

## Structure of Xanthene-9-spiro-2'-[4'-*tert*-butyl-3'-(methylthio)thiete]†

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**Abstract.**  $C_{20}H_{20}OS_2$ ,  $M_r = 340.51$ , monoclinic,  $P2/n$ ,  $a = 11.58$  (1),  $b = 13.76$  (1),  $c = 12.08$  (1) Å,  $\beta = 109.40$  (6)°,  $U = 1816$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.25$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu(\text{Mo } K\alpha) = 0.289$  mm<sup>-1</sup>,  $R_F = 0.089$ , 1505 contributing reflections. The structure of the photochemical product obtained by irradiation ( $\lambda > 530$  nm) of 9-xanthenethione and *tert*-butyl(methylthio)ethyne is established to be that of the title compound. The strained four-membered thiete ring is planar, whereas appreciable departures from planarity are found in the xanthenyl part of the molecule. The *tert*-butyl group is subject to conformational disorder.

**Introduction.** Photochemical (2 + 2)-cycloaddition of 9-xanthenethione,  $O(C_6H_4)_2C=S$ , to *tert*-butyl(methylthio)ethyne,  $tert-C_4H_9-C\equiv C-SCH_3$ , afforded the title compound (Brouwer, 1979). The positions of the *tert*-butyl and methylthio substituents at the double bond of the photochemical product were not known beforehand. In this connection it was uncertain whether Büchi's concept dealing with the regio-specificity of the photochemical addition of ketones to unsymmetrically substituted alkenes (Büchi, Inman & Lipinsky, 1954) and acetylenes (Bos & Boleij, 1969) also applied to the aforementioned reaction, which involves an excited thione  $^3(n, \pi^*)$  rather than an excited ketone [also  $^3(n, \pi^*)$ ]. On the basis of the relative energy levels of the possible intermediate 1,4-biradicals,  $CH_3S-\dot{C}=C(C_4H_9)-S-\dot{C}(C_6H_4)_2O$  and  $C_4H_9-\dot{C}=C(SCH_3)-S-\dot{C}(C_6H_4)_2O$ , it was anticipated that the positions of the substituents in the reaction product were as indicated by the compound name given in the title. On the basis of steric hindrance a different regio-specificity had to be expected.

Cell dimensions and intensities were determined on a CAD-3 diffractometer. Intensity measurements were carried out in the  $\omega$ -scan mode [scan limits 0.5 to 26°

( $\theta$ )] with Zr-filtered Mo  $K\alpha$  radiation. The data were corrected for variation in reference reflections and Lorentz and polarization effects. No absorption corrections were made. After application of the acceptance criterion  $I > 2.5\sigma(I)$ , 1509 unique reflections were retained for use in the structure analysis; 2093 were considered unobserved. Structure solution was achieved with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Apart from the four methyl C atoms, the complete non-hydrogen skeleton was found. The remaining heavy atoms were located in

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) for the non-hydrogen atoms

E.s.d.'s are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	7934 (2)	3110 (2)	4556 (3)
S(2)	10272 (3)	1205 (2)	6873 (3)
O(1)	11273 (6)	4679 (6)	5985 (6)
C(1)	9568 (8)	3071 (7)	5672 (9)
C(2)	9254 (9)	2056 (8)	5983 (9)
C(3)	8081 (9)	1949 (8)	5254 (9)
C(4)	7072 (11)	1188 (10)	4955 (12)
C(51)*	5993	1559	5293
C(52)*	5896	1618	4104
C(61)*	6657	978	3634
C(62)*	7476	312	4380
C(71)*	7578	251	5636
C(72)*	6857	857	6080
C(8)	11193 (11)	1947 (11)	8058 (11)
C(9)	9735 (8)	3830 (7)	6586 (8)
C(10)	9071 (9)	3826 (9)	7379 (10)
C(11)	9201 (10)	4555 (10)	8193 (10)
C(12)	10010 (11)	5315 (9)	8249 (10)
C(13)	10664 (10)	5336 (9)	7489 (10)
C(14)	10573 (9)	4594 (8)	6684 (9)
C(15)	11312 (9)	3908 (9)	5276 (9)
C(16)	12208 (11)	3972 (10)	4764 (11)
C(17)	12329 (10)	3244 (11)	4032 (11)
C(18)	11562 (11)	2434 (10)	3824 (10)
C(19)	10676 (11)	2386 (9)	4364 (10)
C(20)	10537 (8)	3115 (8)	5103 (9)

\* Positions of these atoms were excluded from the refinement (see text).

