1\frac{1}{2}-z$
(ii)	$\frac{1}{2}+x$,	y,	$1\frac{1}{2}-z$
(iii)	$\frac{1}{2}+x$,	y,	$\frac{1}{2}-z$
(iv)	$\frac{1}{2}-x$,	$-y$,	$-\frac{1}{2}+z$

A stereoscopic view of the structure is shown in Fig. 1. The intermolecular bonding consists of three van der Waals interactions between S and N atoms (Table 3 and Fig. 1). The S···N contacts range from 3·08 to 3·18 Å, *i.e.* less than 3·35 Å, the sum of the van der Waals radii. Similar interactions between S and a number of electronegative atoms are often found in crystal structures (Hordvik, 1970).

The positional parameters of the S atoms are identical in the conventional and high-order refinements. The positions of the C and N atoms found in the conventional refinement are displaced by 0·0032 (15) and

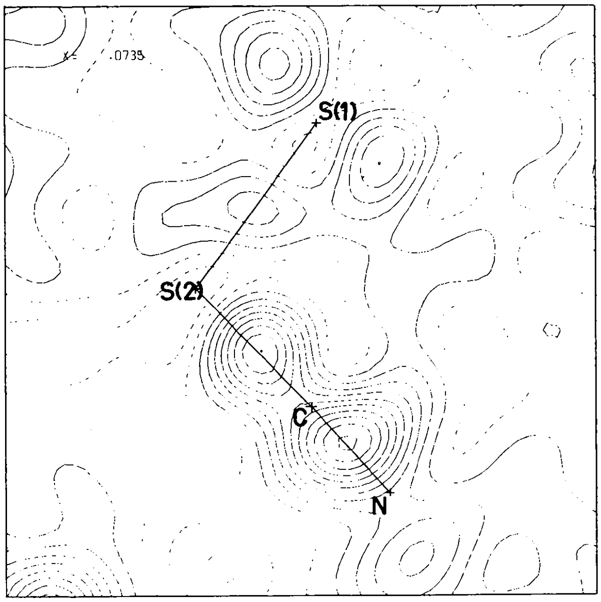

Fig. 2. Difference Fourier synthesis in a section containing the SSCN group, based on parameters from the high-order X-ray refinement. Fourier syntheses with sin $\theta/\lambda \leq$ 0·50 $Å^{-1}$. Contour interval 0·05 e $Å^{-3}$; negative contours broken.

0·0047 (17) Å respectively into the triple CN bond, when compared with the high-order refinement. This effect is generally observed in refinements of X-ray data (Coppens, 1974; Bats, 1976), and results from the aspherical distribution of the bonding electrons. As the structure is refined with a spherical atom model, the reported standard deviations in the atomic parameters do not contain these asphericity effects and are consequently underestimated.

Fig. 2 shows a difference Fourier synthesis in the plane containing the SSCN group, based on the low-order reflections and the high-order atomic parameters. The data cut-off in this difference Fourier synthesis has deliberately been taken low, in order to reduce the noise level. Although quantitative electron density studies require data of greater accuracy than in the present study, residuals due to the aspherical bonding density are apparent in Fig. 2.

Support of this work by the National Science Foundation is gratefully acknowledged.

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Acta Cryst. (1977). **B33**, 2266–2269

6-*endo*-Hydroxy-3-*endo*-aminomethylbicyclo[2.2.1]heptane-2-*endo*-carboxylic Acid Lactam*†

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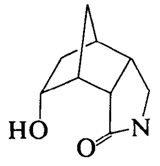
(*Received* 9 *December* 1976; *accepted* 31 *January* 1977)

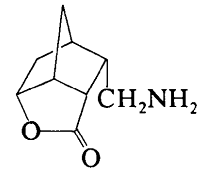
Abstract. $C_9H_{13}NO_2$, monoclinic, $P2_1/c$, 23°C, a = 10·870 (3), b = 7·403 (2), c = 10·721 (4) Å, β = 107·46 (2)°, Z = 4, D_x = 1·350 (2), D_m = 1·35 (1) g cm^{-3}. For 1169 reflections with $I > \sigma$, R = 0·055 and R_w = 0·051. The O(hydroxyl)–C(carbonyl) distance is 2·832 Å, two H atoms are 2·00 Å from each other, and these distances would be even shorter except for distortion of some of the bond angles. Hydrogen bonds from the hydroxyl and amide groups to the carbonyl O atom link the molecules into chains.

Introduction. To explore effects of orientation on rates of chemical reactions analogous to those catalyzed by enzymes, Koshland and co-workers have measured intramolecular reaction rates for norbornane molecules substituted with a variety of functional groups (Storm & Koshland, 1972). The title compound, a hydroxylactam, was synthesized by Hackney (1975) to serve, in its base-catalyzed rearrangement to an aminolactone, as a model for the rate-determining step in the hydrolysis of amides by chymotrypsin.

We determined the crystal structure of this lactam as part of a program to establish the geometry of



hydroxylactam



aminolactone

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* Structures of Bicyclo[2.2.1] Systems. IV.

† Work done in part with support from the US Energy Research and Development Administration.

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