play an important role in the molecular packing. There are five intramolecular contacts between the ring N atoms and the O atoms of the ester groups: $N(3)\cdots O(18)$ 2·601 (7), $N(4)\cdots O(22)$ 2·560 (8), $N(7)\cdots O(21)$ 2·814 (9), $N(12)\cdots O(26)$ 2·627 (6) and $N(13)\cdots O(29)$ 2·633 (8) Å. In addition there is a short contact between O(17) and O(30) [3·182 (6) Å] of the ester groups of rings A and C respectively.

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Reinvestigation of the Structure of Thiourea S,S-Dioxide, $CH_4N_2O_2S$

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Abstract. $M_r = 432·46$, orthorhombic, *Pnma*, $a = 10·644$ (2), $b = 10·106$ (3), $c = 3·9348$ (4) Å, $V = 423·27$ Å^3, $Z = 4$, $D_m = 1·66$, $D_x = 1·697$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·7093$ Å, $\mu = 5·89$ cm^{-1}, $F(000) = 224$, $T = 298$ K, $R = 0·046$ for 562 observed reflections. The C—S bond length 1·8615 (4) Å, close to that of the previous investigation, is much longer than that in thiourea at 123 K [1·716 (8) Å]. This indicates weakening of the C—S bond upon the oxidation of thiourea. The two crystallographically independent N—H⋯O hydrogen bonds are roughly equal [2·84 Å].

Introduction. The structure of the title compound has been determined by Sullivan & Hargreaves (1962) using Weissenberg photographs. This work presents the redetermination using a CAD-4 diffractometer in order to obtain better parameters. We are interested in the rather long C—S bond length, $-SO_2$ conformation and the intermolecular hydrogen bondings.

Experimental. Sample prepared by oxidation of thiourea using hydrogen peroxide. Crystals grown from water, $0·4 \times 0·47 \times 0·13$ mm, CAD-4 diffractometer, unit cell: 20 reflections, 2θ range 15 to 40°. D_m by flotation ($CHCl_3/CHBr_3$). $2\theta_{max} = 60°$. Two equivalent sets hkl, $\bar{h}k\bar{l}$ averaged to yield 649 unique reflection

data with $\Sigma(\Delta I/\bar{I})$ of 0·6%, where ΔI indicates difference between the sets, $\bar{I}$ the arithmetic average intensity of the equivalent sets; the summation is over all the reflections measured. $h \le 14$, $k \le 14$, $l \le 4$. Three standard reflections monitored every 0·5 h; variation 2%. 562 observed with $I \ge \sigma(I)$. Empirical absorption correction based on ψ scans from four reflections with 2θ values from 8 to 42°. H atoms (from ΔF map) refined isotropically, remainder anisotropically, function minimized $\Sigma w(F_o - F_c)^2$; $R = 0·046$, $R_w = 0·027$, $S = 3·89$; weighting scheme from counting statistics. $(\Delta/\sigma)_{max} = 0·9$ (for H atom). Peaks on final $\Delta\rho$ map 0·95 e Å^{-3} (around S atom). Secondary-extinction coefficient 0·241 (length in μm). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computing programs: NRCC *SDP* PDP-11 package (Gabe & Lee, 1981).

Discussion. The atomic coordinates and isotropic temperature factors are shown in Table 1.† The bond lengths and angles are approximately the same as those of the previous work (Sullivan & Hargreaves, 1962). The only significant differences are in the hydrogen

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† Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39624 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and isotropic temperature factors* (Å^2) *of thiourea dioxide*

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

	x	y	z	B_{eq}/B
S	0·45975 (1)	0·25	0·36497 (3)	3·02 (1)
C	0·11194 (3)	0·25	0·9019 (1)	2·57 (2)
N	0·16367 (2)	0·13639 (2)	0·8390 (1)	3·43 (1)
O	0·40051 (1)	0·12865 (2)	0·50769 (4)	3·48 (1)
H(1)	0·2533 (2)	0·1306 (2)	0·7437 (6)	6·4 (1)
H(2)	0·1206 (2)	0·0680 (2)	0·8816 (6)	3·2 (1)

bonds where the two crystallographically independent N···O distances are roughly equal (2·84 Å). The N—H(1)···O bond is believed to be stronger than N—H(2)···O from the closer value of the N—H(1)···O angle to 180° and the lengthening of the N—H(1) bond. A comparison between this work, the previous one and the structure of thiourea at 123 K (Mullen & Hellner, 1978) is given in Table 2. The C—S bond is obviously lengthened in the title compound which indicates single-bond character in the dioxide.

Table 2. *Comparison between thiourea dioxide and thiourea*

	Thiourea dioxide (Sullivan & Hargreaves, 1962)	Thiourea dioxide (This work)	Thiourea (123 K) (Mullen & Hellner, 1978)[*]
C—S	1·85 (2) Å	1·8615 (4) Å	1·716 (8) Å 1·712 (8)
S—O	1·49 (8)	1·4890 (4)	
C—N	1·310 (8)	1·2972 (4)	1·332 (6) 1·334 (8)
N—H(2)	1·27 (9)	0·846 (2)	0·80 (6) 0·93 (6)
N—H(1)	1·09 (8)	1·027 (2)	1·00 (6) 0·93 (5)
N···O	2·85 (2)	2·8392 (5)	
∠N—H(1)···O	166 (7)°	170·4 (2)°	
H(1)···O	1·8 (1) Å	1·821 (2) Å	
H(2)···O	1·6 (1)	2·060 (2)	
N···O	2·84 (2)	2·8429 (9)	
∠N—H(2)···O	161 (6)°	153·5 (1)°	

[*] Two independent molecules.

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Structure of the *tert*-Butyl-*ortho*-tolylcarbinol, 2,2,4,4-Tetramethyl-3-(2-methyl-4-methoxyphenyl)pentan-3-ol, C₁₇H₂₈O₂

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Abstract. $M_r = 264.41$, triclinic, $P\bar{1}$, $a = 8.259$ (3), $b = 7.888$ (3), $c = 13.493$ (3) Å, $\alpha = 102.2$ (3), $\beta = 96.8$ (3), $\gamma = 110.1$ (3)°, $V = 789.2$ (5) Å³, $Z = 2$, $D_x = 1.113$ (1), $D_m = 1.12$ (1) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70926$ Å, $\mu = 0.763$ cm⁻¹, $F(000) = 292$, room temperature. Final $R = 0.05$ for 1736 observed reflections. The geometry indicates severe overcrowding at the alcoholic C atom. The molecular geometry agrees quite well with that predicted by the molecular-mechanics method. The molecule has the synperiplanar

conformation with the hydroxyl group rotated 11·6° out of the plane of the phenyl ring.

Introduction. Over the last few years much attention has been given to steric effects and, in particular, to their influence upon reactivity. One aspect of this work is concerned with highly congested molecules, containing usually one or more *tert*-butyl groups, which show interesting and often unexpected behaviour. Crystallographic studies of such compounds, though not