

Fig. 1. (a) A general view of the O<sub>6</sub>[9]aneS<sub>3</sub> molecule showing the atom-numbering scheme: thermal ellipsoids are drawn at the 30% probability level, except those of H which have artificial radii of 0.1 Å for clarity. (b) An orthogonal view showing the conformation of the nine-membered ring.

of the ring. Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

**Related literature.** Structure determinations have been reported for [9]aneS<sub>3</sub> (Glass, Wilson & Setzer, 1980) and for other oxidation products such as the sulfoxide in [Fe([9]aneS<sub>3</sub>){[9]aneS<sub>2</sub>(SO)}]<sup>2+</sup> (Küppers, Wieghardt, Nuber, Weiss, Bill & Trautwein, 1987) and the bicyclic sulfonium cation 4,7-dithia-1-thioniabicyclo[4.3.0]nonane (Blake, Holder, Hyde, Schröder & Taylor, 1991).

We thank the SERC for support.

#### References

- BLAKE, A. J., HOLDER, A. J., HYDE, T. I., SCHRÖDER, M. & TAYLOR, A. (1991). *New J. Chem.* **15**, 511–514.  
 CLEGG, W. (1981). *Acta Cryst.* **A37**, 22–28.  
 GLASS, R. S., WILSON, G. S. & SETZER, W. N. (1980). *J. Am. Chem. Soc.* **102**, 5068–5069.  
 GOULD, R. O. & TAYLOR, P. (1985). *CALC*. Program for molecular geometry calculations. Univ. of Edinburgh, Scotland.  
 KÜPPERS, H.-J., WIEGHARDT, K., NUBER, B., WEISS, J., BILL, E. & TRAUTWEIN, A. X. (1987). *Inorg. Chem.* **26**, 3762–3769.  
 MALLINSON, P. D. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

*Acta Cryst.* (1991). **C47**, 2718–2720

## Structure of Tris(5-acetyl-3-thienyl)methane–Benzene (2/1) Inclusion Compound

BY P. H. VAN ROOYEN AND H. M. ROOS

*Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa*

(Received 10 December 1990; accepted 25 June 1991)

**Abstract.** 2C<sub>19</sub>H<sub>16</sub>O<sub>3</sub>S<sub>3</sub>·C<sub>6</sub>H<sub>6</sub>, *M<sub>r</sub>* = 855.2, triclinic, *P* $\bar{1}$ , *a* = 14.197 (5), *b* = 13.560 (5), *c* = 11.538 (5) Å,  $\alpha$  = 104.45 (5),  $\beta$  = 103.40 (5),  $\gamma$  = 89.68 (5)°, *V* = 2089 (1) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.36 Mg m<sup>-3</sup>,  $\lambda$ (Mo *K*α) = 0.7107 Å,  $\mu$  = 0.323 mm<sup>-1</sup>, *F*(000) = 892, *T* = 298 K, final *wR* = 0.060, *R* = 0.083 for 4196 observed reflections with *F* > 2σ(*F<sub>o</sub>*) and 580 variable parameters. The clathrate structure consists of two tris(5-acetyl-3-thienyl)methane host molecules and one benzene guest molecule. The shortest non-hydrogen non-bonded distance between host and guest molecules is 3.437 Å [O(6)⋯C(43)]. The guest molecule interacts with only one acetylthienyl substituent of each host molecule.

**Experimental.** The host molecule, tris(5-acetyl-3-thienyl)methane (TATM), is formed by the reaction of chloroform and 2-acetylthiophene (Yakubov, Sudarushkin, Belenkii & Gold'Farb, 1973), and crystallization with many solvents yields 2/1 solute/solvent complexes (Bin Din & Meth-Cohn, 1977). Crystallization of TATM with benzene yielded pale-yellow crystals with approximate dimensions 0.3 × 0.3 × 0.3 mm, m.p. 379–383 K. Philips PW 1100 diffractometer, graphite-monochromated radiation, unit cell from 25 reflections ( $\theta < 13^\circ$ ), 7391 reflections for  $3 \leq \theta \leq 24^\circ$  in the range  $-16 \leq h \leq 16$ ,  $-15 \leq k \leq 15$ ,  $0 \leq l \leq 13$  using  $\omega/2\theta$  scans, scan speed 0.048° s<sup>-1</sup>, scan width 1.20°. Three standard

