

Crystal Structures of *N,N,N',N'*-Bis(tetramethylene)thiuram Disulfide and Tetramethylthiuram Disulfide

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Both compounds crystallize with four molecules in a monoclinic unit cell with dimensions 1: $[S_2CN(CH_2)_4]_2$, $a=9.432(1)$ Å, $b=10.432(1)$ Å, $c=13.851(1)$ Å, $\beta=97.08(1)^\circ$, $V=1353(1)$ Å³, 2: $[S_2CN(CH_3)_2]_2$, $a=9.672(1)$ Å, $b=9.931(2)$ Å, $c=11.882(8)$ Å, $\beta=99.43(3)^\circ$, $V=1120(5)$ Å³. The space groups are 1: $A2/a$, 2: $C2/c$. Both structures were determined with direct methods from 1081(1) and 883(2) reflections, collected with a four-circle X-ray single-crystal diffractometer at room temperature. The structures were refined by the method of least-squares rendering a final $R=0.041$ for both. The structures are similar and consist of van der Waals packed $(S_2CNR_2)_2$ -units. The geometry of the S_2CNC_2 -units in thiuram disulfides and ionic dithiocarbamates is compared. The only significant differences are found in the CS_2 -moiety.

This investigation was made in connection with a project where the geometry of substituted dithiocarbamate ions, $^-S_2CNR_2$ [$R_2=(CH_2)_4$, $(CH_3)_2$, $(C_2H_5)_2$, $(CH(CH_3)_2)_2$] is studied in ionic environments.¹⁻⁴ Recrystallization of $NaS_2CN(CH_3)_2 \cdot 2H_2O$ in aqueous-ethanolic solutions resulted in the formation of an unknown phase, which was analyzed by X-ray crystallography. For organic compounds this method provides a rapid, definite and fairly cheap analysis.⁵ The compound proved to be tetramethylthiuram disulfide, the X-ray structure of which was reported already in 1965.⁶ That study is, however, of low accuracy since it is based on two-dimensional film data. It is interesting to compare the geometry of thiuram disulfides and dithiocarbamates. In thiuram disulfides the $>NCS_2$ -group is covalently bonded

to another S-atom, while in alkali-metal dithiocarbamates it is involved in a hydrogen bond system as well as ionic metal coordination. Besides $[S_2CN(CH_3)_2]_2$ (denoted 2 below) only one crystal structure determination (for compounds of the type $[S_2CNR_2]_2$) has been reported, $[S_2CN(C_2H_5)_2]_2$.⁷ Therefore the crystal structure of $[S_2CH(CN_2)_4]_2$ (denoted 1) was also determined. Compounds 1 and 2 are illustrated in Fig. 1.

EXPERIMENTAL

It is known that dithiocarbamates may be oxidized to thiuram disulfides in acetonitrile according to eqn. (1).⁸

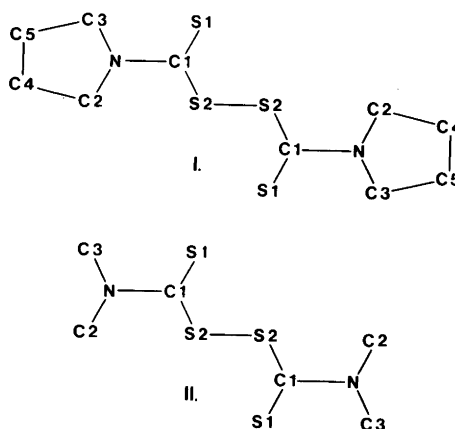
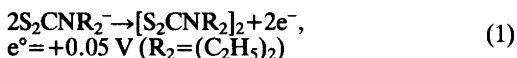
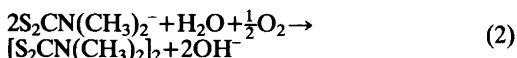


Fig. 1. Atomic numbering of compounds 1 and 2. Multiple bonds are not included.



In mixed water-ethanol solutions of $\text{NaS}_2\text{CN}(\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$ the reaction (2) occurs.



Bubbling air through an aqueous-ethanol solution of $\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$ gave crystals of $[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$ in high yield according to this reaction. For both compounds the crystals are colourless, irregular and hydrophobic.

