The conformation at the C(7)—C(8) bond is markedly different for the (2*R*,3*S*) isomer compared to the other two analogs. The C(6)—C(7)—C(8)—C(9) torsion angle of −61·0 (5)° contrasts with the transplanar arrangement observed in the (2*S*,3*S*) and (2*S*,3*R*) structures for which the torsion angles are 177·6 (5) and 175·9 (4)°, respectively. The observed conformations presumably reflect the most favorable arrangements dictated by formation of H-bonding interactions of the hydroxyl group at C(8).

The crystal structures are stabilized by H-bonding interactions which differ between structures. In the (2*S*,3*R*) structure an intramolecular H bond exists between the carbonyl O(2) atom and the hydroxyl group at C(8). The associated metrical parameters are O(1)···O(2) = 2·700 (3), HO(1)···O(2) = 1·95 (5) Å with an angle at H of 151 (4)°. In the (2*R*,3*S*) structure there is an intermolecular H bond between the donor atom O(1) and the acceptor carbonyl O. The associated metrical parameters are O(1)···O(2) = 2·855 (4) Å, HO(1)···O(2) = 2·14 (5) Å with an angle at H of 159 (5)°. One intermolecular H bond also exists in the (2*S*,3*S*) structure with associated metrical parameters of O(1)···O(2) = 2·711 (3) Å, HO(1)···O(2) = 1·90 (4) Å and an angle at H of 176 (3)°.

The disorder model for the isopropyl methyl group C(14) in the (2*S*,3*S*) structure, while successfully modeling the electron density of the data set, is less than satisfying structurally. In particular, atom C(14) is not in a tetrahedral relationship relative to C(13). Large extensions of the thermal ellipsoids for C(13) and C(12) suggest a disorder in the atomic position for these atoms as well, although no separate occupancy sites could be resolved. Since there are no particularly close intermolecular contacts to explain the observed disorder [shortest intermolecular contacts are 3·54 (2) and 3·93 (1) Å for atoms C(14′) and C(14), respectively], a possible explanation for the current observations is that restrictions on the vibrational and librational motion of this isopropyl group are minimal in an open space within the solid-state structure.

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Structure of Tetramethylthiuram Disulfide (1) and Refinement of Tetraethylthiuram Disulfide (2)

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Abstract. (1), $C_6H_{12}N_2S_4$, $M_r = 240$, monoclinic, $C2/c$, $a = 9.653$ (1), $b = 9.923$ (1), $c = 11.804$ (2) Å, $\beta = 99.38$ (1)°, $V = 1115.5$ (4) Å^3, $Z = 4$, $D_m = 1.45$ (3), $D_x = 1.43$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0.774$ mm^{-1}, $F(000) = 504$, $T = 300$ K, final $R = 0.038$ for 1034 observed reflections. (2), $C_{10}H_{20}N_2S_4$, $M_r = 296$, monoclinic, $P2_1/c$, $a = 11.108$ (2), $b = 15.873$ (2), $c = 8.637$ (3) Å, $\beta = 92.55$ (2)°, $V = 1521.3$ (5) Å^3, $Z = 4$, $D_m = 1.29$ (3), $D_x = 1.30$ Mg m^{-3}. λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0.580$ mm^{-1}, $F(000) = 632$, $T = 300$ K, final $R = 0.036$ for 2850 observed reflections. The corresponding

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bond lengths and angles in the two compounds agree. The C=S double bonds and C—S single bonds in the molecules have average lengths 1·647 (1)/1·643 (2) and 1·805 (1)/1·823 (2) Å respectively. The C—N bonds (average 1·330 Å) are significantly shorter than the normal single bond, possibly attributable to π delocalization. Molecules can be described as two planar portions connected through an S—S single bond with a dihedral angle of ~93°. However, the two structures do differ in their conformation around the S—S bond in a left- or right-handed sense.

Introduction. Tetraethylthiuram disulfide (2) is a useful drug in the treatment of chronic alcoholism. The crystal structure of (2) was previously studied with photographic data (Karle, Estlin & Britts, 1967). Because of the interesting S—S bond and planar arrangement for half of the molecule, $-S_2CNC_2-$, the structure analyses of both tetramethyl and tetraethyl derivatives were undertaken to clarify the molecular structures as well as the molecular conformations.

