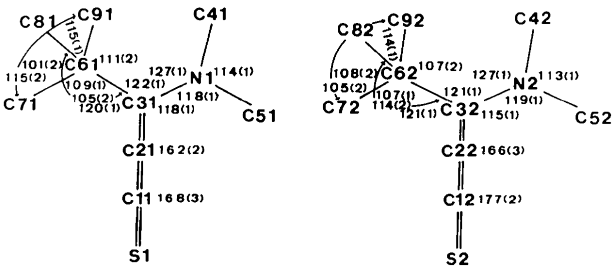

Fig. 2. Angles (°) with standard deviations.

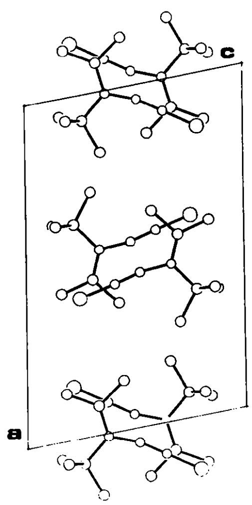

Fig. 3. Title structure viewed along **b**.

Discussion. The interatomic distances and bond angles are given in Figs. 1 and 2.

The distances in the cumulated chain are in agreement with an electronic structure involving an important contribution of the resonance form (II).

C(1)–C(2) (1·23 Å) is much shorter than that observed in a non-conjugated cumulated chain. It is comparable to a triple bond.

C(1)–S is equal to the sum of the covalent radii of a C_{sp} and an S atom.

C(2)–C(3) and C(3)–N indicate conjugation between these bonds. In addition, the cumulated chain and dimethylamino group are coplanar.

The packing of the molecules is shown in Fig. 3.

The authors thank Professor H. G. Viehe for suggesting the problem, M. Parmantier for providing the crystals, and Dr G. Evrard for the data collection. JG and JPD are indebted respectively to the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture and to the Fonds National Belge de la Recherche Scientifique, for financial assistance.

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Identification and Structure of 2-Pivaloylmethylene-4-pivaloyldithiolene

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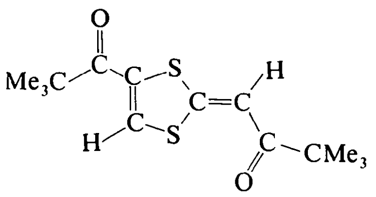
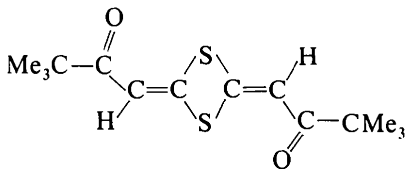
Abstract. $C_{14}H_{20}O_2S_2$, $M_r = 284{\cdot}4$, monoclinic, space group $P2_1/c$, $a = 6{\cdot}080$, $b = 15{\cdot}406$, $c = 9{\cdot}042$ Å, $\beta = 114{\cdot}28°$, $V = 772{\cdot}0$ Å^3, $Z = 2$, $D_x = 1{\cdot}22$ g cm^{-3}, $F(000) = 304$. The structure was refined by rigid-body full-matrix least squares to an R of 0·097 for 1015 counter reflexions. The non-centrosymmetric molecules are situated on inversion centres and are thus disordered.

Introduction. The hydrolysis product of the thia-1,2,3-triene, whose structure has been described in the preceding paper (Galloy, Declercq & Van Meerssche, 1978), is identified as 2-pivaloylmethylene-4-pivaloyldithiolene (I) and not a desaurine (II) as would be expected by analogy with the hydrolysis of ketenes $R_2C{=}C{=}S$ (Ulrich, 1967).



(I)



(II)

The cell constants were determined from 2θ values of six reflexions. Intensities of 1243 reflexions were measured on a Picker semi-automatic diffractometer with Ni-filtered Cu $K\alpha$ radiation (λ = 1·54242 Å) and the ω–2θ scan method ($\Delta 2\theta = \pm 1{\cdot}2°$, $2\theta_{max}$ = 126°); of these, 1015 with $I > 2{\cdot}5\sigma(I)$ were included in the refinement.

The structure was solved by the heavy-atom method. A Fourier map based on the coordinates of the S atom revealed the structure of the desaurine (II). However, the refinement gave a distorted molecule. A new Fourier synthesis based on the coordinates of the S atom and the pivaloyl group gave the result shown in Fig. 1. As the non-centrosymmetric molecule is on a symmetry centre, the structure must be disordered. Refinement was by rigid-body least squares (André, Fourme & Renaud, 1971). Calculations were performed with the *ORION* program. The final R was 0·097; the weighted R was 0·123. θ_1, θ_2 and θ_3 have the values 189·97 (10), −56·60 (5) and 80·83 (8)°. The coordinates of the centre of gravity are −0·0144 (8), −0·0057 (3) and −0·0064 (4). The atomic coordinates and the computed U_{ij} (Schomaker & Trueblood, 1968) are reported in Table