Table 1. Fractional coordinates ( $\times 10^4$ ) and equivalent isotropic thermal factors ( $\text{\AA}^2 \times 10^3$ ) for the non-H atoms in TATM-benzene
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq}$
C(1)	6429 (4)	6501 (4)	3734 (6)	33 (2)
S(1)	3673 (1)	5813 (1)	3762 (2)	45 (1)
C(2)	4669 (4)	6592 (5)	3943 (6)	37 (2)
C(3)	5445 (5)	6048 (5)	3692 (5)	33 (2)
C(4)	5218 (4)	4979 (5)	3356 (5)	32 (2)
C(5)	4291 (4)	4730 (5)	3362 (5)	33 (2)
C(6)	3781 (5)	3734 (5)	3051 (6)	40 (2)
O(1)	2933 (3)	3663 (3)	3093 (5)	59 (1)
C(7)	4326 (5)	2808 (5)	2664 (7)	59 (2)
S(2)	6448 (1)	5698 (2)	130 (2)	53 (1)
C(8)	5954 (5)	6027 (5)	1365 (6)	45 (2)
C(9)	6640 (5)	6191 (4)	2461 (6)	34 (2)
C(10)	7583 (4)	6043 (4)	2261 (6)	33 (2)
C(11)	7616 (4)	5773 (5)	1056 (6)	34 (2)
C(12)	8453 (5)	5581 (5)	553 (6)	41 (2)
O(2)	9261 (3)	5663 (4)	1264 (4)	61 (1)
C(13)	8362 (5)	5300 (6)	-800 (6)	59 (2)
S(3)	6939 (1)	9400 (1)	5788 (2)	50 (1)
C(14)	7004 (5)	8104 (5)	5435 (6)	44 (2)
C(15)	6529 (4)	7633 (5)	4271 (6)	33 (2)
C(16)	6100 (4)	8358 (5)	3610 (6)	36 (2)
C(17)	6261 (4)	9352 (5)	4313 (6)	40 (2)
C(18)	5949 (5)	10308 (6)	4014 (7)	50 (2)
O(3)	6112 (4)	11121 (4)	4780 (5)	68 (1)
C(19)	5449 (6)	10228 (6)	2699 (7)	72 (2)
C(20)	1468 (4)	8008 (5)	3768 (6)	33 (2)
S(4)	1418 (1)	7180 (2)	146 (2)	55 (1)
C(21)	968 (5)	7422 (5)	1417 (6)	46 (2)
C(22)	1657 (4)	7745 (4)	2484 (6)	32 (2)
C(23)	2588 (5)	7807 (5)	2254 (6)	34 (2)
C(24)	2594 (4)	7524 (5)	1032 (6)	39 (2)
C(25)	3414 (6)	7514 (6)	484 (7)	52 (2)
O(4)	4213 (4)	7795 (5)	1120 (5)	82 (2)
C(26)	3265 (6)	7149 (7)	-903 (7)	83 (2)
S(5)	2085 (1)	5996 (1)	5850 (2)	42 (1)
C(27)	2149 (4)	7138 (5)	5456 (6)	37 (2)
C(28)	1579 (4)	7085 (5)	4313 (5)	28 (1)
C(29)	1097 (4)	6119 (5)	3731 (6)	32 (1)
C(30)	1303 (4)	5430 (5)	4453 (5)	33 (2)
C(31)	937 (5)	4384 (6)	4200 (6)	44 (2)
O(5)	1145 (4)	3902 (4)	4977 (5)	66 (1)
C(32)	305 (5)	3895 (5)	2953 (6)	60 (2)
S(6)	-1305 (1)	8693 (1)	3846 (2)	46 (1)
C(33)	-289 (5)	7998 (5)	4018 (6)	41 (2)
C(34)	472 (5)	8414 (5)	3727 (5)	35 (2)
C(35)	215 (5)	9341 (5)	3370 (6)	36 (2)
C(36)	-714 (4)	9571 (5)	3386 (6)	34 (2)
C(37)	-1257 (5)	10436 (5)	3037 (6)	43 (2)
O(6)	-2085 (3)	10537 (3)	3145 (5)	61 (1)
C(38)	-754 (5)	11162 (5)	2565 (7)	64 (2)
C(39)	2587 (13)	10227 (8)	816 (10)	138 (3)
C(40)	1728 (12)	10560 (11)	979 (12)	151 (3)
C(41)	1310 (9)	11311 (12)	413 (12)	158 (3)
C(42)	1802 (11)	11640 (8)	-290 (10)	121 (3)
C(43)	2654 (10)	11341 (10)	-431 (10)	120 (3)
C(44)	3073 (9)	10572 (11)	128 (1)	142 (3)

