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Ethylene bis(dimethyldithiocarbamate) and butane-1,4-diyl bis(dimethyldithiocarbamate)

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Abstract

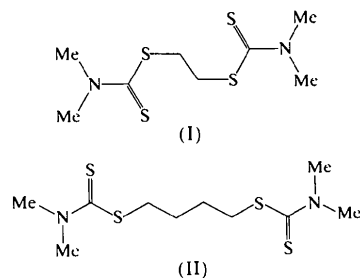
In the crystals of the title compounds, C₈H₁₆N₂S₄, (I), and C₁₀H₂₀N₂S₄, (II), the molecules lie about inversion centres. In both structures, the C=S bonds in the two dithiocarbamate units are oriented *trans* to each other. In (I), the ethylene bridge and the bridged S atoms adopt a *trans* planar conformation and form a dihedral angle of 84.4(2)° with the dimethyldithiocarbamate plane. The molecule of (II) is nearly planar; in the crystal, the molecules are arranged in sheets which are stacked, 3.874(2) Å apart, parallel to (206) planes.

Comment

Since the discovery of alkylene dithiocarbamate [*R*¹*R*²NC(=S)SR³SC(=S)NR²*R*¹; *R*¹ = H, C₁₋₁₈; *R*² = C₁₋₁₈; *R*³ = C₁₋₁₀, divalent hydrocarbon] as a plant-protective fungicide, many of its derivatives have been synthesized (Yagihara *et al.*, 1975; Kubota *et al.*, 1977; Roethling *et al.*, 1983). It was recently discovered that various alkylene bis(dialkyldithiocarbamates) could be used as flotation agents in Au and Cu recovery (Di Biase & Bush, 1991) and as vulcanization accelerator agents in the curing of diene rubbers. This paper reports the structural details of two such derivatives.

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In the crystals of both (I) and (II), the asymmetric unit contains one half of the molecule, the other half being inversion related. In both structures, each S₂CNMe₂ subunit has one C—S single bond [1.758(3) in (I) and 1.778(2) Å in (II)] and one C=S double bond [1.664(3) in (I) and 1.675(2) Å in (II)]. The S₂CNMe₂ units are bonded to the bridging ethylene and butylene by C—S single bonds. In both compounds, the two C=S bonds are oriented *trans* to each other. Shorter C—N bond distances in the S₂CN units [1.328(4) in (I) and 1.328(2) Å in (II)] are indicative of considerable double-bond character. All these bond distances (S—C, S=C and C—N) are comparable with the corresponding distances in the methylene bis(dialkyldithiocarbamate) structure (Sharma *et al.*, 1991; Gimeno *et al.*, 1996).



In (I), the dimethyldithiocarbamate group is planar to within 0.023(3) Å and atoms S1, C4, C4ⁱ and S1ⁱ adopt a *trans* planar conformation; these two planes form a dihedral angle of 84.4(2)°. The non-H atoms in (II) are nearly coplanar with maximum deviations of -0.071(1) and 0.071(1) Å for S1 and S1ⁱ, respectively.

In both structures, the S2...C4 contact distances [3.101(5) and 3.113(2) Å] are significantly shorter than the sum of the van der Waals radii (3.55 Å) indicating the formation of an incipient bond between these atoms and the occurrence of ring-opening/ring-closing tautomerism (Schumaker *et al.*, 1991). Other significant intramolecular short contacts in these structures are S1...N1 [2.585(4) and 2.607(2) Å], S1...C2 [2.852(4) and 2.858(2) Å], S2...N1 [2.650(4) and 2.660(2) Å], S2...C1 [3.011(5) and 3.019(2) Å] and S1...C5 [2.710(2) Å in (II)]. The shortest intermolecular contact in the two structures is S1...C4(1-x, -y, 1-z) [2.769(4) Å], which is observed in (I). In the crystal of (II), the molecules form a zigzag arrangement in a plane, the molecular sheets being stacked parallel to (206) planes, 3.874(2) Å apart.

