Service at Daresbury used for crystallographic literature searches.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55392 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1015]

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Structures of 1-Cyano-2,2-bis(methylthio)vinyl *N,N*-Dimethyldithiocarbamate (2) and 1,2,2-Tris(methylthio)vinyl *N,N*-Dimethyldithiocarbamate (3)

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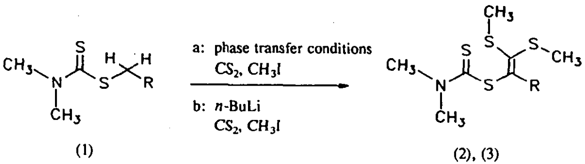
Abstract

The *N,N*-dimethyldithiocarbamate moiety in both title compounds is planar. The C5—N1 bond lengths are 1.332 (4) and 1.327 (7) Å in (2) and (3) respectively, markedly shorter than the normal value for a C—N single bond. The ethylene skeleton in (2) and (3) is non-planar. The dithiocarbamate and ethylene moieties are nearly perpendicular to each other.

Comment

As systems with a doubly activated methylene group, dimethyldithiocarbamates (1) react with carbon disulfide and alkyl halides in the presence of a strong base. Different products may be obtained according to the particular reaction conditions and the activating ability of the substituent *R*. 1,3-Dithiole derivatives are formed by the reaction of (1) with CS_2 in dry tetrahydrofuran in the presence of sodium *tert*-butylate and subsequent methylation (Dölling, Friedemann, Heinemann & Hartung, 1991; Dölling, Khoudary, Augustin, Baumeister & Hartung, 1988). Under phase transfer conditions and in the presence of an equimolar amount of triethylbenzylammonium chloride, (2) is formed after alkylation with methyl iodide (see reaction *a* below) (Dölling, Sperk & Augustin, 1990). As a result of the very weak activation of the methylene group by the SCH_3 substituent, compound (3) can be prepared only by dithiocarboxylation of (1) in the presence of a very strong base such as *n*-BuLi (reaction *b*).



a: R = CN (2)
b: R = S-CH_3 (3)

Compounds (2) and (3) were identified by X-ray analysis. Their structures, which are reported here, are of interest with regard to the conformational behaviour of the trithio- and tetrathioethylene system. The *N,N*-dimethyldithiocarbamate group (S1, S2, N1, C5, C6, C7) adopts a more or less planar conformation; in (2), this fragment is exactly planar, but there are significant deviations from planarity in (3) where C6 deviates by 0.104 (7) Å from the least-squares plane defined by the six atoms. This is also illustrated by the corresponding torsion angles (Table 2). The deviations of about 7° from the ideal values (0 and 180° respectively) for C6—N1—C5—S1 and C6—N1—C5—S2 indicate that the C6 methyl group is tilted out of plane in (3). The C5—N1 distances of 1.332 (4) Å for (2) and 1.327 (7) Å for (3) are both markedly shorter than the normal C—N single bond length of 1.47 Å (Testa, 1983). This shortening indicates that the N lone pair participates strongly in the π system of the

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thiocarbonyl group and makes a substantial contribution to the zwitterionic resonance form of the overall structure as recently reported for the related compound *S*-[1-benzoyl-2-bis(methylthio)vinyl] pentamethylenedithiocarbamate (Dölling *et al.*, 1988). The ethylene skeleton C8(S5), S1, C1, C2, S3, S4 is clearly non-planar in both compounds but the sp^2-hybridized atoms C1 and C2 are coordinated in a planar arrangement, except for C1 in (3) which deviates slightly (0.045 (6) Å) from the C1, C2, S1, S5 plane. The Csp^2 planes are twisted around the C1—C2 bond by 9.2 and 8.4° in (2) and (3) respectively. This result agrees quite well with the conformation found in *S*-[1-benzoyl-2-bis(methylthio)vinyl] pentamethylenedithiocarbamate (Dölling *et al.*, 1988). The ethylene and *N*,*N*-dimethyldithiocarbamate fragments are orientated nearly perpendicular to each other, the interplanar angles of the least-squares planes being 84.8 and 81.2° in (2) and (3) respectively.

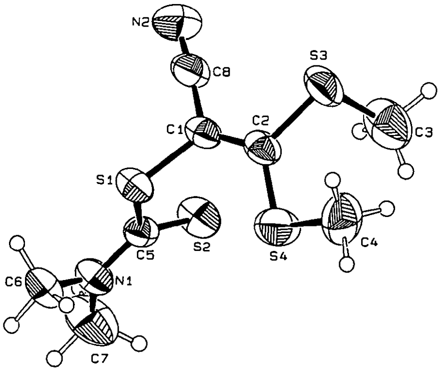

Fig. 1. Molecular structure and atomic numbering of (2). The thermal ellipsoids are drawn at the 50% level and the H atoms are shown as spheres of arbitrary radii.