Table 2. Bond lengths ( $\text{\AA}$ ) and valence angles ( $^\circ$ ) for the non-H atoms in TATM-benzene

C(1)—C(3)	1.515 (9)	C(1)—C(9)	1.522 (9)
C(1)—C(15)	1.499 (8)	S(1)—C(2)	1.711 (7)
S(1)—C(5)	1.724 (6)	C(2)—C(3)	1.368 (9)
C(3)—C(4)	1.423 (9)	C(4)—C(5)	1.362 (9)
C(5)—C(6)	1.458 (9)	C(6)—O(1)	1.223 (9)
C(6)—C(7)	1.497 (10)	S(2)—C(8)	1.691 (7)
S(2)—C(11)	1.740 (6)	C(8)—C(9)	1.374 (8)
C(9)—C(10)	1.416 (9)	C(10)—C(11)	1.358 (9)
C(11)—C(12)	1.434 (10)	C(12)—O(2)	1.233 (8)
C(12)—C(13)	1.487 (10)	S(3)—C(14)	1.710 (7)
S(3)—C(17)	1.736 (6)	C(14)—C(15)	1.351 (8)
C(15)—C(16)	1.439 (10)	C(16)—C(17)	1.377 (9)
C(17)—C(18)	1.463 (11)	C(18)—O(3)	1.213 (8)
C(18)—C(19)	1.495 (11)	C(20)—C(22)	1.521 (9)
C(20)—C(28)	1.527 (10)	C(20)—C(34)	1.510 (9)
S(4)—C(21)	1.691 (8)	S(4)—C(24)	1.740 (6)
C(21)—C(22)	1.358 (8)	C(22)—C(23)	1.413 (10)
C(23)—C(24)	1.368 (9)	C(24)—C(25)	1.447 (11)
C(25)—O(4)	1.205 (8)	C(25)—C(26)	1.516 (10)
S(5)—C(27)	1.727 (7)	S(5)—C(30)	1.728 (5)
C(27)—C(28)	1.363 (8)	C(28)—C(29)	1.412 (8)
C(29)—C(30)	1.386 (10)	C(30)—C(31)	1.448 (10)
C(31)—O(5)	1.218 (10)	C(31)—C(32)	1.499 (9)
S(6)—C(33)	1.719 (7)	S(6)—C(36)	1.714 (7)
C(33)—C(34)	1.366 (10)	C(34)—C(35)	1.437 (9)
C(35)—C(36)	1.357 (9)	C(36)—C(37)	1.488 (10)
C(37)—O(6)	1.213 (9)	C(37)—C(38)	1.493 (12)
C(39)—C(40)	1.34 (3)	C(39)—C(44)	1.33 (2)
C(40)—C(41)	1.40 (2)	C(41)—C(42)	1.34 (2)
C(42)—C(43)	1.31 (2)	C(43)—C(44)	1.42 (2)
C(3)—C(1)—C(9)	110.0 (4)	C(3)—C(1)—C(15)	112.4 (5)
C(9)—C(1)—C(15)	112.6 (6)	C(2)—S(1)—C(5)	92.1 (3)
S(1)—C(2)—C(3)	112.0 (5)	C(1)—C(3)—C(2)	125.5 (6)
C(1)—C(3)—C(4)	122.7 (6)	C(2)—C(3)—C(4)	111.7 (6)
S(1)—C(4)—C(5)	113.5 (6)	S(1)—C(5)—C(4)	110.8 (5)
S(1)—C(5)—C(6)	119.1 (5)	C(4)—C(5)—C(6)	130.1 (6)
C(5)—C(6)—O(1)	120.7 (6)	C(5)—C(6)—C(7)	118.0 (6)
O(1)—C(6)—C(7)	121.4 (6)	C(8)—S(2)—C(11)	92.4 (3)
S(2)—C(8)—C(9)	112.4 (5)	C(1)—C(9)—C(8)	125.2 (6)