Experimental. (1), tetramethylthiuram disulfide, was prepared from $HNMe_2$ and CS_2 (Cummings & Simmons, 1928). Suitable single crystals obtained by evaporation from C_2H_5OH solution. Crystal 0·2 × 0·2 × 0·3 mm. CAD-4 diffractometer. D_m by flotation (KI/H_2O). Absorption corrections according to experimental ψ rotation; normalized transmission coefficients 0·94–1·00. $2\theta_{max} = 60°$, $-13 \leq h \leq 13$, $0 \leq k \leq 13$, $0 \leq l \leq 16$, 2θ scan range $(1·6 + 0·7\tan\theta)°$. Unit-cell parameters from least-squares refinement of 25 reflections with $20 < 2\theta < 25°$. 3 monitored reflections; variation < 1%. 1623 unique reflections measured, 1034 with $I > 3\sigma(I)$, $R(F) = 0·038$, $wR(F) = 0·049$, $S = 2·1$, $w = 1/[\sigma^2(F_o) + (0·01F_o)^2]$. Structure solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Atomic parameters refined by least squares. H atoms located in ΔF map and refined. Parameters of H atoms fixed before final cycles of full-matrix least-squares refinement of non-H atoms. Final $(\Delta/\sigma)_{max} = 0·1$. Peaks in final $\Delta\rho$ map $< \pm 0·3$ e Å^{-3}. Secondary isotropic extinction coefficient 4·5 (length in μm). Atomic scattering factors calculated with analytical form using coefficients given in *International Tables for X-ray Crystallography* (1974). Anomalous dispersion for non-H atoms applied according to *International Tables for X-ray Crystallography* (1962). Programs from *NRCC* (Gabe & Lee, 1981) and *SDP* (Enraf–Nonius, 1979).

(2), crystal 0·3 × 0·3 × 0·4 mm. D_m by flotation (KI/H_2O). Absorption applied according to ψ rotation; transmission coefficient range 0·94–1·00. $2\theta_{max} = 50°$, $-15 \leq h \leq 15$, $0 \leq k \leq 22$, $0 \leq l \leq 12$, 2θ scan range $(1·6 + 0·7\tan\theta)°$. Unit cell: 25 reflections with $20 < 2\theta < 45°$. 3 monitored reflections, variation < 3%. 4424 unique reflections measured, 2850 with $I > 3\sigma(I)$. $R(F) = 0·036$, $wR(F) = 0·028$, $S = 2·6$, $w = 1/\sigma^2(F_o)$. Atomic parameters taken from previous work (Karle, Estlin & Britts, 1967) and refined by least squares. H atoms located on difference Fourier map and then refined. Final $(\Delta/\sigma)_{max} = 0·05$. Peak in final $\Delta\rho$ $< \pm 0·3$ e Å^{-3}. Secondary-extinction coefficient 5·5 (length in μm).

Discussion. The molecular structures and bond distances of both compounds are shown in Figs. 1(*a*) and 1(*b*). The fractional atomic coordinates and equivalent isotropic thermal parameters of non-H atoms are given in Table 1.* Selected bond angles are listed in Table 2. The corresponding interatomic distances and angles of (1) and (2) are the same within the e.s.d.'s except the C—S single bonds of (2) which are somewhat longer than that of (1). The C—S bond length does vary significantly between compounds, *e.g.* 1·729 Å in 3*H*-1,2-dithiole-3-thiones (Wei, 1983; Wang, Lin & Wei, 1985) to *e.g.* 1·862 Å in thiourea *S*,*S*-dioxide

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43038 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

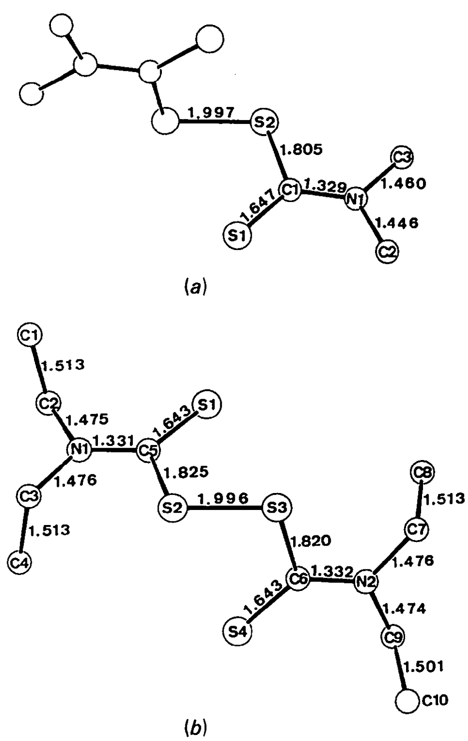

Fig. 1. The molecular structure with bond distances and atom labelling for (*a*) (1) and (*b*) (2). E.s.d.'s of (1) 0·001 Å; e.s.d.'s of (2): S—S 0·001 Å, four ethyl C—C 0·003 Å, remainder 0·002 Å.