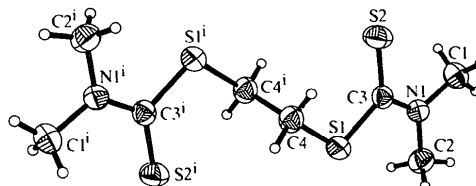


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

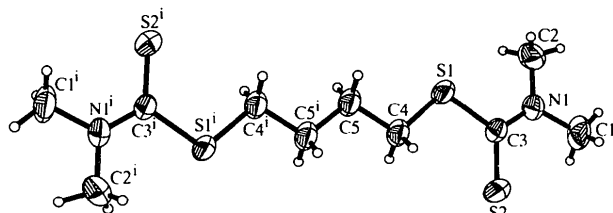


Fig. 2. The structure of (II) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

Sodium *N,N'*-dimethyldithiocarbamate [$\text{Na}(\text{S}_2\text{CNMe}_2)$] dissolved in ethanol was added to 1,2-dichloroethane for (I) and 1,4-dibromobutane for (II) at 353–358 K with stirring, followed by refluxing for 4–5 h and condensing. The products were washed with water and dried overnight under vacuum. Recrystallization was from $\text{CH}_3\text{Cl}/\text{EtOH}$. Single crystals suitable for X-ray analysis were grown from EtOH by slow evaporation at room temperature for two weeks.

Compound (I)

Crystal data

$\text{C}_8\text{H}_{16}\text{N}_2\text{S}_4$
 $M_r = 268.47$
 Monoclinic
 $P2_1/c$
 $a = 6.069$ (7) Å
 $b = 7.829$ (2) Å
 $c = 13.455$ (3) Å
 $\beta = 91.76$ (3)°
 $V = 639.0$ (8) Å³
 $Z = 2$
 $D_x = 1.395$ Mg m⁻³
 D_m not measured

Data collection

Siemens P4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: empirical ψ scans (XSCANS; Siemens, 1994)
 $T_{\min} = 0.755$, $T_{\max} = 0.826$
 1692 measured reflections
 1123 independent reflections
 822 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.095$
 $S = 1.043$
 1123 reflections
 66 parameters
 H-atoms: see text
 $w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 0.1707P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 40 reflections
 $\theta = 6.85$ – 12.49 °
 $\mu = 0.710$ mm⁻¹
 $T = 295$ (2) K
 Block
 $0.42 \times 0.30 \times 0.28$ mm
 Pale yellow

$R_{\text{int}} = 0.028$
 $\theta_{\text{max}} = 25$ °
 $h = -7 \rightarrow 7$
 $k = 0 \rightarrow 9$
 $l = 0 \rightarrow 15$
 3 standard reflections every 97 reflections
 intensity decay: <3%

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.253$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.200$ e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (I)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U^{ij}a^i a^j \cdot a_j$$

	x	y	z	U_{eq}
S1	0.51668 (14)	0.02118 (11)	0.33644 (6)	0.0457 (3)
S2	0.13289 (15)	0.24008 (12)	0.39141 (6)	0.0519 (3)
N1	0.2131 (4)	0.1234 (3)	0.21123 (17)	0.0367 (6)
C1	0.0149 (6)	0.2082 (5)	0.1732 (2)	0.0514 (9)
C2	0.3404 (6)	0.0312 (4)	0.1376 (2)	0.0482 (8)
C3	0.2718 (5)	0.1325 (4)	0.3070 (2)	0.0347 (7)
C4	0.5617 (5)	0.0614 (4)	0.4677 (2)	0.0425 (8)

Table 2. Selected bond lengths (Å) for (I)

S1—C3	1.758 (3)	N1—C1	1.453 (4)
S1—C4	1.807 (3)	N1—C2	1.465 (4)
S2—C3	1.664 (3)	C4—C4'	1.509 (6)
N1—C3	1.328 (4)		

Symmetry code: (i) $1 - x, -y, 1 - z$.