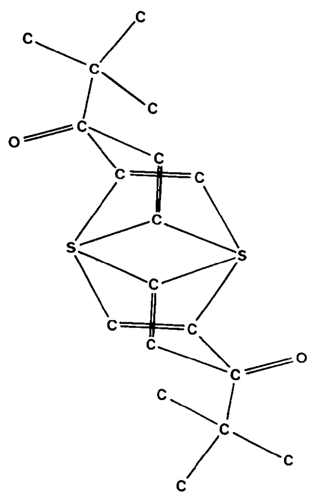


Fig. 1. Superposition of the two possible orientations of the molecule.

Table 1. *Final coordinates* (× 10⁴) *and anisotropic thermal parameters* (Å² × 10³)

The anisotropic temperature factor is of the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	−2553 (5)	−167 (3)	−464 (5)	37	64	73	−3	23	−8
S(2)	2502 (5)	117 (3)	201 (5)	39	80	69	−10	24	−11
C(1)	195 (5)	257 (3)	761 (5)	38	51	59	−1	19	4
C(2)	472 (5)	722 (3)	2083 (5)	46	53	59	−2	22	4
C(8)	−1510 (5)	−678 (3)	−1867 (5)	37	54	64	0	19	−1
C(9)	820 (5)	−536 (3)	−1589 (5)	39	69	68	−5	23	−7
C(31)	2702 (5)	1117 (3)	3117 (5)	52	63	58	−8	20	1
C(32)	−3304 (5)	−1178 (3)	−3178 (5)	41	64	74	−3	19	−10
C(41)	2905 (5)	1548 (3)	4639 (5)	67	64	58	−8	23	1
C(42)	−3160 (5)	−1645 (3)	−4581 (5)	51	66	74	−2	20	−12
C(51)	834 (5)	2289 (3)	4067 (5)	85	62	66	−1	27	−4
C(52)	−1368 (5)	−2391 (3)	−3996 (5)	66	68	84	6	25	−15
C(61)	1842 (5)	885 (3)	5515 (5)	101	69	62	−13	37	2
C(62)	−2539 (5)	−955 (3)	−5665 (5)	88	77	67	−9	26	−12
C(71)	5526 (5)	1767 (3)	5873 (5)	75	98	67	−14	17	−14
C(72)	−5421 (5)	−2120 (3)	−5418 (5)	58	87	92	−13	22	−30
O(1)	4521 (5)	1023 (3)	2760 (5)	49	98	73	−19	23	−19
O(2)	−5291 (5)	−1170 (3)	−3110 (5)	41	95	96	−12	24	−32

Table 2. *Rigid-body thermal parameters*

The translational, **T**, rotational, **L**, and correlation, **S**, tensors are referred to a Cartesian coordinate system defined by unit vectors **â**, **b̂*** and **â** × **b̂***.

T (× 10^2) (Å^2)	3·72 (9)	−0·22 (3)	−0·62 (4)
		5·15 (15)	0·33 (7)
			5·96 (13)
L (× 10^2) (rad^2)	0·09 (1)	−0·03 (1)	−0·05 (1)
		0·56 (3)	0·61 (3)
			0·98 (5)
S (× 10^4) (Å rad)	0 (6)	2 (4)	−15 (4)
	−2 (3)	12 (6)	5 (3)
	−17 (5)	26 (7)	−12 (0)
R.m.s. amplitudes (Å) along principal axes of **T**	0·25	0·22	0·19
R.m.s. amplitudes (°) along principal axes of **L**	6·81	2·06	2·71

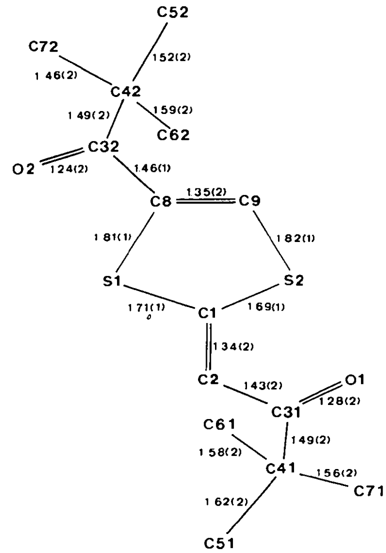


Fig. 3. Bond distances (Å) with standard deviations.