Data collected on a CAD4 diffractometer revealed the Laue class 2/m and the systematic extinctions hkl , $h+k$ odd and $h0l$, l odd, for both compounds, consistent with the space group $C2/c$. For 1 the space group $A2/a$ was chosen. The different sizes of the molecules are reflected in the length of the c -axis. Intensity data for all independent reflections in the interval $3 < \theta \leq 70^\circ$ (1, $\text{CuK}\alpha$ radiation) and $3 < \theta \leq 30^\circ$ (2, $\text{MoK}\alpha$) were measured on the CAD4 using graphite

monochromator. Table 1 gives information concerning the data collection, the data reduction and the least-squares refinements. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects ($\sigma_c(I)$ is based on counting statistics).

STRUCTURE DETERMINATIONS AND REFINEMENTS

The non-hydrogen atoms were located with MULTAN⁹ and the hydrogen atoms in succeeding difference Fourier calculations. The structures were refined using full-matrix least-squares minimizing $\sum w(|F_o| - |F_c|)^2$ with weights $w = [\sigma_c^2/4|F_o|^2 + (C_1 \cdot |F_o|)^2 + C_2]^{-1}$, so that constant values of $\langle w(|F_o| - |F_c|)^2 \rangle$ were obtained in different F_o and $\sin\theta$ -intervals. The presence of extinction effects in the data sets were investigated by including an isotropic extinction parameter¹⁰ in the calculations. Ten (1) and two (2) reflections had extinction corrections larger than 10 %, with

Table 1. Crystal data, collection and reduction of intensity data and least-squares refinements.

	$[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$	$[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$
Crystal size (mm)	0.21×0.19×0.19	0.50×0.20×0.30
Space group	$A2/a$	$C2/c$
a (Å)	9.432(1)	9.672(1)
b (Å)	10.432(1)	9.931(2)
c (Å)	13.851(1)	11.882(8)
β (°)	97.08(1)	99.43(3)
V (Å ³)	1353(1)	1120(5)
D_x (Mg m ⁻³)	1.436	1.426
Wavelength (Å)	1.5418 (CuK α)	0.71069 (MoK α)
θ -interval (°)	3–70	3–30
ω - 2θ scan width (°)	0.80+0.5tan θ	0.80+0.6tan θ
Maximum recording time(s)	120	180
$\sigma_c(I)/I$ requested in a scan	0.03	0.03
μ (mm ⁻¹)	5.99	0.77
Range of transmission factors	0.35–0.49	0.74–0.84
Total number of reflections	1449	1786
Number of reflections with zero weight ($I < 3\sigma$)	368	868
Number of reflections in final LS-cycle ($I \geq 3\sigma$), m	1081	883
Number of parameters refined, n	106	80
$R = \sum \Delta F / \sum F_o $	0.041	0.041
$R_w = [\sum w(\Delta F)^2 / \sum w(F_o)^2]^{1/2}$	0.061	0.053
$S = [\sum w(\Delta F)^2 / (m-n)]^{1/2}$	1.43	0.907
C(1) (weighting function)	0.03	0.05
C(2) (weighting function)	0.25	0.10
$g \cdot 10^{-4}$ (extinction)	0.63(8)	0.29(8)

Table 2. Positional and isotropic thermal parameters with e.s.d.s for (a): $[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$ and (b): $[\text{S}_2\text{CN}(\text{CH}_3)_2 \cdot B_{\text{eq}} = \frac{4}{3} \sum \sum \beta_j a_i \cdot a_j$ is given for the non-H atoms. Positional parameters for non-hydrogen atoms have been multiplied by 10^4 and for hydrogen atoms by 10^3 .

(a)				
S(1)	6155(1)	2267(1)	1033(1)	4.3(0)
S(2)	8197(1)	130(1)	607(1)	4.3(0)
N	8165(3)	1212(2)	2289(2)	3.4(1)
C(1)	7475(3)	1280(3)	1392(2)	3.1(1)
C(2)	9381(4)	357(3)	2610(2)	4.2(1)
C(3)	7771(4)	2001(4)	3095(2)	4.5(1)
C(4)	9909(4)	822(5)	3623(3)	5.4(1)
C(5)	8605(5)	1343(7)	3980(3)	6.0(1)
H1C(2)	593(4)	446(4)	240(3)	4.7(8)
H2C(2)	491(5)	543(5)	285(4)	6.9(11)
H1C(3)	666(5)	200(4)	308(3)	5.8(9)
H2C(3)	797(5)	288(5)	300(4)	6.6(12)
H1C(4)	462(6)	513(6)	101(4)	8.4(14)
H2C(4)	433(6)	665(6)	140(4)	8.9(14)
H1C(5)	887(4)	214(4)	402(3)	3.7(8)
H2C(5)	809(6)	60(7)	424(5)	10.0(17)
(b)				
S(1)	3047(1)	3916(1)	2968(1)	4.5(0)
S(2)	5287(1)	1738(1)	3356(1)	5.4(0)
C(1)	4182(3)	3007(3)	3845(2)	3.6(1)
N	4394(3)	3106(3)	4985(2)	4.4(1)
C(2)	5409(5)	2311(6)	5750(4)	6.7(1)
C(3)	3618(5)	4057(5)	5566(3)	5.7(1)
HC(2)	528(4)	136(4)	566(3)	8.3(9)
HC(2)	579(4)	280(3)	643(4)	9.8(8)
HC(2)	619(4)	232(4)	552(3)	8.7(9)
HC(3)	331(4)	348(4)	613(4)	8.6(8)
HC(3)	442(4)	460(4)	622(3)	10.0(7)
HC(3)	329(4)	470(4)	519(3)	8.5(9)