C(1)—C(9)—C(10)	123.7 (5)	C(8)—C(9)—C(10)	111.2 (6)
C(9)—C(10)—C(11)	114.5 (5)	S(2)—C(11)—C(10)	109.6 (5)
S(2)—C(11)—C(12)	122.4 (5)	C(10)—C(11)—C(12)	128.0 (5)
C(11)—C(12)—O(2)	119.0 (6)	C(11)—C(12)—C(13)	121.2 (6)
O(2)—C(12)—C(13)	119.8 (7)	C(14)—S(3)—C(17)	91.5 (3)
S(3)—C(14)—C(15)	113.6 (5)	C(1)—C(15)—C(14)	125.0 (6)
C(1)—C(15)—C(16)	123.8 (5)	C(14)—C(15)—C(16)	111.2 (5)
C(15)—C(16)—C(17)	113.1 (5)	S(3)—C(17)—C(16)	110.5 (5)
S(3)—C(17)—C(18)	118.6 (5)	C(16)—C(17)—C(18)	130.9 (6)
C(17)—C(18)—O(3)	121.9 (7)	C(17)—C(18)—C(19)	116.1 (6)
O(3)—C(18)—C(19)	122.0 (7)	C(22)—C(20)—C(28)	111.1 (5)
C(22)—C(20)—C(34)	110.0 (5)	C(28)—C(20)—C(34)	111.0 (6)
S(4)—C(21)—C(22)	91.6 (3)	S(4)—C(21)—C(22)	113.4 (5)
C(20)—C(22)—C(23)	125.1 (6)	C(20)—C(22)—C(23)	123.7 (5)
C(22)—C(23)—C(24)	111.2 (6)	C(22)—C(23)—C(24)	114.0 (5)
S(4)—C(24)—C(23)	109.8 (5)	S(4)—C(24)—C(25)	122.1 (5)
C(23)—C(24)—C(25)	128.1 (6)	C(24)—C(25)—O(4)	120.5 (7)
C(24)—C(25)—C(26)	119.7 (6)	O(4)—C(25)—C(26)	119.8 (8)
C(27)—S(5)—C(30)	92.2 (3)	S(5)—C(27)—C(28)	111.2 (4)
C(20)—C(28)—C(27)	121.8 (5)	C(20)—C(28)—C(29)	124.9 (5)
C(27)—C(28)—C(29)	113.3 (6)	C(28)—C(29)—C(30)	112.8 (5)
S(5)—C(30)—C(29)	110.5 (4)	S(5)—C(30)—C(31)	120.0 (5)
C(29)—C(30)—C(31)	129.5 (5)	C(30)—C(31)—O(5)	121.0 (5)
C(30)—C(31)—C(32)	118.7 (7)	O(5)—C(31)—C(32)	120.2 (6)
C(33)—S(6)—C(36)	91.1 (3)	S(6)—C(33)—C(34)	112.9 (5)
C(20)—C(34)—C(33)	127.1 (6)	C(20)—C(34)—C(35)	122.0 (6)
C(33)—C(34)—C(35)	110.9 (6)	C(34)—C(35)—C(36)	112.8 (6)
S(6)—C(36)—C(35)	112.3 (5)	S(6)—C(36)—C(37)	118.6 (5)
C(35)—C(36)—C(37)	129.0 (7)	C(36)—C(37)—O(6)	119.8 (7)
C(36)—C(37)—C(38)	118.2 (6)	O(6)—C(37)—C(38)	122.0 (7)
C(40)—C(39)—C(44)	123.0 (13)	C(39)—C(40)—C(41)	120 (2)
C(40)—C(41)—C(42)	116.7 (14)	C(41)—C(42)—C(43)	124.4 (13)
C(42)—C(43)—C(44)	118.9 (13)	C(39)—C(44)—C(43)	117.4 (13)

