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Triclinic Form of Dipyrrolidinylthiuram Disulfide

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(*Received 26 May 1995; accepted 20 September 1995*)

Abstract

A new polymorphic form of the title compound, di-1,4-butanediylthiuram disulfide [1,1′-dithiodicarbonothioylbis(pyrrolidine)], $C_{10}H_{16}N_2S_4$, has been determined in the triclinic system. There are two simultaneous reports on structure determinations of this compound in the monoclinic system [Ymen (1983). *Acta Chem. Scand. Ser. B*, **37**, 707–713; Williams, Statham & White (1983). *Aust. J. Chem.* **36**, 1371–1377]. The two forms show differences in the conformation of one of the two pyrrolidine rings of the molecule.

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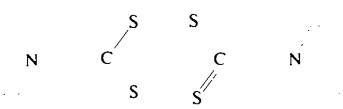
Comment

It is known that several metal dithiocarbamates are being used as pesticides, vulcanizing agents, antioxidants and lubricants, and therefore studies on these compounds has attracted interest since as early as 1908 (Thorn & Ludwig, 1962). However, the instability of some metal dithiocarbamates in several solvents leads to decomposition of the complex instead of recrystallization. As an example, crystals of the title compound, dipyrrolidinylthiuram disulfide (DPTD), were obtained by slow evaporation of tetrakis(pyrrolidine-1-carbodithioato)thorium(IV) from dimethyl sulfoxide (Williams, Statham & White, 1983). DPTD crystals were also obtained by bubbling air through an aqueous ethanol solution of $NaS_2CN(CH_3)_2.2H_2O$ (Ymen, 1983). The DPTD crystals thus obtained belonged to the monoclinic space group $C2/c$, the molecule having C_2 symmetry. In our studies on the reactivity of some metal dithiocarbamates, recrystallization of $[Fe\{S_2CN(CH_2)_4\}_3]$ from methanol gave some single crystals suitable for X-ray diffraction studies. Surprisingly, the crystals were found to be those of DPTD but belonging to the triclinic space group $P\bar{1}$ instead. In the triclinic form, the molecule occupies a general equivalent position and does not have any symmetry. DPTD has been reported as a potent inhibitor of the cytoplasmic aldehyde dehydrogenases of sheep liver (Kitson, 1976), hence the present report may be useful in assessing which form is more active in this regard.



DPTD

A displacement ellipsoid plot of the DPTD molecule with the numbering scheme is shown in Fig. 1. The two pyrrolidine rings adopt two different conformations; ring 1 (N1, C2, C3, C4, C5) is a half-chair and ring 2 (N1*A*, C2*A*, C3*A*, C4*A*, C5*A*) adopts an envelope conformation. The deviations of atoms C3 and C4 from the plane of the other ring 1 atoms (N1, C2, C5) are −0.321 (6) and 0.226 (6) Å, respectively. In ring 2, C3*A* is the pivot atom of the envelope and deviates by 0.360 (7) Å from the plane formed by the remainder of the atoms (N1*A*, C2*A*, C5*A*, C4*A*). The asymmetry parameters according to Nardelli (1983*a*) are D_2(N1) = 0.011 (2) for ring 1 and D_s(C3*A*) = 0.006 (3) for ring 2. In the monoclinic form, the pyrrolidine rings both have half-chair conformations, and the bond lengths and angles show some deviations from those of ring 1 in the present triclinic form. The two S_2CN groups in the triclinic form (S1, S2, C1, N1 and S1*A*, S2*A*, C1*A*, N1*A*) are individually planar and make a dihedral angle of 91.13 (5)° with respect to one another, which is close to the angle of 86.01 (3)° found in the monoclinic form. The two terminal S atoms, S1 and S1*A*, tend to be further apart in the triclinic form (4.175 Å) than in the monoclinic form (4.048 Å).

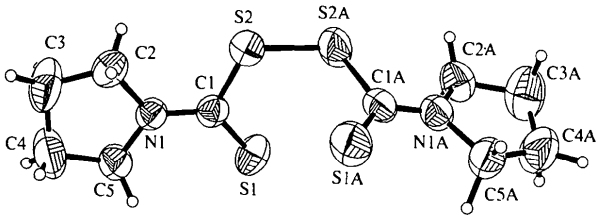


Fig. 1. Displacement ellipsoid plot (50% probability) of the title molecule with the numbering scheme.

The molecules of DPTD are linear and lie in layers parallel to the (110) planes.

Experimental

Crystals of DPTD were obtained by recrystallization of $[Fe\{S_2CN(CH_2)_4\}_3]$ from methanol (see *Comment*). The crystal density D_m was measured in KBr solution.