maximum corrections of 41 % (1) for $22\bar{2}$ and 14 % (2) for $22\bar{1}$. Atomic scattering factors with corrections for anomalous dispersion were taken from *International Tables for X-Ray Crystallography*.¹¹ δR -plots comparing observed and calculated structure amplitudes¹² resulted in approximately straight lines with slopes 1.295(5) (1) and 0.952(5) (2), intercepts 0.105(5) (1) and 0.071(5) (2) and correlation coefficients 0.992 (1) and 0.990 (2).

DISCUSSION

Final positional and isotropic thermal parameters are given in Table 2* and selected

* Lists of structure factors and anisotropic thermal parameters may be obtained from the author.

distances and angles together with those for $[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$ ⁷ in Table 3. The structures are depicted in Fig. 2. Both structures consists of van der Waals packed $[\text{S}_2\text{CNR}_2]_2$ molecules. The packing is similar in the two compounds, but in 1 there is a non-parallel arrangement of the organic ends compared to 2 where they are packed in a parallel manner. The $[\text{S}_2\text{CNR}_2]_2$ molecules are located with the S-S bonds across 2-fold axes parallel to *b*. Some short van der Waals distances are 1: C(1)···H2C(4)=2.78(6), H2C(5)···H2C(5')=2.50(13) Å, 2: C(1)···HC(3)=2.74(4), HC(2)···HC(3)=2.96(6) Å. The geometries in relevant parts of the molecules are similar to that observed in $[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$ (Table 3).

The influence from the lone pairs on the sulfur atoms gives torsion angles C(1)-S(2)-S(2')-

