diamond already had a clearly established philosophy, succinctly expressed in the quote: 'Great precision was not attempted; to attain it would have been needlessly troublesome'. We think the time has come to heed the advice implicit in that statement.

We emphasize, however, that we do not advocate careless work. Reasonable precautions must always be taken to ensure acceptable crystal quality, to detect twinning and other problems, and to obtain data for correct space-group assignments. If this is not done, the gains of fast data acquisition may be offset by subsequent computing problems.

A great proportion of our routine structures will hereafter be based on data collected with techniques similar to those described here. Also, since these results were obtained it has become feasible to introduce crystal structure determination as an undergraduate physical chemistry laboratory exercise in this department. So far about ten such projects have been successfully completed.

The materials used in this study were obtained from the laboratories of Professors W. K. Musker (I), K. M. Smith (II), and C. P. Nash (III). We thank them for their interest. Detailed descriptions of the structures will be published elsewhere.

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Structure of Xanthene-9-spiro-2′-[3′,4′-bis(*tert*-butylthio)thiete]

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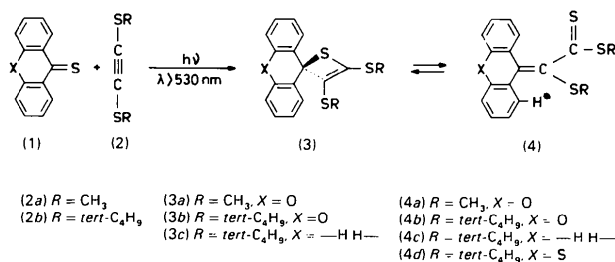*Organisch Chemisch Laboratorium, Rijksuniversiteit, Croesestraat 79, Utrecht, The Netherlands*

Abstract

$C_{23}H_{26}OS_3$ is obtained by irradiating a solution of 9-xanthenethione and bis(*tert*-butylthio)ethyne. The crystals are monoclinic, $P2_1/n$, with $a = 14.890$ (5), $b = 9.296$ (5), $c = 16.342$ (11) Å, $\beta = 101.14$ (5)°, $Z = 4$. The structure was determined from 3427 independent diffractometer intensities with $I > 2.5\sigma(I)$ by the heavy-atom method and refined to $R = 0.054$. Bond lengths and angles in the planar thiete ring indicate appreciable strain; the xanthene system is slightly curved.

Introduction

Brouwer, George, Seykens & Bos (1979) reported the isolation of the red crystalline α,β-unsaturated dithio-

ester (4a) after irradiating a solution of 9-xanthenethione (1) and bis(methylthio)ethyne (2a). The thiete (3a), a (2 + 2) cycloadduct,

(1)   (2)   (3)   (4)

(2a) R = CH₃
(2b) R = tert-C₄H₉

(3a) R = CH₃, X = O
(3b) R = tert-C₄H₉, X = O
(3c) R = tert-C₄H₉, X = —H H—

(4a) R = CH₃, X = O
(4b) R = tert-C₄H₉, X = O
(4c) R = tert-C₄H₉, X = —H H—
(4d) R = tert-C₄H₉, X = S

was postulated as an intermediary, giving a rearrangement known to occur for oxetes (Brandsma, Bos & Arens, 1969) which are oxygen analogues of thietes. To investigate the scope of this reaction and to demonstrate the intermediacy of a thiete, we studied the

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addition of 9-xanthenethione (1) ($X = O$) to bis-(*tert*-butylthio)ethyne (2b) in dichloromethane. Recrystallization of the reaction product (a red oil) from dichloromethane–pentane initially only afforded red crystals of dithioester (4b), m.p. 404–406 K. However, recrystallization of this dithioester yielded yellow crystals only (m.p. 392–393 K), possibly of thiete (3b). (3b) and (4b) (introduced as solids) showed the same mass spectra (Brouwer, 1979).

In carbon disulphide solution at room temperature the compounds appeared to be in rapid equilibrium, showing a simple ^{1}H NMR spectrum at 90 MHz. At 218 K separate signals of the dithioester and of its isomer (ratio 40:60) were observed, indicating structure (3b) for the latter. To confirm the structure of this yellow compound an X-ray structure determination was undertaken.

In the course of our investigation a preliminary report on the crystal structure of a stable thiete, which did not contain any geometrical detail, was published by Gotthardt & Huss (1978). Also, we have determined the crystal structure on an unsymmetrically substituted thiete (Verhoeckx, Kroon, Brouwer & Bos, 1980), whose structure will be compared with that of the title compound.

Experimental

All measurements were made on a CAD-3 diffractometer with Zr-filtered Mo $K\alpha$ radiation. Crystal data are given in Table 1. Intensities were collected in the ω-scan mode [scan limits 1 to 26° (θ)]. The data were corrected for variation in reference reflections and Lorentz and polarization effects but not for absorption. 3427 unique reflections with $I > 2\cdot5\sigma(I)$ were retained for use in the analysis; 967 were considered unobserved.

