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A Centric Thiuram Disulfide. Structure of Tetraisopropylthiuram Disulfide

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Abstract. $C_{14}H_{28}N_2S_4$, $M_r = 352\cdot6$, monoclinic, $P2_1/n$, $a = 6\cdot137\,(1)$, $b = 11\cdot392\,(2)$, $c = 13\cdot446\,(2)$ Å, $\beta = 91\cdot98\,(1)°$, $V = 939\cdot4\,(2)$ Å^3, $Z = 2$, $D_m = 1\cdot30\,(2)$, $D_x = 1\cdot25$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot5418$ Å, $\mu = 4\cdot41$ mm^{-1}, $F(000) = 380$, $T = 293$ K, final $R = 0\cdot041$ for 1631 observed reflections. The unusual structural features are (i) the C—S—S—C torsion angle of 180·0° and (ii) the S—S bond length of 2·069 (1) Å which is the longest observed in thiuram disulfides. The molecule is centrosymmetric. In the central part of the molecule, the C—S—S—C moiety adopts a strictly *trans* planar conformation. No intermolecular short contacts are observed.

Introduction. Thiuram disulfides are the immediate oxidation products of dithiocarbamic acids and are known to be formed as one of the products during redox complexation reactions of dithiocarbamates with metal ions like Te^{IV}, Se^{IV} *etc.* (Bode, Tusche & Wahrhausen, 1962; Fabiani, Spagna, Vaciago & Zambonelli, 1971; Schnabel, Deuten & Klar, 1980). In the course of our investigation on the diisopropyldithiocarbamate complexes of Te^{IV}, we noticed the formation of the thiuram disulfide. The structure determination was carried out to study the structural features of the disulfide, namely the S—S bond and the two torsion angles, C—S—S—C and N—C—S—S. Other structures of thiuram disulfide which have been reported are those of tetramethylthiuram disulfide (Maroy, 1967), tetraethylthiuram disulfide (Karle, Estlin & Britts, 1967), dipyrrolidyl disulfide (Geoffrey, Statham & White, 1983) and bis(4-morpholinethiocarbonyl) disulfide (Rout, Seshasayee & Aravamudan, 1982). For the first time we report a torsion angle of 180° in the free disulfide.

Experimental. The title compound was prepared by the controlled oxidation of sodium diisopropyldithiocarbamate by iodine dissolved in an aqueous solution of potassium iodide. The yellow solid formed was redissolved in ethyl acetate. This on slow evaporation at room temperature gave pale yellow needles, dimensions 0·975 × 0·450 × 0·225 mm; D_m by flotation in acetone/carbon tetrachloride; $P2_1/n$ from systematic absences; Enraf–Nonius CAD-4 diffractometer, Cu $K\alpha$ radiation, graphite monochromator; cell parameters by least squares from setting angles of 15 reflections with $60° \le 2\theta \le 100°$. 2032 reflections with $2° \le 2\theta \le 140°$ and $0 \le h \le 7$, $0 \le k \le 13$, $-16 \le l \le 16$ were collected using ω–2θ scan, two standard reflections measured every hour showed no significant change; correction for Lorentz, polarization and absorption effects, maximum and minimum transmission factors are 0·4301 and 0·1548 respectively; crystal bound by the faces (100), (0$\bar{1}$1), (012); 1631 reflections with $I > 3\sigma(I)$ used for structure determination; structure solved by direct methods using *SHELXS86* (Sheldrick, 1986); non-H atoms refined on F with anisotropic and H atoms with isotropic temperature factors; maximum electron density less than 0·3 e Å^{-3}, $R = 0\cdot041$, $wR = 0\cdot049$, $w = 1/[\sigma^2(F_o) + 0\cdot0037|F_o|^2]$, $(\Delta/\sigma)_{\max} = 0\cdot008$ and $S = 0\cdot8382$. Scattering factors used were those in *SHELXS86*.

Discussion. Table 1 contains the atomic coordinates and the thermal parameters of all non-H atoms.

