Table 5. *Intermolecular contact distances* (Å) *for* (I) *and* (II)

	(I)		(II)
I⁻–I⁻	5·496 (2)*		
I⁻–S(2)	3·911 (4)	I⁻–S(2)	3·734 (2)
I⁻–S(1)	4·202 (5)	I⁻–S(101)	3·970 (–)
I⁻–H(3)	3·04 (13)	I⁻–H(10)	2·92 (8)
I⁻–H(5)	3·11 (8)	I⁻–N(1)	4·366 (8)
S(1)–S(2)	4·01 (1)	S(1)–S(3)	3·76 (3)
		S(2)–S(2)	3·70 (4)†

* Symmetry operator $x, y, 1 + z$.
† Symmetry operator $-x, 2 - y, -z$.

be found for (I); the shortest, for $S(1)\cdots S(2)$, is 4·01 Å. For (II), intermolecular contact distances of 3·70 and 3·76 Å (see Table 4) are about twice the van der Waals radii given by Pauling (1969), e.g. 3·70 Å for sulphur in crystalline sulphides.

Molecule-orbital overlap can thus be postulated to a certain degree, the π electrons not being used for the binding of the S atoms. This means that electron transfer is much more possible than with compound (I). Thus the thiophene ring as π-electron donor and also a stronger intermolecular interaction are both responsible for a higher electrical conductivity (Table 4). This effect has been found with several compounds containing thiophene ring systems (Zobel, 1977; Zobel & Ruban, 1978) and supported by electrical measurements on single crystals. There it could be shown that the conductivity in the direction of the shortest intermolecular S–S distance is significantly higher than in other directions. For the title compounds such measurements on single crystals were not possible because only very small samples were available.

References

BOCIONEK, P. (1978). Thesis, FU Berlin.
BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., p. 213. Birmingham: Kynoch Press.
JOHNSON, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
KOSSMEHL, G., BOCIONEK, P. & MANECKE, G. (1979). *Makromol. Chem.* **180**, 1441–1463.
LABISCHINSKI, H. (1976). Private communication.
LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
PAULING L. (1969). *Grundlagen der Chemie*. Weinheim: Verlag Chemie.
STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446, Computer Science Center, Univ. of Maryland, College Park, Maryland.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
WILLIAMS, D. E. (1972). *Acta Cryst.* A**28**, 629–635.
ZOBEL, D. (1977). Thesis. FU Berlin.
ZOBEL, D. & RUBAN, G. (1978). *Acta Cryst.* B**34**, 1652–1657.

Structure of *tert*-Butyl 2-(*tert*-Butylthio)-2-(9-thioxanthenylidene)dithioacetate

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Abstract

$C_{23}H_{26}S_4$, $M_r = 430\cdot72$, is obtained by irradiating a solution of thioxanthenethione and bis(*tert*-butylthio)-ethyn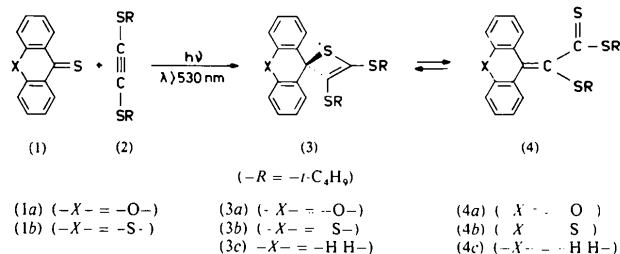e. The crystals are monoclinic, space group $P2_1/n$, with $a = 10\cdot899$ (3), $b = 17\cdot052$ (6), $c = 12\cdot304$ (6) Å, $\beta = 98\cdot40$ (4)°, $V = 2262$ Å³, $Z = 4$, $F(000) = 912$, $D_x = 1\cdot265$ Mg m⁻³, μ(Mo $K\alpha$) = $0\cdot411$ mm⁻¹, λ(Mo $K\alpha$) = 0·71069Å. $R = 0\cdot038$ for 2695 reflexions. The ratio thiete/unsaturated dithioester found in solution for xanthenyl and thioxanthenyl derivatives is apparently governed by ring strain *versus*

overcrowding, which strongly depends on the different curvatures of the xanthene and thioxanthene groups.

Introduction

Brouwer, George, Seykens & Bos (1979) reported the photoaddition of xanthenethione (1a) to bis(tert-butyl-thio)ethyne (2) with formation of a red oil. Crystallization of this oil from dichloromethane–pentane initially only afforded red crystals of dithioester (4a).