Structure determination

The S atoms were located from a Patterson synthesis, and a subsequent Fourier map yielded the complete non-hydrogen skeleton. All the heavy atoms were refined anisotropically. Since most of the H atoms did

Table 1. *Crystal data*

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

Formula	$C_{23}H_{26}OS_3$	$F(000)$	880
M_r	414·65	Z	4
Space group	$P2_1/n$	D_x (Mg m^{-3})	1·23
a (Å)	14·890 (5)	μ(Mo $K\alpha$) (mm^{-1})	0·351
b (Å)	9·296 (5)	λ(Mo $K\alpha$) (Å)	0·7107
c (Å)	16·342 (11)	Crystal shape	Block
β (°)	101·14 (5)	size (mm)	0·6 × 0·6 × 0·5
V (Å^3)	2219		

Table 2. *Fractional atomic coordinates* ($\times 10^5$ *for* S, $\times 10^4$ *for* O *and* C, $\times 10^3$ *for* H *atoms*) *with e.s.d.'s in parentheses and isotropic U values* (Å$^2 \times 10^4$)

U_{eq} is the average of the three eigenvalues of each anisotropic vibration tensor.

	x	y	z	U_{eq}/U
S(1)	1514 (8)	10955 (12)	68141 (7)	383
S(2)	−11011 (8)	−24644 (12)	76263 (7)	378
S(3)	−13272 (9)	−8246 (13)	55935 (7)	460
O(1)	1366 (2)	790 (4)	9399 (2)	541
C(1)	226 (3)	−55 (5)	7813 (3)	327
C(2)	−476 (3)	−1065 (4)	7281 (3)	320
C(3)	−632 (3)	−370 (5)	6542 (3)	343
C(4)	−1841 (3)	914 (5)	5158 (3)	421
C(5)	−2324 (4)	1654 (8)	5792 (4)	694
C(6)	−2535 (4)	426 (7)	4388 (4)	730
C(7)	−1117 (4)	1864 (6)	4894 (3)	596
C(8)	−615 (3)	−4227 (5)	7374 (3)	449
C(9)	−138 (3)	755 (5)	8485 (3)	342
C(10)	−1067 (3)	1144 (5)	8393 (3)	450
C(11)	−1384 (4)	1915 (6)	9001 (3)	508
C(12)	−788 (4)	2303 (6)	9719 (3)	538
C(13)	136 (4)	1921 (6)	9842 (3)	508
C(14)	447 (3)	1146 (5)	9223 (3)	395
C(15)	1691 (3)	−147 (5)	8874 (3)	417
C(16)	2595 (3)	−647 (6)	9168 (3)	566
C(17)	2996 (3)	−1558 (7)	8681 (4)	589
C(18)	2506 (4)	−2004 (7)	7907 (3)	563
C(19)	1618 (3)	−1518 (6)	7629 (3)	477
C(20)	1190 (3)	−592 (5)	8114 (3)	361
C(21)	−368 (4)	−4207 (6)	6504 (4)	633
C(22)	215 (5)	−4632 (7)	8033 (4)	834
C(23)	−1421 (5)	−5282 (6)	7405 (4)	699
H(51)	−259	254	557	662
H(52)	−279	105	591	662
H(53)	−189	184	629	662
H(61)	−280	130	416	632
H(62)	−224	−6	400	632
H(63)	−299	−20	454	632
H(71)	−138	275	467	561
H(72)	−65	206	536	561
H(73)	−87	138	447	561
H(10)	−149	87	790	458
H(11)	−201	218	893	511
H(12)	−101	284	1014	547
H(13)	55	219	1035	490
H(16)	292	−36	970	523
H(17)	361	−189	887	579
H(18)	278	−264	757	570
H(19)	129	−182	709	481
H(211)	−13	−511	638	637
H(212)	−91	−402	611	637
H(213)	7	−348	649	637
H(221)	46	−554	791	713
H(222)	67	−392	807	713
H(223)	31	−472	856	713
H(231)	−117	−617	728	659
H(232)	−157	−529	794	659
H(233)	−194	−503	701	659

not show up in a difference synthesis, they were all included in the structure-factor calculations at idealized positions with C—H = 0·95 Å. The sp^2 or sp^3 hybridization states of the carrier atoms were taken into account. The conformations of the methyl groups

were taken such that the *tert*-butyl groups were in the LEM form (Corosine, Crasnier, Labarre, Labarre & Leibovici, 1973). The H atoms were assigned the isotropic temperature factors of their carrier atoms. During the block-diagonal least-squares refinement, their positions and temperature factors remained fixed. The final R for the observed reflections (four reflections were removed as they were apparently affected by secondary extinction) was 0·054 ($R_{wF} = 0·072$). A final difference synthesis contained no structurally significant density. All calculations were carried out with a locally adapted version of XRAY 76 (Stewart, 1976). Scattering factors for S, C and O were from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). The final parameters are listed in Table 2.*