Crystal data

$C_{10}H_{16}N_2S_4$
$M_r = 292.49$
Triclinic
$P\bar{1}$
$a = 8.270\ (2)$ Å
$b = 9.361\ (2)$ Å
$c = 10.689\ (2)$ Å
$\alpha = 113.88\ (1)°$
$\beta = 98.81\ (2)°$
$\gamma = 105.94\ (1)°$
$V = 693.9\ (3)$ Å^3
$Z = 2$
$D_x = 1.400$ Mg m^{-3}
$D_m = 1.39$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 36 reflections
$\theta = 10$–$25°$
$\mu = 0.661$ mm^{-1}
$T = 293\ (2)$ K
Needle
$0.60 \times 0.44 \times 0.12$ mm
Light yellow

Data collection

Siemens $P4$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3578 measured reflections
2947 independent reflections
1760 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0165$

$\theta_{max} = 27.49°$
$h = -1 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 100 reflections
intensity decay: <4%

Refinement

Refinement on F^2
$R(F) = 0.0430$
$wR(F^2) = 0.1146$
$S = 0.869$
2947 reflections
209 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.322$ e Å^{-3}
$\Delta\rho_{min} = -0.311$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
S1	0.74799 (9)	−0.12482 (11)	0.27574 (9)	0.0742 (3)
S2	1.08535 (10)	0.16131 (9)	0.34061 (9)	0.0741 (3)
N1	1.0650 (2)	−0.1390 (2)	0.2918 (2)	0.0500 (5)
C1	0.9619 (3)	−0.0522 (3)	0.3009 (2)	0.0509 (6)
C2	1.2580 (4)	−0.0735 (4)	0.3265 (4)	0.0609 (7)
C3	1.3077 (5)	−0.2115 (6)	0.3348 (6)	0.0958 (13)
C4	1.1546 (6)	−0.3674 (6)	0.2341 (7)	0.1043 (15)
C5	0.9961 (4)	−0.3198 (4)	0.2476 (4)	0.0674 (8)
S1A	0.86133 (12)	0.14910 (11)	0.05301 (8)	0.0782 (3)
S2A	0.91102 (13)	0.27324 (11)	0.37108 (8)	0.0821 (3)
N1A	0.6675 (3)	0.2898 (3)	0.1997 (2)	0.0576 (6)
C1A	0.7981 (4)	0.2348 (3)	0.1947 (3)	0.0568 (6)
C2A	0.6106 (5)	0.3648 (5)	0.3275 (4)	0.0712 (8)
C3A	0.4879 (7)	0.4400 (7)	0.2853 (5)	0.1014 (14)
C4A	0.4209 (8)	0.3493 (9)	0.1287 (5)	0.112 (2)
C5A	0.5533 (5)	0.2778 (5)	0.0721 (4)	0.0731 (8)

Table 2. *Selected geometric parameters (Å, °)*

S2—S2A	1.995 (1)	N1—C2	1.469 (3)
S1—C1	1.646 (3)	C2—C3	1.490 (5)
S2—C1	1.811 (3)	C3—C4	1.479 (6)
N1—C1	1.319 (3)	C4—C5	1.504 (5)
N1—C5	1.467 (4)		
C1—S2—S2A	103.7 (1)	S1—C1—S2	123.1 (2)
C1—N1—C5	122.4 (2)	N1—C2—C3	103.8 (3)
C1—N1—C2	126.8 (2)	C4—C3—C2	104.7 (3)
C5—N1—C2	110.8 (2)	C3—C4—C5	105.0 (3)
N1—C1—S1	125.9 (2)	N1—C5—C4	103.5 (3)
N1—C1—S2	111.0 (2)		
C1—S2—S2A—C1A	87.7 (1)	N1—C2—C3—C4	−29.8 (5)
C5—N1—C1—S2	174.2 (2)	C2—C3—C4—C5	36.0 (6)
S2A—S2—C1—N1	173.8 (2)	C2—N1—C5—C4	8.9 (4)
C5—N1—C2—C3	12.8 (4)	C3—C4—C5—N1	−27.4 (5)

The structure was solved by direct methods and refined by full-matrix least squares. All the H atoms were located from difference maps and refined isotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93. Geometric calculations: *PARST* (Nardelli, 1983*b*).