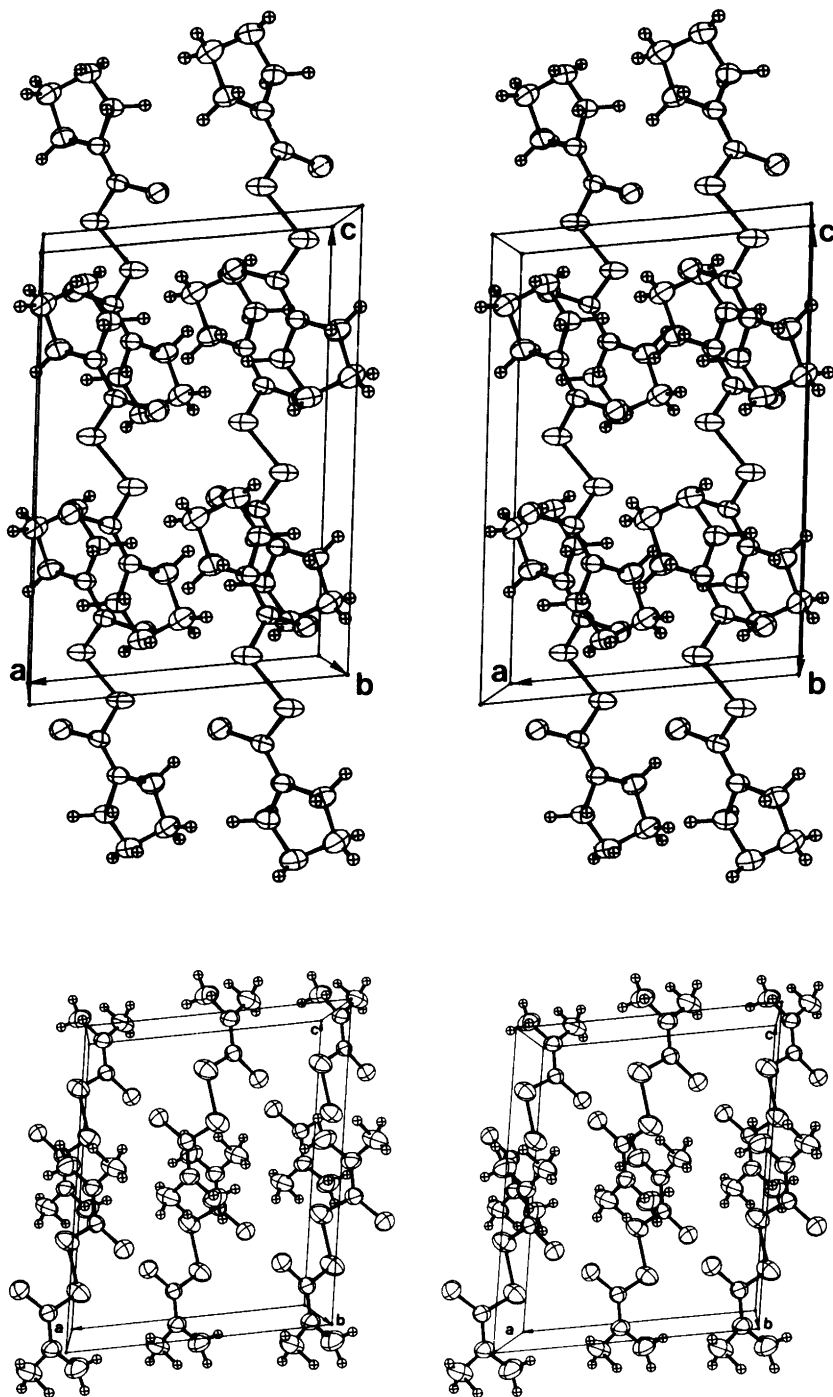


Fig. 2. Stereoscopic views of the unit-cells for compounds 1 (a) and 2 (b).

Table 3. Selected distances (Å) and angles (°) with e.s.d.s.

	[S ₂ CN(CH ₂) ₄] ₂	[S ₂ CN(CH ₃) ₂] ₂	[S ₂ CN(C ₂ H ₅) ₂] ₂
S(2)–S(2')	2.003(2)	2.009(2)	1.999(5)
S(1)–C(1)	1.644(3)	1.649(3)	1.634(11)
	–	–	1.662(11)
S(2)–C(1)	1.807(3)	1.807(3)	1.818(13)
	–	–	1.813(14)
C(1)–N	1.332(4)	1.334(4)	1.362(14)
	–	–	1.334(15)
N–C(2)	1.477(4)	1.454(6)	1.482(13)
	–	–	1.492(14)
N–C(3)	1.471(4)	1.447(5)	1.465(16)
	–	–	1.453(18)
C(2)–C(4)	1.510(5)	–	1.515(18)
	–	–	1.530(17)
C(3)–C(5)	1.535(6)	–	1.520(20)
	–	–	1.544(18)
C(4)–C(5)	1.484(6)	–	–
S(2)–S(2')–C(1)	104.4(1)	104.0(1)	103.4(4)
	–	–	103.6(4)
S(1)–C(1)–S(2)	124.1(2)	123.2(2)	122.2(7)
	–	–	122.0(7)
S(1)–C(1)–N	125.5(2)	124.8(2)	125.6(9)
	–	–	124.6(10)
S(2)–C(1)–N	110.4(2)	112.0(2)	112.1(8)
	–	–	113.4(8)
C(1)–N–C(2)	125.8(3)	124.4(3)	122.6(10)
	–	–	122.0(10)
C(1)–N–C(3)	122.5(3)	121.5(3)	120.2(9)
	–	–	122.0(9)
C(2)–N–C(3)	111.7(2)	114.1(3)	116.9(9)
	–	–	115.9(9)
N–C(2)–C(4)	103.9(3)	–	110.8(9)
	–	–	110.7(9)
N–C(3)–C(5)	101.8(3)	–	110.8(9)
	–	–	109.5(9)
C(2)–C(4)–C(5)	103.6(3)	–	–
C(3)–C(5)–C(4)	105.1(3)	–	–
C(1)–S(2)–S(2')–C(1')	93.6(1)	88.2(1)	90.2(6)
S(1)–C(1)–N–C(2)	–177.9(2)	–179.5(3)	–174.6(9)
	–	–	–175.6(9)
S(1)–C(1)–N–C(3)	2.8(4)	0.0(4)	2.7(16)
	–	–	–2.6(16)
S(2)–C(1)–N–C(2)	1.7(4)	0.8(4)	6.5(14)
	–	–	8.3(14)
S(2)–C(1)–N–C(3)	–177.5(2)	–179.7(3)	–176.3(8)
	–	–	–178.7(8)
C(1)–N–C(2)–C(4)	170.6(3)	–	89.4(13)
	–	–	85.9(13)
C(1)–N–C(3)–C(5)	166.7(3)	–	88.5(13)
	–	–	87.8(13)
N–C(2)–C(4)–C(5)	29.4(4)	–	–
N–C(3)–C(5)–C(4)	31.2(4)	–	–
C(2)–C(4)–C(5)–C(3)	–38.1(4)	–	–