Discussion

Crystal and molecular structure

Fig. 1 shows a view of the molecule and the numbering of the atoms; in the tables the H atoms are given the numbers of the C atoms to which they are bonded. Bond lengths and angles are given in Table 3. The molecular geometry as a whole resembles that of xanthene-9-spiro-2'-[4'-*tert*-butyl-3'-(methylthio)thiete] (Verhoeckx, Kroon, Brouwer & Bos, 1980). In the title compound the strain in the four-membered thiete ring is evident from a long C(1)–S(1) bond of 1·937 (4) Å and an acute C(1)–S(1)–C(3) angle of 73·6 (2)°. S(2) and S(3) deviate by 0·27 and 0·03 Å respectively from the least-squares ring plane. The same curvature of the xanthene group as in the asymmetrically substituted compound is found, *i.e.* it is convex on the side of the endocyclic S atom; its central

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35615 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
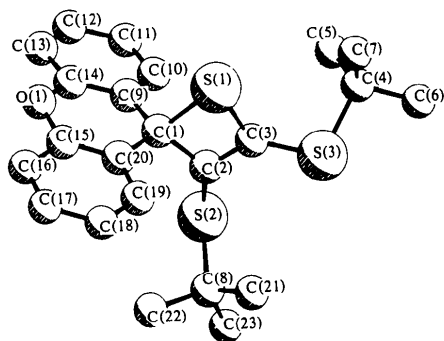

Fig. 1. Perspective view of the molecule showing the numbering of the non-hydrogen atoms.

Table 3. *Bond lengths* (Å) *and angles* (°) *for the non-hydrogen atoms*

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

|			
S(1)–C(1)	1·937 (4)	C(8)–C(21)	1·536 (8)
S(1)–C(3)	1·793 (4)	C(8)–C(22)	1·521 (8)
S(2)–C(2)	1·755 (4)	C(8)–C(23)	1·558 (8)
S(2)–C(8)	1·870 (5)	C(9)–C(10)	1·410 (6)
S(3)–C(3)	1·742 (4)	C(9)–C(14)	1·393 (6)
S(3)–C(4)	1·869 (5)	C(10)–C(11)	1·379 (8)
O(1)–C(14)	1·383 (5)	C(11)–C(12)	1·376 (7)
O(1)–C(15)	1·374 (6)	C(12)–C(13)	1·396 (8)
C(1)–C(2)	1·543 (6)	C(13)–C(14)	1·392 (7)
C(1)–C(9)	1·515 (6)	C(15)–C(16)	1·417 (7)
C(1)–C(20)	1·510 (6)	C(15)–C(20)	1·382 (6)
C(2)–C(3)	1·349 (6)	C(16)–C(17)	1·375 (8)
C(4)–C(5)	1·533 (8)	C(17)–C(18)	1·396 (7)
C(4)–C(6)	1·536 (7)	C(18)–C(19)	1·388 (7)
C(4)–C(7)	1·520 (8)	C(19)–C(20)	1·404 (7)
C(1)–S(1)–C(3)	73·6 (2)	S(2)–C(8)–C(23)	102·1 (4)
C(2)–S(2)–C(8)	109·0 (2)	C(21)–C(8)–C(22)	110·6 (5)
C(3)–S(3)–C(4)	105·0 (2)	C(21)–C(8)–C(23)	111·2 (4)
C(14)–O(1)–C(15)	118·4 (3)	C(22)–C(8)–C(23)	110·3 (5)
S(1)–C(1)–C(2)	86·5 (2)	C(1)–C(9)–C(10)	122·1 (4)
S(1)–C(1)–C(9)	111·5 (3)	C(1)–C(9)–C(14)	120·4 (4)
S(1)–C(1)–C(20)	110·7 (3)	C(10)–C(9)–C(14)	117·5 (4)
C(2)–C(1)–C(9)	114·4 (4)	C(9)–C(10)–C(11)	121·4 (4)
C(2)–C(1)–C(20)	118·7 (4)	C(10)–C(11)–C(12)	119·8 (5)
C(9)–C(1)–C(20)	112·2 (3)	C(11)–C(12)–C(13)	120·7 (5)
S(2)–C(2)–C(1)	127·8 (3)	C(12)–C(13)–C(14)	119·0 (4)
S(2)–C(2)–C(3)	129·2 (3)	O(1)–C(14)–C(9)	123·1 (4)
C(1)–C(2)–C(3)	101·2 (3)	O(1)–C(14)–C(13)	115·4 (4)
S(1)–C(3)–S(3)	130·6 (3)	C(9)–C(14)–C(13)	121·6 (4)
S(1)–C(3)–C(2)	98·7 (3)	O(1)–C(15)–C(16)	115·0 (4)
S(3)–C(3)–C(2)	130·6 (3)	O(1)–C(15)–C(20)	123·8 (4)
S(3)–C(4)–C(5)	110·0 (4)	C(16)–C(15)–C(20)	121·2 (5)
S(3)–C(4)–C(6)	102·6 (4)	C(15)–C(16)–C(17)	119·7 (4)
S(3)–C(4)–C(7)	110·5 (3)	C(16)–C(17)–C(18)	119·9 (5)
C(5)–C(4)–C(6)	111·0 (4)	C(17)–C(18)–C(19)	119·9 (5)
C(5)–C(4)–C(7)	112·5 (5)	C(18)–C(19)–C(20)	121·4 (4)
C(6)–C(4)–C(7)	109·9 (4)	C(1)–C(20)–C(15)	120·5 (4)
S(2)–C(8)–C(21)	111·5 (3)	C(1)–C(20)–C(19)	121·6 (4)
S(2)–C(8)–C(22)	110·9 (4)	C(15)–C(20)–C(19)	117·8 (4)