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a difference synthesis. Block-diagonal least-squares refinement resulted in high temperature factors for the methyl C atoms of the *tert*-butyl group. A subsequent difference synthesis indicated conformational disorder of this group. The C atom positions of the second conformation were obtained from this difference map, requiring the *tert*-butyl group geometry to be ideal ( $C-C = 1.53 \text{ \AA}$ ; tetrahedral bond angles). In the following refinement the occupancy ratio between the two conformations was varied. The positions of the six C atoms involved in the disorder were kept fixed and the thermal motions of the C atoms at the less occupied sites were treated isotropically, whereas the other heavy atoms were refined anisotropically. The subsequent difference map showed maxima at the expected positions of all H atoms, those belonging to the disordered group excepted. The indicated H atoms were included in the structure factor calculations, placed at idealized positions ( $C-H = 0.95 \text{ \AA}$ ,  $sp^2$  or  $sp^3$  hybridization states of the carrier atoms). Their positions and isotropic temperature factors ( $B = 5 \text{ \AA}^2$ ) were kept fixed during the subsequent refinement. The final  $R$  over the observed reflections (four reflections were removed as they were apparently affected by secondary extinction) was 0.089. A final difference synthesis contained no structurally significant density.

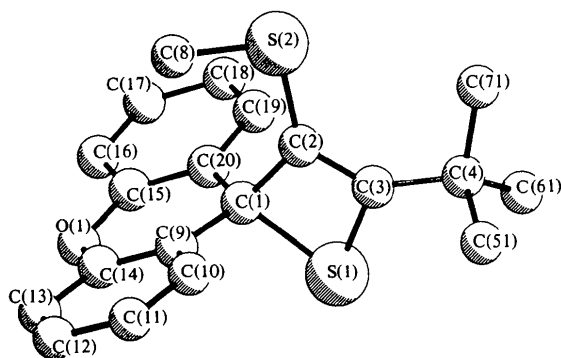


Fig. 1. Perspective view of the molecule showing the numbering of the non-hydrogen atoms. Only the predominant *tert*-butyl conformation is shown.

Table 2. Fractional atomic coordinates ( $\times 10^3$ ) for the hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>
H(81)	1194	163	847
H(82)	1140	255	776
H(83)	1076	214	856
H(10)	853	330	735
H(11)	873	454	871
H(12)	1010	582	882
H(13)	1120	586	755
H(16)	1277	451	494
H(17)	1294	329	367
H(18)	1164	193	331
H(19)	1015	184	422

Table 3. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the non-hydrogen atoms

E.s.d.'s are given in parentheses.

S(1)—C(1)	1.926 (8)	C(9)—C(14)	1.408 (14)
S(1)—C(3)	1.788 (11)	C(10)—C(11)	1.378 (18)
S(2)—C(2)	1.753 (10)	C(11)—C(12)	1.391 (18)
S(2)—C(8)	1.793 (12)	C(12)—C(13)	1.372 (20)
O(1)—C(14)	1.356 (15)	C(13)—C(14)	1.389 (16)
O(1)—C(15)	1.373 (14)	C(15)—C(16)	1.376 (19)
C(1)—C(2)	1.521 (15)	C(15)—C(20)	1.384 (15)
C(1)—C(9)	1.486 (14)	C(16)—C(17)	1.374 (20)
C(1)—C(20)	1.500 (16)	C(17)—C(18)	1.394 (19)
C(2)—C(3)	1.360 (13)	C(18)—C(19)	1.389 (20)
C(3)—C(4)	1.521 (17)	C(19)—C(20)	1.386 (17)
C(9)—C(10)	1.415 (17)		
C(1)—S(1)—C(3)	74.2 (4)	C(9)—C(10)—C(11)	121.7 (11)
C(2)—S(2)—C(8)	102.1 (6)	C(10)—C(11)—C(12)	119.6 (13)
C(14)—O(1)—C(15)	118.2 (9)	C(11)—C(12)—C(13)	119.7 (12)
S(1)—C(1)—C(2)	86.5 (5)	C(12)—C(13)—C(14)	121.5 (11)
S(1)—C(1)—C(9)	110.8 (7)	O(1)—C(14)—C(9)	123.3 (9)
S(1)—C(1)—C(20)	112.9 (7)	O(1)—C(14)—C(13)	116.8 (10)
C(2)—C(1)—C(9)	116.4 (9)	C(9)—C(14)—C(13)	119.8 (11)
C(2)—C(1)—C(20)	115.3 (9)	O(1)—C(15)—C(16)	114.7 (10)
C(9)—C(1)—C(20)	112.3 (8)	O(1)—C(15)—C(20)	123.3 (11)
S(2)—C(2)—C(1)	126.7 (7)	C(16)—C(15)—C(20)	122.0 (11)
S(2)—C(2)—C(3)	130.4 (9)	C(15)—C(16)—C(17)	119.8 (12)
C(1)—C(2)—C(3)	102.0 (8)	C(16)—C(17)—C(18)	120.2 (13)
S(1)—C(3)—C(2)	97.3 (8)	C(17)—C(18)—C(19)	118.6 (12)
S(1)—C(3)—C(4)	123.9 (7)	C(18)—C(19)—C(20)	122.0 (11)
C(2)—C(3)—C(4)	138.7 (10)	C(1)—C(20)—C(15)	120.6 (10)
C(1)—C(9)—C(10)	122.3 (9)	C(1)—C(20)—C(19)	122.0 (10)
C(1)—C(9)—C(14)	120.3 (10)	C(15)—C(20)—C(19)	117.4 (11)
C(10)—C(9)—C(14)	117.4 (10)		