Table 1. *Positional parameters and* U_{eq} (Å^2) *for non-*H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sin^2\beta(U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	U_{eq}
S1	0·1083 (1)	0·4309 (1)	0·5092 (1)	0·0474 (4)
S2	−0·0420 (1)	0·4530 (1)	0·2948 (1)	0·0459 (4)
N	0·2199 (3)	0·2847 (1)	0·3698 (1)	0·0386 (13)
C1	0·1030 (3)	0·3813 (2)	0·3822 (1)	0·0356 (14)
C2	0·0348 (5)	0·1778 (3)	0·2263 (2)	0·0627 (25)
C3	0·2457 (4)	0·2278 (3)	0·2707 (2)	0·0446 (18)
C4	0·2466 (6)	0·1079 (3)	0·4751 (3)	0·0746 (32)
C5	0·3410 (4)	0·2267 (2)	0·4534 (1)	0·0450 (15)
C6	0·3705 (5)	0·3053 (3)	0·2009 (2)	0·0632 (25)
C7	0·5820 (5)	0·2213 (4)	0·4366 (3)	0·0753 (30)

Table 2. *Bond lengths* (Å) *and angles* (°) *of non-*H *atoms with e.s.d.'s in parentheses*

C(1)—S(1)—S(1^i)	97·8 (1)	S(1)—C(1)	1·798 (3)
S(2)—C(1)—N	126·6 (2)	S(1)—S(1^i)	2·069 (1)
C(1)—N—C(3)	123·1 (2)	S(2)—C(1)	1·664 (3)
N—C(3)—C(2)	113·5 (3)	N—C(1)	1·327 (4)
N—C(3)—C(6)	111·7 (3)	N—C(3)	1·495 (3)
C(1)—N—C(5)	122·2 (2)	N—C(5)	1·483 (4)
C(3)—N—C(5)	114·6 (2)	C(2)—C(3)	1·517 (6)
N—C(5)—C(4)	111·2 (3)	C(3)—C(6)	1·515 (5)
N—C(5)—C(7)	111·9 (3)	C(4)—C(5)	1·505 (6)
C(2)—C(3)—C(6)	114·7 (3)	C(5)—C(7)	1·505 (5)
C(4)—C(5)—C(7)	112·3 (3)	S(1)—C(1)—S(2)	120·5 (2)
		S(1)—C(1)—N	112·9 (2)

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

Bond distances and angles are given in Table 2.* Fig. 1 shows the *ORTEP* (Johnson, 1965) plot of the molecule while Fig. 2 shows the packing of the molecules in the unit cell.

The crystal symmetry dictates that only half the molecule is unique, the two halves being related by an inversion center. The title compound adopts the *trans* conformation with an N—C—S—S torsion angle of −175·7 (2)°. The atoms C(1)—S(1)—S(1^i)—C(1^i) (i: x, $1-y$, $1-z$) in the central part of the molecule adopt a *trans* conformation. The observed S(1)—S(1^i) bond length is 2·069 (1) Å. The C—S—S—C torsion angle is 180·0°. Both these are unusual compared to those observed in other thiuram disulfides cited earlier. The S—S distances and the corresponding torsion angles are 2·009 Å and 88·0° in tetramethylthiuram disulfide, 2·00 Å and 96·4° in tetraethylthiuram disulfide, 2·002 Å and 87·9° in dipyrrolidylthiuram disulfide and 2·009 Å and 99·0° in bis(4-morpholinethiocarbonyl) disulfide. Simmons, Lundeen & Seff (1979) have reported a value of 180° for the C—S—S—C torsion angle in the Cu$^{\mathrm{I}}$ complex of (2-pyrimidyl) disulfide and Bor, Gervasio, Rossetti & Stanghellini (1978) have reported the same value in the organometallic compound (CO)$_9$Co$_3$CSSCCo$_3$(CO)$_9$. Hordvik (1966) reported a relationship between the S—S bond length and the C—S—S—C torsion angle. Shefter (1970) noted the lack of such a correlation. He found the S—S bond length to correlate with another torsion angle, X—C—S—S, X = C or N. The S—S bond length of the present compound does not support the X—C—S—S criterion of Shefter. The sum of the three angles around C(1) is almost 360° in accord with a planar structure. The sulfur valency angle C(1)—S(1)—S(1^i) is 97·8°. The sum of the angles around each N atom shows that the three

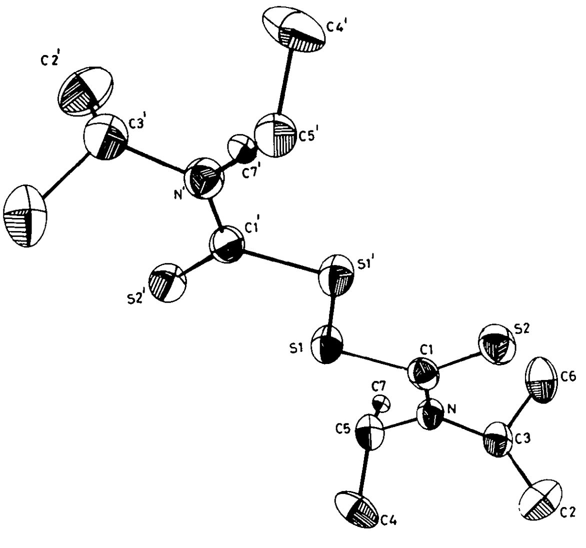

Fig. 1. *ORTEP* plot of the molecule.