The authors would like to thank the Malaysian Government, Universiti Kebangsaan Malaysia and Universiti Sains Malaysia for research grants Nos. 2-07-03-008 and 123-3417-2201, respectively. One of the authors (KS) thanks the Universiti Sains Malaysia for a Visiting Post Doctoral Research Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1200). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 953–955

(*S*)-1-Acetoxymethyl-2-acetyl-1,2,3,4-tetrahydro-6,7-dimethoxy-1-methylisoquinoline

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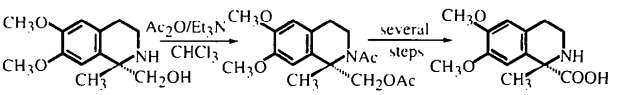
(*Received 26 June 1995; accepted 20 October 1995*)

Abstract

The title compound [(*S*)-2-acetyl-1,2,3,4-tetrahydro-6,7-dimethoxy-1-methyl-1-isoquinolinylmethyl acetate, $C_{17}H_{23}NO_5$] is a key chiral intermediate in the synthesis of some natural isoquinoline derivatives with a C1 quaternary centre. This diacetyl derivative has been proposed as a stable intermediate storage compound. The absolute structure has been verified.

Comment

In the course of our first enantioselective synthesis (Czarnocki, Suh, MacLean, Hultin & Szarek, 1992) of mammalian alkaloid (Collins, 1983), we prepared (*S*)-1,2,3,4-tetrahydro-1-hydroxymethyl-6,7-dimethoxy-1-methylisoquinoline, (1), as a key synthetic intermediate. This amino alcohol proved to be quite unstable, especially in solution. In order to avoid its extensive decomposition during storage, we decided to transform it into the title diacetyl derivative, (2), which appears to be indefinitely stable and may be transformed back into the parent amino alcohol by basic hydrolysis. A further synthetic sequence led to the synthesis of (*S*)-1,2,3,4-tetrahydro-6,7-dimethoxy-1-methylisoquinoline-1-carboxylic acid, (3), as a final product. The absolute stereochemistry of this compound was established by comparison with the results obtained by Chrzanowska, Schonenberger, Brossi & Flippen-Anderson (1987) for (*S*)-salsoline-1-carboxylic acid. In this report, we describe the X-ray crystal structure and absolute configuration of (2).



The optical purity of (2) is greater than 95%, as indicated by chiral HPLC (Czarnocki *et al.*, 1992), and the absolute configuration was confirmed as the expected *S* by refinement of the Flack (1983) enantiopole parameter to 0.14 (24). The C5–C10 aromatic ring is planar (r.m.s. deviation = 0.012 Å). The methoxy groups at the C6 and C7 atoms are slightly rotated around the C6—O4 and C7—O5 bonds (Fig. 1), the dihedral angles between the plane of the aromatic ring and the planes defined by atoms C6, O4, C17 and C7, O5, C18 being 15.7 (3) and 11.0 (3)°, respectively. The C4 atom lies almost in the plane of the aromatic ring, whereas atom C1 is slightly displaced from it [the deviations of atoms C4 and C1 from the ring plane are 0.028 (4) and −0.095 (3) Å, respectively]. Atoms C11 and C12, bonded to the chiral C1 atom, lie in the plane almost perpendicular to the mean plane of both rings, with the dihedral angle between the plane of the aromatic ring and the plane defined by atoms C11, C1 and C12 being 89.7 (1)°. The acetyl group at the N atom is planar (r.m.s. deviation = 0.004 Å) and only slightly rotated from the 'best plane' of both condensed rings (r.m.s. deviation = 0.200 Å), whereas the planar acetoxy group at the C11 atom (r.m.s. deviation = 0.000 Å) is almost

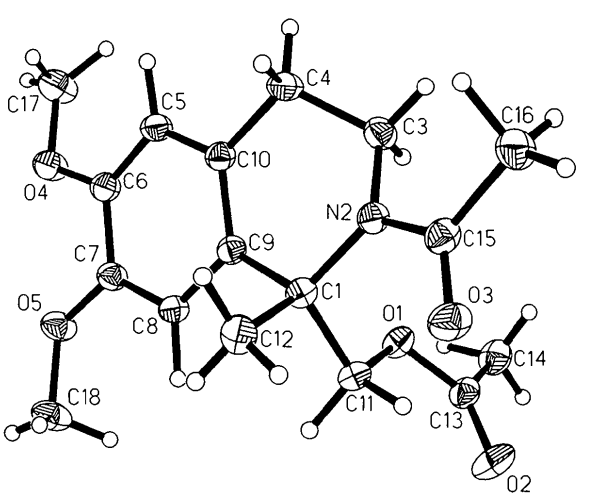


Fig. 1. The molecular structure of the title compound showing the atom-numbering scheme and 30% probability ellipsoids for non-H atoms.