All calculations were carried out with a locally adapted version of the XRAY 76 system (Stewart, 1976). Scattering factors for S, C and O were from Cromer & Mann (1968), and for H from Stewart, Davidson & Simpson (1965). The final positional parameters are listed in Tables 1 and 2.\*

**Discussion.** Fig. 1 gives a general view of the molecule and the atom numbering. The relative positions of the substituents at the double bond in the thiethane ring appear to be as predicted by Büchi's concept. Bond distances and angles are given in Table 3. All angles in the strained four-membered thiethane ring, which is planar within the limits of accuracy, are small and the bond lengths are abnormally large. The exocyclic S atom deviates 0.240  $\text{\AA}$  from the ring plane, whereas the central C atom of the *tert*-butyl group is coplanar with it. The xanthene group is curved with a boat-shaped central part; it is convex at the side of the endocyclic S atom. Deviations from coplanarity up to 0.21  $\text{\AA}$  are found. The *tert*-butyl group is disordered between two conformational arrangements with an occupancy ratio of

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34863 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

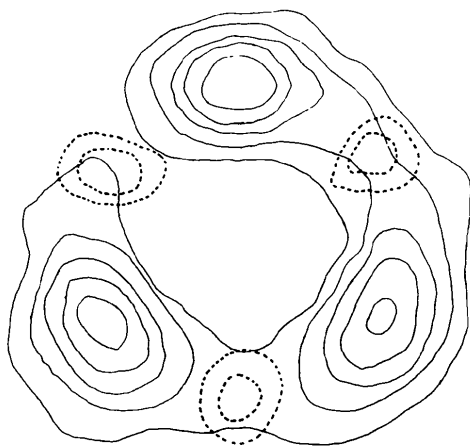


Fig. 2. Composite difference electron-density synthesis: section through the methyl C atoms of the *tert*-butyl group. Solid lines:  $F_c$  without *tert*-butyl methyl C atom contributions; contours from  $0.50 \text{ e } \text{Å}^{-3}$ , at intervals of  $0.20 \text{ e } \text{Å}^{-3}$ . Dashed lines:  $F_c$  with the contributions of the C atoms located at the maxima in the previous difference synthesis. Contours from  $0.30 \text{ e } \text{Å}^{-3}$ , at intervals of  $0.10 \text{ e } \text{Å}^{-3}$ .

5 (1). In both cases one of the methyl C atoms is coplanar with the thiete ring, so that the rotational angle between the two conformations is nearly  $60^\circ$ . The electron-density distributions in the plane through the *tert*-butyl methyl C atoms were obtained by two consecutive difference syntheses and are displayed in a composite map shown in Fig. 2. Fig. 3 shows the Newman projections for both conformations along C(3)–C(4). The intermolecular packing is limited to van der Waals contacts.

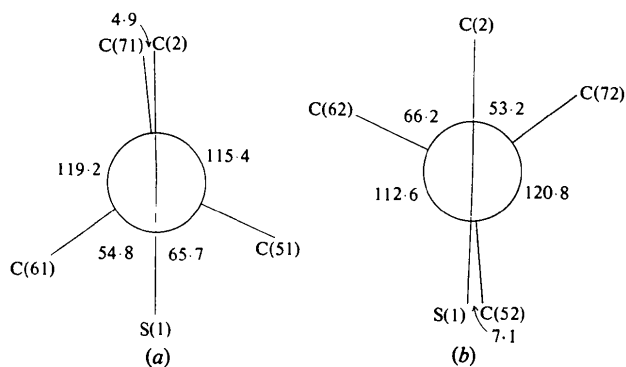


Fig. 3. Newman projections along C(3)–C(4). (a) Conformation with an occupancy factor of 0.84. (b) Conformation with an occupancy factor of 0.16. Since the positional parameters of the methyl C atoms were not included in the refinement no e.s.d.'s are given. (Torsion angles in deg.)

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## The Structure of Dihydrnimbin\*

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**Abstract.**  $\text{C}_{30}\text{H}_{38}\text{O}_9$ , monoclinic,  $P2_1$ ,  $a = 16.24$  (1),  $b = 7.61$  (1),  $c = 11.47$  (2) Å,  $\beta = 95.9$  (2)°,  $\rho_o = 1.264$ ,  $\rho_c = 1.278 \text{ Mg m}^{-3}$  for  $Z = 2$ . The structure was solved by direct methods with 1494 reflections. The molecular structure obtained from the present study is in agreement with the structures and stereochemistries deduced earlier for nimbin, nimbolide and

other related products from chemical, PMR and other studies.

**Introduction.** The crystalline bitter principle, nimbin, isolated from the seeds, bark and other parts of the neem tree (*Melia azadirachta*), has been shown to be a triterpenoid of the apoeuphol or tirucallol type with the unique feature that its C ring is oxidized and broken (Narayanan, Pachapurkar, Pradhan, Shah &

\* NCL Communication No. 2405.