part is in a boat form. Departures from coplanarity in the xanthene group up to 0·18 Å are found. The deviations from trigonal symmetry of the *tert*-butyl group are evident from the unequivalency of the S–C–C angles (Table 3); this feature will be discussed in detail elsewhere. The packing is limited to van der Waals contacts.

Equilibrium between dithioester (4b) and thiete (3b)

Ring opening of a thiete such as (3b) will give relief of the ring strain and formation of a conjugated system $(aryl)_2C=C–(C=S)SR$. However, dithioesters (4a) and (4b) show an equilibrium with their thietes. This must be due to non-bonded interactions between H*, as marked in structure (4), of the flattened xanthene ring system with the neighbouring S–*tert*-C_4H_9 group, as was inferred from space-filling molecular models

(Brouwer, 1979). In the unbridged dithioester (4*c*) (*X* = —H H—) no such interactions take place because the aromatic systems are no longer in one plane. Therefore, it is not surprising that, in solution, (4*c*) shows no tendency to be in equilibrium with its thiete.

That dithioester (6) is not found to occur in equilibrium with its thiete (5) at room temperature is undoubtedly due to the lack of delocalization energy in the —C(=S)—*tert*-C₄H₉ group.
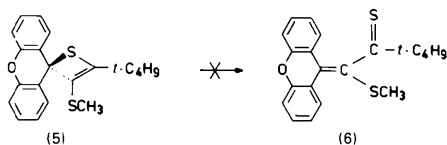
It is remarkable that the red crystals of dithioester (4*b*) on storing at 263 K for about a year had crumbled and partially turned yellow. On the basis of infrared spectra, rearrangement into thiete (3*b*) must have occurred (Brouwer, 1979).

A structural investigation of dithioester (4*d*) is under way.

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Stereochemical Investigations of Heterocyclic Compounds.
X. The Structure of a Novel Compound: 1,4-Dihydro-3,5-dimethoxy-1-tosylimino-1λ⁴,2,4,6-thiatriazine

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Abstract

$C_{11}H_{14}N_4O_4S_2$ is monoclinic, space group $P2_1/c$, with $a = 14·415$ (1), $b = 7·534$ (1), $c = 15·473$ (2) Å, $\beta = 120·46$ (1)°, $Z = 4$. Final $R = 0·035$ for 2698 reflexions. As in related compounds the thia(IV)triazine ring is non-planar. The lengths of the S^{IV}—N multiple bonds maintained by S^{IV} situated at the top of a distorted trigonal pyramid are governed by the bond-order rule [Kálmán, Argay, Fischer & Rembarz (1979). *Acta Cryst.* B**35**, 860–866]. Participation of the *exo* N atom in a strong NH···N hydrogen bond seems to influence the competition between the S^{IV}—N and S^{VI}—N

multiple bonds which build up the $RS^{VI}O_2$—N=S^{IV} moieties (*cf. e.g.* N-sulphonylsulphilimines). The tautomeric proton which maintains a NH···N hydrogen bond was located unambiguously at N(4).

Introduction

A new synthesis (Fischer & Teller, 1979) leads to 1-arylimino-1λ⁴,2,4,6-thiatriazines in high yields. Thus the reaction of *O,O*-dimethyldiisobiuret with N-tosylsulphinylamine in anhydrous benzene gives 1,4-dihydro-3,5-dimethoxy-1-tosylimino-1λ⁴,2,4,6-thiatri-