(Chen & Wang, 1984*b*) and dibenzyl disulfide (Lee & Bryant, 1969); as does the C=S double bond, *e.g.* 1·712 Å in thiourea (Mullen & Hellner, 1978) and 1·655 Å in a 3*H*-1,2-dithiol-3-thione (Wei, 1983). All the C=S double-bond lengths in the two title compounds are about the same and belong to the shorter end of the range (1·64–1·71 Å) found in the literature. The C—S single-bond lengths in these two compounds are, on the other hand, close to the longer end of the range (1·73–1·87 Å). The configurations around C1 in (1) and C5, C6 in (2) are planar (sp^2) with S—C—N (av. 112°) much smaller than S=C—S (av. 122·5°) and S=C—N (av. 125·5°, see Table 2). Such an asymmetric arrangement was also observed in a thiourea coordination compound (Lis & Starynowicz, 1985). The C—N bond lengths adjacent to the S atoms in these two compounds are obviously shorter than the normal C—N single bond which appeared in the amine substituents of the same molecule. Some degree of π delocalization is believed to exist in such a planar molecule (Peng, Wang & Chiang, 1984). The configurations around the N atoms are planar, too, with C(*R*)—N—C(*R*) less than the other two C(*R*)—N—C(S) angles.

Table 1. *The fractional atomic coordinates and equivalent isotropic thermal parameters for tetramethylthiuram disulfide* (1) *and tetraethylthiuram disulfide* (2)

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq} (Å^2)
(1)				
S1	0·19534 (3)	0·39158 (3)	0·20335 (2)	4·36 (1)
S2	−0·02813 (3)	0·17379 (3)	0·16477 (3)	5·40 (2)
N1	0·06057 (9)	0·31049 (9)	0·00167 (8)	4·18 (5)
C1	0·0825 (1)	0·3004 (1)	0·1155 (1)	3·43 (4)
C2	0·1385 (1)	0·4055 (1)	−0·0563 (1)	5·63 (7)
C3	−0·0415 (1)	0·2305 (2)	−0·0752 (1)	6·42 (10)
(2)				
S1	0·33138 (6)	0·32794 (4)	0·22721 (9)	4·92 (4)
S2	0·17073 (5)	0·45307 (4)	0·05163 (7)	3·76 (3)
S3	0·32619 (5)	0·51472 (4)	0·08606 (7)	3·78 (3)
S4	0·17307 (6)	0·57822 (5)	0·34316 (9)	5·37 (4)
N1	0·0981 (1)	0·3071 (1)	0·1572 (2)	3·1 (1)
N2	0·4045 (1)	0·6139 (1)	0·3118 (2)	3·5 (1)
C1	0·1297 (2)	0·1559 (1)	0·1070 (3)	4·5 (1)
C2	0·1020 (2)	0·2221 (1)	0·2262 (3)	3·8 (1)
C3	−0·0225 (2)	0·3360 (1)	0·1013 (2)	3·5 (1)
C4	−0·0881 (2)	0·3796 (2)	0·2287 (3)	4·8 (1)
C5	0·1974 (2)	0·3538 (1)	0·1538 (2)	3·1 (1)
C6	0·3042 (2)	0·5745 (1)	0·2625 (2)	3·2 (1)
C7	0·5226 (2)	0·6035 (1)	0·2421 (3)	3·9 (1)
C8	0·5914 (2)	0·5301 (2)	0·3143 (3)	4·9 (1)
C9	0·4038 (2)	0·6670 (2)	0·4517 (3)	4·7 (1)
C10	0·3636 (2)	0·7552 (2)	0·4141 (4)	6·4 (2)

Table 2. *Selected bond angles* (°) *for tetramethylthiuram disulfide* (1) *and tetraethylthiuram disulfide* (2)

(1)							
S2	S2	C1	104·28 (3)	C1	N1	C2	121·21 (9)
C1	N1	C3	124·5 (1)	C2	N1	C3	114·3 (1)
S1	C1	S2	123·00 (6)	S1	C1	N1	125·09 (8)
S2	C1	N1	111·91 (7)				
(2)							
S3	S2	C5	103·33 (7)	S2	S3	C6	103·48 (7)
C2	N1	C3	115·2 (1)	C2	N1	C5	120·6 (1)
C3	N1	C5	124·2 (1)	C6	N2	C7	124·3 (1)
C6	N2	C9	119·8 (1)	C7	N2	C9	115·8 (1)
N1	C2	C1	111·4 (1)	N1	C3	C4	111·3 (1)
S1	C5	S2	121·8 (1)	S1	C5	N1	126·2 (1)
S2	C5	N1	112·0 (1)	S3	C6	S4	121·9 (1)
S3	C6	N2	111·8 (1)	S4	C6	N2	126·3 (1)
N2	C7	C8	111·1 (1)	N2	C9	C10	111·6 (2)