(−R = −t-C₄H₉)

(1a) (−X− = −O−)	(3a) (−X− = −O−)	(4a) (X · · O)
(1b) (−X− = −S−)	(3b) (−X− = S−)	(4b) (X S)
	(3c) −X− = −H H−)	(4c) (−X− _ − H H−)

Recrystallization of this dithioester yielded yellow crystals of thiete (3a), whose structure was determined by X-ray analysis (de Vos, Kroon, Brouwer & Bos, 1981). The above red crystals (4a), after storage at about 263 K for about one year, had crumbled and partially turned yellow, because of rearrangement into thiete (3a). In carbon disulphide at room temperature (3a) and (4a) appeared to be in fast equilibrium, showing a simple ^{1}H NMR spectrum at 90 MHz. At 218 K separate signals of (3a) and (4a) (ratio about 60/40) were observed (Brouwer, 1979). The unbridged dithioester (4c) (−X− = −H H−) shows no tendency at all to be in fast equilibrium with its thiete (3c). As was inferred from space-filling models, non-bonded interactions in (4a) could be an explanation for the difference in behaviour between (4a) and (4c). For an insight into these features it would be relevant to determine the structure of (4a). Unfortunately, crystals of this compound could not be obtained again. The same cycloaddition with thioxanthenethione, (1b), also afforded a red oil. Crystallization from dichloromethane–pentane yielded red crystals (m.p. 461–462 K dec.) only. In carbon disulphide solution the ratio between (3b) and (4b) is now about 30/70 at 188 K. The availability of these red crystals enabled us to study the molecular structure of (4b), the sulphur analogue of (4a). This paper reports its X-ray structure determination.

Experimental

Intensities were collected on a Nonius CAD-4 diffractometer with Zr-filtered Mo $K\alpha$ radiation with a block-shaped crystal $0.6 \times 0.4 \times 0.4$ mm. Intensities up to $\theta = 27.5°$ were collected in the ω–2θ scan mode

with a scan width of $(1 + 0.7 \tan \theta)°$. The intensities were corrected for variation in two reference reflexions and for Lorentz and polarization effects, but not for extinction or absorption. 2695 of the non-equivalent terms measured obeyed the condition $I \geq 2.5\sigma(I)$ and were used in subsequent calculations; 2461 reflexions 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. In a difference synthesis most of the H atoms showed up; only H(232) and H(233) were placed at idealized positions (with C−H = 1.02 Å, and the sp^3 hybridization state of the carrier atoms taken into account). The H atoms were assigned the isotropic temperature factors of their carrier atoms. During the block-diagonal least-squares anisotropic refinement their temperature factors remained fixed. The final R for the observed reflexions was 0.038 (R_{wF} = 0.039). A final difference synthesis was essentially featureless. All calculations were carried out with a locally adapted version of XRAY 76 (Stewart, 1976). Scattering factors for S and C were from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). The final parameters are listed in Table 1.*

Discussion

A view of the molecule and the numbering of the atoms are shown in Fig. 1. Bond lengths and angles are given

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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 36042 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
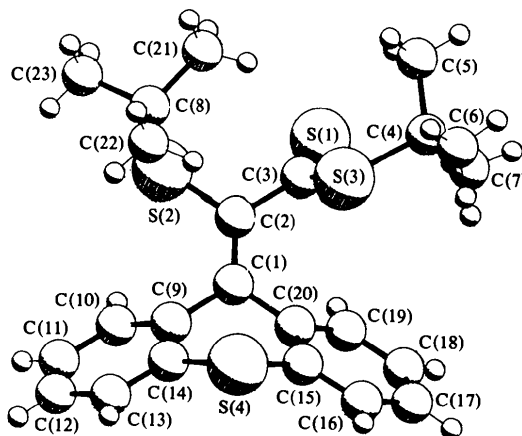
Fig. 1. Perspective view of the molecule showing the numbering of the non-hydrogen atoms.

in Table 2. The H atoms of the *tert*-butyl groups have the LEM geometry (Corosine, Crasnier, Labarre, Labarre & Leibovici, 1973). The curvature of the thioxanthene group is much more pronounced than that of the xanthene group in xanthene-9-spiro-2'-

Table 1. *Fractional atomic coordinates* ($\times 10^4$; *for* S $\times 10^5$; *for* H $\times 10^3$) *and isotropic U values* ($\times 10^3$)

U_{eq} is the average of the three eigenvalues of each anisotropic vibration tensor. E.s.d.'s in the least significant digits are in parentheses.