Compound (II)

Crystal data

$\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4$
 $M_r = 296.52$
 Monoclinic
 $P2_1/n$
 $a = 7.4875$ (1) Å
 $b = 7.4424$ (2) Å
 $c = 13.7568$ (3) Å
 $\beta = 97.536$ (1)°
 $V = 759.98$ (3) Å³
 $Z = 2$
 $D_x = 1.296$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 3850 reflections
 $\theta = 2.95$ – 33.19 °
 $\mu = 0.604$ mm⁻¹
 $T = 293$ (2) K
 Needle
 $0.60 \times 0.16 \times 0.14$ mm
 Yellow

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.713$, $T_{\max} = 0.920$
 3823 measured reflections

1329 independent reflections
 1179 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.0158$
 $\theta_{\text{max}} = 25$ °
 $h = -8 \rightarrow 8$
 $k = 0 \rightarrow 8$
 $l = 0 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.075$
 $S = 1.103$
 1329 reflections
 75 parameters
 H-atoms: see text
 $w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.1038P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.218$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.146$ e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U^{ij}a^i a^j \cdot a_j$$

	x	y	z	U_{eq}
S1	0.71341 (6)	0.36232 (5)	0.41993 (4)	0.0521 (2)
S2	1.02722 (6)	0.18790 (7)	0.33841 (4)	0.0599 (2)

N1	0.96496 (19)	0.5391 (2)	0.34654 (10)	0.0503 (4)
C1	1.1308 (3)	0.5720 (3)	0.30258 (16)	0.0717 (6)
C2	0.8657 (3)	0.6980 (2)	0.37231 (14)	0.0623 (5)
C3	0.9150 (2)	0.3726 (2)	0.36473 (11)	0.0420 (4)
C4	0.6849 (2)	0.1241 (2)	0.44011 (14)	0.0509 (4)
C5	0.5187 (2)	0.0990 (2)	0.49248 (14)	0.0512 (4)

Table 4. Selected bond lengths (Å) for (II)

S1—C3	1.778 (2)	N1—C2	1.465 (2)
S1—C4	1.812 (2)	N1—C1	1.471 (2)
S2—C3	1.675 (2)	C4—C5	1.529 (2)
N1—C3	1.328 (2)	C5—C5'	1.519 (3)

Symmetry code: (i) $1 - x, -y, 1 - z$.

The data collection for (II) covered a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω . The crystal-to-detector distance was 4 cm and the detector swing angle was -35°. Crystal decay was monitored by repeating thirty initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible.

Both structures were solved by direct methods and refined by full-matrix least-squares techniques. The H atoms of both (I) and (II) were fixed geometrically and allowed to ride on the attached atoms; rotating-group refinement was used for the methyl groups of both structures.

Data collection: XSCANS (Siemens, 1994) for (I); SMART (Siemens, 1996) for (II). Cell refinement: XSCANS for (I); SAINT (Siemens, 1996) for (II). Data reduction: XSCANS for (I); SAINT for (II). For both compounds, program(s) used to solve structures: SHELXTL (Sheldrick, 1997); program(s) used to refine structures: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1520). Services for accessing these data are described at the back of the journal.

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p-Methoxybenzaldehyde isonicotinoyl-hydrazone monohydrate

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Abstract

X-ray analysis reveals that the title compound, C₁₄H₁₃N₃O₂·H₂O, is in keto tautomeric form and the configuration at the azomethine C=N double bond is *E*. The pyridine plane makes a dihedral angle of 39.9(1)° with the plane through the central hydrazone bridge. The crystal structure is stabilized by extensive hydrogen bonding involving the water molecule and the hydrazone bridge.

Comment

Aroylhydrazone compounds containing a pyridyl group have received considerable attention recently. In addition to the existence of a strong coordinating hydrazone group, the pyridyl unit can also serve as a coordination site to form polynuclear complexes. As a continuation of our work on the synthesis and characterization of aroylhydrazone compounds (Fun *et al.*, 1996; Lu, Duan *et al.*, 1996; Lu, Shan *et al.*, 1996; Ma *et al.*, 1994), we report the structure of *p*-methoxybenzaldehyde isonicotinoylhydrazone monohydrate, (I).