The S—S bonds in this work are some of the shortest S—S single bonds observed. Typical S—S single bonds can be represented by the bond lengths of cyclooctasulfur 2·045 Å* (Coppens, Yang, Blessing, Cooper & Larsen, 1977) and of some disulfide compounds, *e.g.* 2·026 (1) Å in bis(phenylsulfonyl) trisulfide (Chen & Wang, 1984*a*) and 2·038 (4) Å in a thiourea coordination complex (Lis & Starynowicz, 1985). Other similar short ones are 1·987, 1·997 Å in BaS_2O_3 and $(NH_4)_2S_2O_3$ (Teng, Fuess & Bats, 1979; Armagan, 1983). The structure can be described as two planar —S—(CS)—N(C)$_2$ moieties connected by an S—S single bond with a dihedral angle of 92·98 (1) and 94·05 (3)° [93·00 (1) and 93·94 (3)° if planes are defined by —S_2CN only] for (1) and (2) respectively. As mentioned in the previous work (Karle, Estlin & Britts, 1967), there are rotations of 4·0 (2), 4·8 (1)° around C6—N2 and C5—N1 in (2) but only 0·9 (1)° in (1). This configuration about the S—S bonds is similar to that in H_2S_2 and other disulfides, 94·4, 96·1° (Lis & Starynowicz, 1985). Although the magnitudes of the dihedral angles between the planes and the torsional angle C—S—S—C are roughly the same for both compounds, the exact conformations could be described with a left- or right-handed sense as given for the disulfides of cystine salts (Rajeswaran & Parthasarathy, 1985; Donzel, Kamber, Wuthrich & Schwyzer, 1972), *i.e.* with a positive or negative dihedral angle relative to a certain plane. The molecular conformations of the two title compounds are different in this way; Fig. 2 is a composite drawing of the two molecules with part of each molecule [S1=C1(S2)(N1) of (1) and S4=C6(S3)(N2) of (2)] superimposed, then the rest of each molecule is nicely demonstrated as a left- or right-hand rotation from this plane. Thus, (1) has an exact twofold molecular symmetry at the mid-point of the S—S bond but (2) does not.

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* This bond distance is from the low-temperature data, the corresponding room-temperature distance should be 0·02 Å shorter.

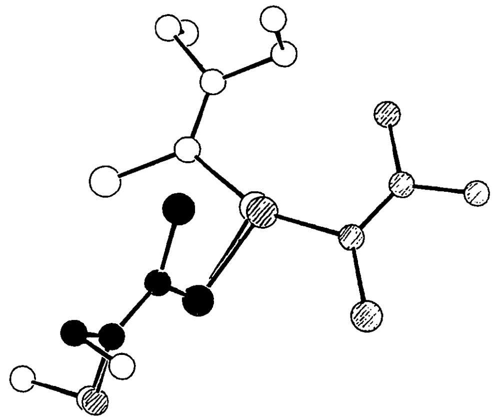

Fig. 2. Molecular conformations of (1) and (2). The shaded atoms refer to (1), the unshaded ones to (2), with superimposed atoms black.

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5,6-Benzochroman-4-one*

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Abstract. $C_{13}H_{10}O_2$, $M_r = 198 \cdot 2$, orthorhombic, *Pccn*, $a = 11 \cdot 6430$ (3), $b = 19 \cdot 4230$ (4), $c = 8 \cdot 5480$ (2) Å, $V = 1933 \cdot 06$ (8) Å^3, $Z = 8$, $D_m = 1 \cdot 35$ (2) (flotation), $D_x = 1 \cdot 362$ (1) Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1 \cdot 5418$ Å, $\mu = 0 \cdot 698$ mm^{-1}, $F(000) = 832$, $T = 294$ K, $R = 0 \cdot 052$ for 1443 observed reflections. The dihydropyran ring system is a modified half-chair distorted toward the *d,e* diplanar arrangement. The benzene ring common to the naphthalene and benzopyran groups deviates from planarity owing to fusion strains.

Introduction. The benzopyran nucleus is a widely prevalent ring system, present in a variety of naturally occurring compounds like carbohydrates, xanthones, flavones *etc.* The crystal structure determination of the title compound is part of a research programme which is being carried out on the conformation of the oxygen heterocyclic compounds.

Experimental. The title compound was prepared according to the procedure of Kasturi & Arunachalam (1970). Crystals from benzene–hexane mixture,

* IUPAC name: 2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-one. *Cf. Acta Cryst.* (1986). C**42**, 1043–1044 for the structure of a similar compound.
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‡ Contribution No. 682.

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