	x	y	z	U_{eq}/U (Å^2)
S(1)	−9800 (9)	26578 (6)	23616 (9)	47·4 (5)
S(2)	19161 (8)	21190 (5)	19259 (8)	38·4 (5)
S(3)	−14343 (8)	11194 (5)	11252 (8)	39·7 (4)
S(4)	10579 (9)	−8804 (6)	22275 (9)	47·0 (5)
C(1)	991 (3)	821 (2)	2830 (3)	31 (2)
C(2)	729 (3)	1496 (2)	2268 (3)	32 (2)
C(3)	−578 (3)	1793 (2)	1957 (3)	34 (2)
C(4)	−3063 (3)	1443 (2)	791 (3)	47 (2)
C(5)	−3159 (4)	2159 (3)	54 (4)	65 (3)
C(6)	−3655 (4)	739 (3)	156 (4)	77 (3)
C(7)	−3640 (4)	1565 (3)	1834 (4)	67 (3)
C(8)	1819 (4)	2086 (2)	411 (3)	48 (2)
C(9)	2244 (3)	465 (2)	3048 (3)	32 (2)
C(10)	3297 (3)	860 (2)	3543 (3)	40 (2)
C(11)	4437 (3)	501 (2)	3686 (3)	50 (2)
C(12)	4548 (3)	−264 (2)	3348 (4)	55 (2)
C(13)	3514 (4)	−680 (2)	2911 (3)	48 (2)
C(14)	2366 (3)	−323 (2)	2778 (3)	35 (2)
C(15)	−41 (3)	−460 (2)	2971 (3)	37 (2)
C(16)	−989 (4)	−923 (2)	3282 (3)	48 (2)
C(17)	−1825 (4)	−601 (2)	3885 (3)	53 (2)
C(18)	−1733 (3)	170 (2)	4193 (3)	47 (2)
C(19)	−818 (3)	637 (2)	3874 (3)	38 (2)
C(20)	23 (3)	336 (2)	3232 (3)	32 (2)
C(21)	666 (4)	2478 (3)	−167 (4)	70 (3)
C(22)	1904 (6)	1247 (3)	42 (4)	85 (4)
C(23)	2954 (5)	2564 (3)	232 (4)	77 (3)
H(51)	−279 (3)	206 (2)	−61 (3)	61·5
H(52)	−272 (3)	257 (2)	39 (3)	61·5
H(53)	−399 (3)	230 (2)	−18 (3)	61·5
H(61)	−328 (4)	60 (2)	−51 (3)	71·2
H(62)	−363 (4)	31 (2)	67 (3)	71·2
H(63)	−447 (3)	89 (2)	−14 (3)	71·2
H(71)	−352 (3)	109 (2)	220 (3)	66·3
H(72)	−448 (3)	163 (2)	164 (3)	66·3
H(73)	−329 (3)	199 (2)	227 (3)	66·3
H(10)	325 (3)	138 (2)	377 (3)	40·6
H(11)	515 (3)	78 (2)	402 (3)	47·5
H(12)	531 (3)	−48 (2)	349 (3)	52·4
H(13)	357 (3)	−116 (2)	270 (3)	47·6
H(16)	−98 (3)	−143 (2)	306 (3)	45·7
H(17)	−245 (3)	−93 (2)	411 (3)	52·8
H(18)	−225 (3)	40 (2)	462 (3)	50·9
H(19)	−69 (3)	116 (2)	408 (2)	38·1
H(211)	55 (3)	299 (2)	11 (3)	69·8
H(212)	−11 (4)	221 (2)	−18 (3)	69·8
H(213)	75 (3)	247 (2)	−92 (3)	69·8
H(221)	264 (4)	108 (3)	41 (3)	84·1
H(222)	197 (4)	124 (3)	−70 (3)	84·1
H(223)	116 (4)	95 (2)	15 (3)	84·1
H(231)	366 (4)	234 (2)	58 (3)	71·3
H(232)	302 (4)	252 (2)	−56 (3)	71·3
H(233)	280 (4)	309 (2)	48 (3)	71·3

Table 2. *Bond lengths* (Å) *and angles* (°)

E.s.d.'s are in parentheses. For bond lengths and angles involving H atoms mean values with their e.s.d.'s in the least significant digits are given.

S(1)–C(3)	1·637 (4)	S(2)–C(2)	1·772 (3)	S(2)–C(8)	1·853 (4)
S(3)–C(3)	1·719 (3)	S(3)–C(4)	1·847 (4)	S(4)–C(14)	1·764 (3)
S(4)–C(15)	1·762 (4)	C(1)–C(2)	1·352 (4)	C(1)–C(9)	1·483 (4)
C(1)–C(20)	1·481 (5)	C(2)–C(3)	1·507 (5)	C(4)–C(5)	1·516 (6)
C(4)–C(6)	1·524 (6)	C(4)–C(7)	1·523 (6)	C(8)–C(21)	1·506 (6)
C(8)–C(22)	1·507 (7)	C(8)–C(23)	1·525 (7)	C(9)–C(10)	1·391 (5)
C(9)–C(14)	1·394 (5)	C(10)–C(11)	1·373 (5)	C(11)–C(12)	1·381 (6)
C(12)–C(13)	1·373 (5)	C(13)–C(14)	1·380 (5)	C(15)–C(16)	1·397 (5)
C(15)–C(20)	1·395 (5)	C(16)–C(17)	1·372 (6)	C(17)–C(18)	1·369 (6)
C(18)–C(19)	1·377 (5)	C(19)–C(20)	1·392 (5)	C(sp²)–H	0·92 (2)
C(sp³)–H	0·95 (1)				