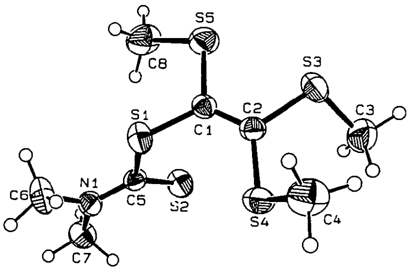

Fig. 2. Molecular structure and atomic numbering of (3). The thermal ellipsoids are drawn at the 50% level and the H atoms are shown as spheres of arbitrary radii.

Experimental

Compound (2)

Crystal data

$C_8H_{12}N_2S_4$
M = 264.45
Monoclinic
$P2_1/n$
a = 9.939 (2) Å
b = 11.403 (2) Å
c = 12.472 (1) Å
β = 113.04 (1)°
V = 1300.8 Å^3
Z = 4
D_x = 1.350 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 82 reflections
θ = 12–17.5°
μ = 0.67 mm^{-1}
T = 293 K
Irregular
0.46 × 0.38 × 0.27 mm
Pale yellow

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
7280 measured reflections
1700 independent reflections
1678 observed reflections [$I \geq 2\sigma(I)$]
R_{int} = 0.018

θ_{max} = 22.5°
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity variations: 5.4, 5.4, 11.9%

Refinement

Refinement on F
Final R = 0.039
wR = 0.035
S = 0.762
1678 reflections
139 parameters

H-atom parameters not refined
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.215
$\Delta\rho_{max}$ = 0.280 e Å^{-3}
$\Delta\rho_{min}$ = −0.230 e Å^{-3}

Compound (3)

Crystal data

$C_8H_{15}NS_5$
M_r = 285.54
Monoclinic
$P2_1/c$
a = 11.203 (2) Å
b = 9.042 (2) Å
c = 13.693 (2) Å
β = 100.85 (2)°
V = 1362.2 Å^3
Z = 4
D_x = 1.392 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 14 reflections
θ = 12–14.5°
μ = 7.33 mm^{-1}
T = 291 K
Irregular
0.32 × 0.30 × 0.21 mm
Pale yellow

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.828, T_{max} = 1.391
2025 measured reflections
1813 independent reflections
1497 observed reflections [$I \geq 3.92\sigma(I)$]

R_{int} = 0
θ_{max} = 57.5°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -16 \rightarrow 16$
2 standard reflections monitored every 100 reflections
intensity variations: 4.2, 5.2%

Refinement

Refinement on F
Final R = 0.052
wR = 0.058

H-atom parameters not refined
$w = 1/\sigma^2(F)$

$S = 5.26$
1497 reflections
142 parameters
$(\Delta/\sigma)_{\max} = 0.366$
$\Delta\rho_{\max} = 0.349$ e Å^{-3}
$\Delta\rho_{\min} = -0.405$ e Å^{-3}

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
(2)				
S1	0.12744 (9)	0.67158 (7)	0.88463 (7)	0.0541 (3)
S2	0.3305 (1)	0.84448 (8)	1.05431 (8)	0.0695 (4)
S3	0.2032 (1)	0.5071 (1)	1.21902 (8)	0.0793 (5)
S4	0.3657 (1)	0.5008 (1)	1.0558 (1)	0.0840 (5)
N1	0.2695 (3)	0.8356 (2)	0.8272 (2)	0.060 (1)
N2	−0.0577 (4)	0.7444 (4)	1.0768 (3)	0.096 (2)
C1	0.1319 (3)	0.6334 (3)	1.0232 (3)	0.052 (1)
C2	0.2246 (4)	0.5536 (3)	1.0925 (3)	0.057 (1)
C3	0.3755 (5)	0.5456 (5)	1.3326 (4)	0.106 (2)
C4	0.4094 (5)	0.3583 (4)	1.1222 (4)	0.097 (2)
C5	0.2514 (3)	0.7936 (3)	0.9203 (3)	0.047 (1)
C6	0.1975 (4)	0.7871 (4)	0.7101 (3)	0.077 (2)
C7	0.3676 (6)	0.9351 (4)	0.8388 (4)	0.108 (3)
C8	0.0276 (4)	0.6932 (3)	1.0561 (3)	0.065 (2)
(3)				
S1	0.6475 (2)	−0.0362 (2)	0.6866 (1)	0.0471 (6)
S2	0.7944 (2)	0.2159 (2)	0.7930 (1)	0.0546 (6)
S3	0.7595 (2)	−0.2338 (2)	0.9785 (1)	0.0545 (6)
S4	0.8921 (2)	−0.1860 (2)	0.8069 (1)	0.0514 (6)
S5	0.5417 (2)	−0.0532 (2)	0.8744 (1)	0.0601 (7)
N1	0.7131 (4)	0.1970 (5)	0.5981 (3)	0.043 (2)
C1	0.6653 (5)	−0.0855 (6)	0.8129 (4)	0.037 (2)
C2	0.7617 (5)	−0.1579 (6)	0.8602 (4)	0.038 (2)
C3	0.9099 (6)	−0.2064 (9)	1.0458 (5)	0.070 (3)
C4	0.9172 (7)	−0.3829 (8)	0.8218 (6)	0.069 (3)
C5	0.7225 (5)	0.1402 (6)	0.6886 (4)	0.036 (2)
C6	0.6375 (7)	0.1322 (8)	0.5083 (4)	0.064 (3)
C7	0.7704 (6)	0.3405 (7)	0.5844 (5)	0.054 (3)
C8	0.4570 (7)	0.0932 (9)	0.8048 (6)	0.077 (3)