1. Rigid-body thermal parameters are given in Table 2.* All other computations were performed with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The weighting scheme was $w = (3{\cdot}01 + |F_o| + 0{\cdot}022|F_o|^2)^{-1}$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

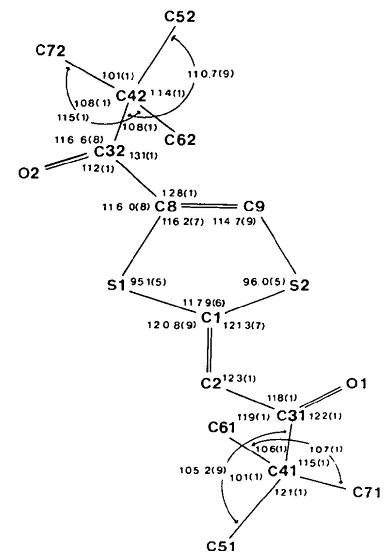


Fig. 4. Angles (°) with standard deviations.

Discussion. A perspective drawing of the molecule with inertia axes is shown in Fig. 2. Non-hydrogen atoms are represented by 50% probability thermal ellipsoids (Johnson, 1965). The bond lengths and angles are shown in Figs. 3 and 4. Except for the *tert*-butyl substituent, the molecule is planar within experimental error. The *s-cis* configuration about C(2)—C(31) and C(8)—C(32) is favourable to S···O interactions. Indeed, the intramolecular distances S(1)···O(2) [2·76 (1) Å] and S(2)···O(1) [2·54 (1)Å] lie between a single-bond length (1·65 to 1·70 Å) and the sum of the van der Waals radii (3·05 Å).

Fig. 5 shows the packing of the molecules. Only one molecular orientation is drawn.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33129 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

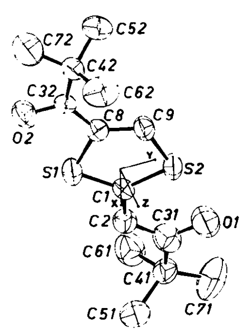


Fig. 2. The molecule drawn relative to its inertial axes.

The authors thank Professor H. G. Viehe for suggesting the problem, M. Parmantier for providing the crystals and Dr J.-P. Putzeys for the data collection. JG and JPD are indebted respectively to the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture and to the Fonds

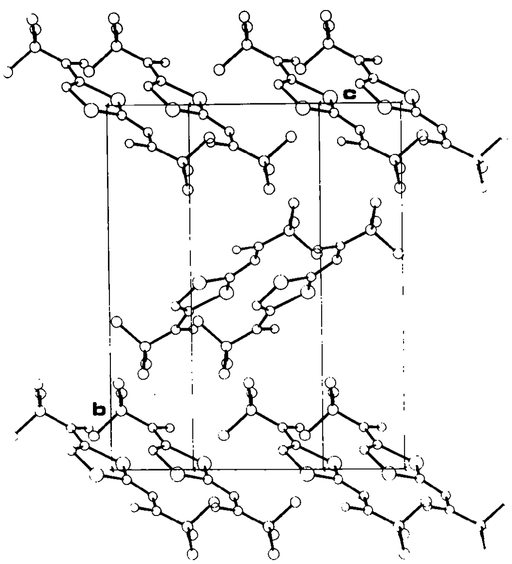


Fig. 5. Packing of the molecules in the unit cell.

National Belge de la Recherche Scientifique, for financial assistance.

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10-(1,3-Dimethyl-3-piperidylmethyl)phenothiazine Hydrochloride

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Abstract. $C_{20}H_{24}N_2S.HCl$, monoclinic, $P2_1/c$, $Z = 4$, $M_r = 360{\cdot}93$, $a = 13{\cdot}791$ (2), $b = 10{\cdot}900$ (2), $c = 13{\cdot}192$ (2) Å, $\beta = 104{\cdot}44$ (2)°, $V = 1920{\cdot}40$ Å^3, $D_x = 1{\cdot}248$, $D_m = 1{\cdot}26$ g cm^{-3} (by flotation), λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 27·45 cm^{-1}, final residual R = 0·062. The folding angle of the phenothiazine ring is smaller than that in other *N*-derivatives of phenothiazine.

Introduction. Single crystals of the title compound were grown in the form of clear prisms from isopropyl alcohol solutions. The unit-cell parameters were obtained from the measurement of '+' and '−' 2θ values of 20 reflections, and the intensity data were collected on a Nonius CAD-4 automatic diffractometer. The space group, $P2_1/c$, was deduced from systematic absences ($h0l$ absent with l odd, $0k0$ absent with k odd). An $\omega/2\theta$ scanning mode with Ni-filtered Cu $K\alpha$ radiation was used to measure 3625 independent reflections with 2θ values below 140°, of which 3124 reflections were considered as observed by the criterion $I > 2{\cdot}0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors, and no absorption corrections were applied.

The structure was determined by the heavy-atom method. The refinement was carried out by the full-matrix least-squares method (Busing, Martin & Levy, 1962) with isotropic temperature factors and the block-diagonal least-squares method (Shiono, 1971) with anisotropic temperature factors. All the H atoms were located on difference Fourier syntheses. The isotropic temperature factors were used for H atoms in the final