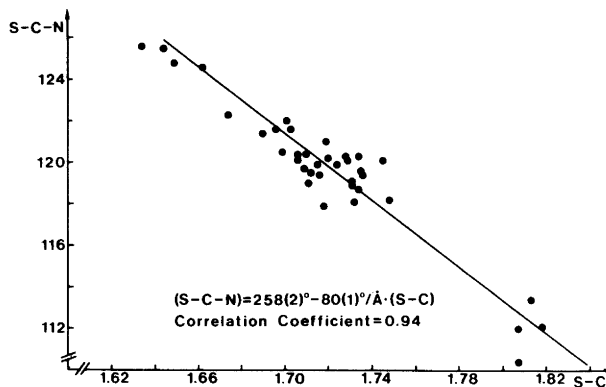


Fig. 3. The angle S-C-N as a function of the distance S-C for 13 ionic dithiocarbamates and 3 thiuram disulfides. The four extreme values above 1.80 Å and below 1.665 Å represent the thiuram disulfides.

C(1') in the vicinity of 90° as expected. At any other angle there would be overlapping between filled orbitals.^{13,14} The S(2)-S(2') distances are of the same size as in other compounds containing -S-S- bonds *i.e.* ~2.0 Å.¹⁵⁻¹⁷ The rms-deviations from the least-squares planes defined by S(1), S(2), C(1) and N are 5.17 (1) and 3.90 Å · 10⁴ (2). The other atoms deviate from these planes by C(2): -56(41), C(3): 119(51) (2) and C(2): 417(36), C(3): -540(38), C(4): 2657(43) and C(5): -3731(53) Å · 10⁴ (1). These values indicate that the S₂CNR₂-moiety in 2 is planar while the atoms C(2), C(3), C(4) and C(5) in 1 undergo conformational reorientation similar to the one found for NaS₂CH(CH₂)₄ · 2H₂O.¹

The geometries observed in the thiuram disulfides may be compared to those observed in 13 ionic dithiocarbamates.^{1-4, 18-27} In the R₂N-parts of thiuram disulfides and ionic dithiocarbamates with equal R₂-groups no significant differences are observed. The two S-C(1) distances in ionic dithiocarbamates may be different, but their sum is often constant. This indicates different hybridization²⁸ on the C(1)-atom, which ought to be reflected in the angles around C(1). The angle S-C(1)-N (*y*) is roughly a linear function of the distance S-C(1) (*x*) for ionic dithiocarbamates and thiuram disulfides, with $y = 258(2) - 80(1)^\circ/\text{Å} \cdot x$ and correlation coefficient 0.94. The thiuram disulfides represent extreme values (Fig. 3).

From a literature study of 68 S-C distances²⁹ the mean values 1.610(6) Å for an S=C double

bond and 1.818(1) Å for a single bond are found. According to this the weighted mean value for the S(2)-C(1) bond distance [1.807(2) Å] in the thiuram disulfides represents a single bond. Similarly, the weighted mean value for the S(1)-C(1) distance 1.647(3) Å, indicates an appreciable amount of double bonding. From the 13 ionic dithiocarbamates a weighted²⁹ mean value of 1.722(2) Å for the S-C(1) (*i.e.* [S(1)-C(1)+S(2)-C(1)]/2) distances is found. This value is not significantly different from the value 1.726(2) Å found for the thiuram disulfides. The weighted mean values 1.334(3) Å (thiuram disulfides) and 1.332(3) Å (ionic dithiocarbamates) for the C(1)-N bond distances are not significantly different. Compared to >C=N- double bonds (1.224(10)-1.283(6) Å)³⁰⁻³⁵ and >C-N< bonds [1.447(5)-1.492(14) Å] (Table 3) these values also indicate an appreciable amount of double bonding. The change from ionic coordination to the formation of a covalent -S-S- bond thus has no detectable effects on the C(1)-N bond.

It is concluded that the only significant difference in the comparable parts of these two types of compounds is in the CS₂-moiety. The sum of distances in S₂C-N is equal but the S-C bond order is redistributed. Furthermore, the angles around C(1) are drastically changed upon formation of the -S-S- bond.

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