Table 2. *Geometric parameters* (Å, °)

	(2)	(3)		(2)	(3)
S1—C1	1.765 (4)	1.760 (5)	S5—C8		1.794 (8)
S1—C5	1.795 (3)	1.801 (6)	N1—C5	1.332 (4)	1.327 (7)
S2—C5	1.649 (3)	1.652 (6)	N1—C6	1.460 (5)	1.477 (8)
S3—C2	1.755 (4)	1.763 (6)	N1—C7	1.467 (6)	1.475 (8)
S3—C3	1.798 (5)	1.780 (7)	N2—C8	1.138 (5)	
S4—C2	1.743 (4)	1.770 (6)	C1—C2	1.342 (5)	1.324 (8)
S4—C4	1.798 (5)	1.808 (7)	C1—C8	1.429 (5)	
S5—C1		1.775 (6)			
C1—S1—C5	101.3 (2)	104.1 (3)	S5—C1—C2		119.1 (4)
C2—S3—C3	102.8 (2)	104.2 (3)	C2—C1—C8	122.1 (3)	
C2—S4—C4	105.4 (2)	102.6 (3)	S3—C2—S4	121.7 (2)	118.6 (3)
C1—S5—C8		104.5 (3)	S3—C2—C1	119.3 (2)	119.4 (4)
C5—N1—C6	123.8 (3)	123.8 (4)	S4—C2—C1	119.0 (2)	122.0 (4)
C5—N1—C7	120.2 (3)	120.0 (4)	S1—C5—S2	122.2 (2)	122.0 (3)
C6—N1—C7	116.0 (3)	115.9 (4)	S1—C5—N1	112.1 (2)	112.0 (4)
S1—C1—C2	123.1 (2)	122.5 (4)	S2—C5—N1	125.7 (2)	126.0 (4)
S1—C1—C8	114.8 (2)		N2—C8—C1	176.2 (3)	
S1—C1—S5		118.1 (3)			
C5—S1—C1—S5		99.2 (3)			
C5—S1—C1—C2	−91.9 (3)	−87.5 (5)	C6—N1—C5—S2	179.7 (3)	−173.6 (6)
C5—S1—C1—C8	88.7 (3)		C7—N1—C5—S1	−179.6 (3)	−179.2 (5)
C1—S1—C5—S2	−2.2 (2)	3.2 (4)	C7—N1—C5—S2	0.5 (3)	0.3 (6)
C1—S1—C5—N1	177.9 (2)	−177.3 (4)	S1—C1—C2—S3	−171.2 (2)	−167.9 (4)
C3—S3—C2—S4	57.9 (2)	39.3 (4)	S1—C1—C2—S4	10.1 (3)	10.2 (5)
C3—S3—C2—C1	−120.8 (3)	−142.5 (5)	S5—C1—C2—S3		5.4 (5)
C4—S4—C2—S3	26.6 (2)	49.0 (4)	S5—C1—C2—S4		−176.5 (4)
C4—S4—C2—C1	−154.6 (3)	−129.1 (5)	C8—C1—C2—S3	8.2 (4)	
C8—S5—C1—S1		−24.5 (4)	C8—C1—C2—S4	−170.6 (3)	
C8—S5—C1—C2		161.9 (5)	S1—C1—C8—N2	−4 (5)	
C6—N1—C5—S1	−0.4 (3)	7.0 (6)	C2—C1—C8—N2	177 (6)	

In both cases, the compounds were recrystallized from ethanol. Structures were solved by direct methods. Refinement was by full-matrix least-squares methods. All H atoms were placed at calculated positions. Atomic scattering factors were taken from *SHELX*76 (Sheldrick, 1976).

Programs used for data collection: (2) *DIF*4 (Stoe & Cie, 1991*a*) using the learnt-profile method (Clegg, 1981), (3) *XTL* (Syntex Corporation, 1973). Programs used for data reduction: (2) *REDU*4 (Stoe & Cie, 1991*b*). (3) *PRADIR* (Jaskolski, 1990). Program used to solve structures: *SHELXS*86 (Sheldrick, 1986). Program used to refine structures: *SHELX*76. Programs used to draw diagrams: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978). Software used for geometrical calculations: *EDIT* (Jaskólski, 1982).

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55331 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1007]

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