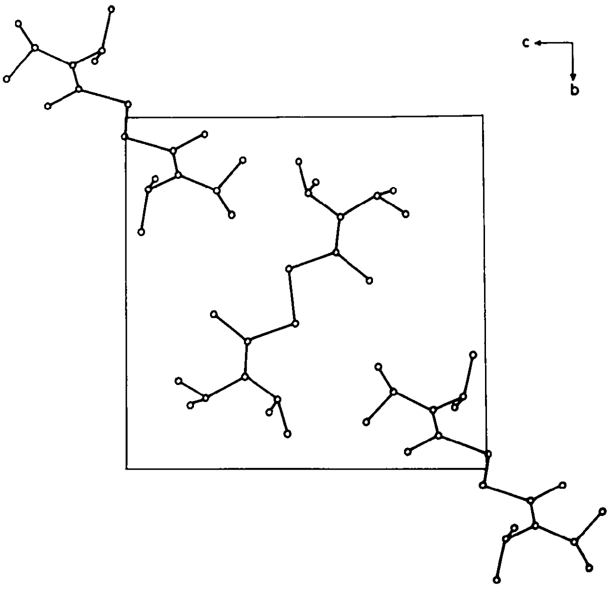

Fig. 2. Packing of the molecules in the unit cell.

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* Lists of structure factors, H-atom parameters and anisotropic thermal parameters of non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52473 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonds to each N atom are coplanar rather than in a pyramidal arrangement. As in the other thiuram disulfides, the C—N bond adjacent to the S atom is quite short while the other C—N bond lengths are long. No intermolecular short contacts are observed. In summary, there are two unusual structural features with respect to the previously reported thiuram disulfides. Whether the long S—S bond leads to greater chemical reactivity is being investigated.

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Structure of κ-Agonist, U-50488

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Abstract. $C_{19}H_{26}Cl_2N_2O.CH_3SO_3H.CH_3OH$, $M_r = 497{\cdot}44$, triclinic, $P1$, $a = 12{\cdot}276$ (4), $b = 12{\cdot}398$ (4), $c = 8{\cdot}841$ (2) Å, $\alpha = 99{\cdot}37$ (6), $\beta = 90{\cdot}86$ (8), $\gamma = 109{\cdot}64$ (4)°, $V = 1246$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}326$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 34·28 mm^{-1}, $F(000) = 528$, $T = 295$ K, $R = 0{\cdot}0482$ for 3813 reflections with $F > 3\sigma F$. *trans*-(+)-3,4-Dichloro-*N*-methyl-*N*-[2-(1-pyrrolidinyl)cyclohexyl]-phenylacetamide (U-50488) methane sulfonic acid was cocrystallized with methanol. The pyrrolidine ring is in a protonated state and forms an ion pair with methanesulfonate. The latter molecule is further linked with methanol solvent *via* a hydrogen bond. The molecule takes an opened conformation to avoid short contacts among the three bulky rings.

Introduction. Conformational studies for μ- and δ-opioid receptor selective antagonists or agonists have provided much information on the structure–function relationship of opioid receptors (Hansen & Morgan, 1984). However, it is well known that there are several opioid sub-receptors other than μ- and δ-receptors. To understand the multifarious functions of the opioid receptor, the stable conformation of the ligand which exhibits high selectivity to each opioid sub-receptor should be elucidated. Some morphine derivatives display analgesic actions, and one of them, U-50488, has high selectivity to the so-called κ-opioid receptor (Vonvoigtlander, Lahti & Ludens, 1983). As part of a series of structural studies of opioid ligands, we report here the crystal structure of U-50488.

Experimental. Cubic crystals were grown from a methanol/ethyl acetate solution of U-50488 methanesulfonic acid. Unit-cell parameters were refined using 22 reflections ($47 \leq 2\theta \leq 58°$) on a Rigaku AFC-5 diffractometer. Intensity data were collected to $\sin\theta/\lambda = 0{\cdot}588$ Å^{-1} using Cu $K\alpha$ radiation with the θ–2θ scan mode, from a crystal of dimensions 0·4 × 0·4 × 0·3 mm. The data were corrected for Lorentz and polarization effects. An absorption correction was not applied. 4275 independent reflections were measured for $-14 \leq h \leq 14$, $-14 \leq k \leq 14$ and $-10 \leq l \leq 0$, in which 3813 had $F > 3\sigma(F)$. Four reflections monitored periodically during the data correction showed negligible variation indicating instrumental and crystal stability. The structure was solved by direct methods using *MULTAN*87 (Debaerdemaeker, Germain, Main,