C(20)–C(1)–C(9)	113·2 (3)	C(20)–C(1)–C(2)	122·5 (3)
C(2)–C(1)–C(9)	124·2 (3)	C(1)–C(2)–C(3)	122·5 (3)
C(3)–C(2)–S(2)	115·7 (2)	S(2)–C(2)–C(1)	121·7 (2)
C(2)–C(3)–S(1)	120·7 (2)	S(1)–C(3)–S(3)	129·5 (2)
S(3)–C(3)–C(2)	109·7 (2)	C(3)–S(3)–C(4)	110·7 (2)
S(3)–C(4)–C(5)	110·8 (3)	S(3)–C(4)–C(6)	101·5 (3)
S(3)–C(4)–C(7)	110·8 (3)	C(5)–C(4)–C(6)	109·9 (3)
C(6)–C(4)–C(7)	110·1 (4)	C(7)–C(4)–C(5)	113·2 (4)
C(2)–S(2)–C(8)	106·5 (2)	S(2)–C(8)–C(21)	112·5 (3)
S(2)–C(8)–C(22)	109·6 (3)	S(2)–C(8)–C(23)	101·6 (3)
C(21)–C(8)–C(22)	111·3 (4)	C(22)–C(8)–C(23)	112·2 (4)
C(23)–C(8)–C(21)	109·4 (4)	C(1)–C(9)–C(10)	124·0 (3)
C(10)–C(9)–C(14)	118·0 (3)	C(14)–C(9)–C(1)	117·9 (3)
C(9)–C(10)–C(11)	120·9 (3)	C(10)–(11)–C(12)	120·0 (3)
C(11)–C(12)–C(13)	120·2 (3)	C(12)–C(13)–C(14)	119·8 (3)
C(13)–C(14)–C(9)	120·9 (3)	C(9)–C(14)–S(4)	120·7 (2)
C(13)–C(14)–S(4)	118·4 (3)	C(14)–S(4)–C(15)	98·9 (2)
S(4)–C(15)–C(20)	120·0 (3)	S(4)–C(15)–C(16)	119·9 (3)
C(16)–C(15)–C(20)	120·1 (3)	C(15)–C(16)–C(17)	119·9 (3)
C(16)–C(17)–C(18)	120·4 (4)	C(17)–C(18)–C(19)	120·3 (4)
C(18)–C(19)–C(20)	120·8 (3)	C(19)–C(20)–C(1)	123·0 (3)
C(19)–C(20)–C(15)	118·3 (3)	C(15)–C(20)–C(1)	118·7 (3)
C(sp²)–C(sp²)–H	119·8 (9)	C(sp³)–C(sp³)–H	109·9 (11)
H–C(sp³)–H	109·2 (13)		

[3',4'-bis(*tert*-butylthio)thiete] (de Vos, Kroon, Brouwer & Bos, 1981); the acute angles between the least-squares planes through the phenyl groups are 45·7 and 9·8° respectively. The torsion angle C(1)–C(2)–C(3)–S(1) of 58·1° and the intramolecular distance S(2)···C(10) of 3·167 Å are indicative of severe overcrowding, which would be even more serious in the case of the xanthene spiro thietes with their fairly planar xanthene groups. The difference between the ratio thiete/unsaturated dithioester found in solution for the xanthenyl and thioxanthenyl derivatives is compatible with this finding. The intermolecular packing is limited to van der Waals contacts.

References

BROUWER, A. C. (1979). Thesis, Utrecht.

BROUWER, A. C., GEORGE, A. V. E., SEYKENS, D. & BOS, H. J. T. (1979). *Tetrahedron Lett.* pp. 4839–4840.

COROSINE, M., CRASNIER, F., LABARRE, M. C., LABARRE, J. F. & LEIBOVICI, C. (1973). *Chem. Phys. Lett.* **20**, 111–115.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

STEWART, J. M. (1976). XRAY 76. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

VOS, A. M. DE, KROON, J., BROUWER, A. C. & BOS, H. J. T. (1981). *Acta Cryst.* B**37**, 161–164.