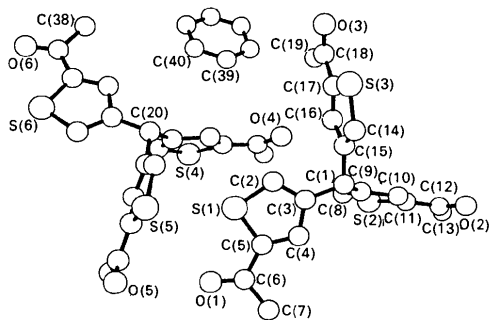


Fig. 1. Perspective view with atomic numbering scheme.

reflections ( $1\bar{2}3$ , 603, 324) were measured every hour, Lorentz-polarization correction, but no decay or absorption corrections applied. Structure solved using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), blocked least-squares refinement using *SHELX76* (Sheldrick,

1976),  $F$  magnitudes,  $\sigma^{-2}(F)$  weights, all non-H atoms anisotropic, all H atoms isotropic in calculated positions (C—H = 1.08 Å, H—C—H = 109.4°) with a common thermal parameter that was also refined [ $U_{\text{iso}}(\text{H}) = 0.138$  (6) Å<sup>2</sup>], 580 variables refined,  $\sum w|\Delta F|^2$  minimized. Final  $wR = 0.060$ ,  $R = 0.083$ ,  $(\Delta/\sigma)_{\text{max}} < 0.1$ , maximum residual electron density = 0.43 e Å<sup>-3</sup>. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 1 gives the atom parameters, Table 2 the bond lengths and valence angles, and Fig. 1 shows the molecular structure and atomic numbering scheme drawn by *ORTEP* (Johnson, 1965).\*

**Related literature.** In the TATM—EtOAc clathrate studied recently (van Rooyen & Roos, 1990) the

\* Lists of structure factors, bond angles involving H atoms, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54396 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

interaction of the guest molecule is with two acetylthienyl substituents of each host molecule.

The authors wish to thank Dr O. Meth-Cohn for the title compound.

#### References

- BIN DIN, L. & METH-COHN, O. (1977). *J. Chem. Soc. Chem. Commun.* pp. 741–742.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.  
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 VAN ROOYEN, P. H. & ROOS, H. M. (1990). *Acta Cryst.* **C47**, 2468–2470.  
 YAKUBOV, A. P., SUDARUSHKIN, YU. K., BELENKII, L. I. & GOLD'FARB, YA. L. (1973). *J. Org. Chem. USSR*, **9**, 1549–1552.

*Acta Cryst.* (1991). **C47**, 2720–2723

## Bis(carbodifluoro) and Tris(carbodifluoro) Derivatives of Zaluzanin D\*

BY E. DÍAZ,† H. BARRIOS, R. VILLENA AND R. A. TOSCANO

*Instituto de Química, UNAM, Circuito Exterior, Ciudad Universitaria, Coyoacán, DF 04510 Mexico*

(Received 3 December 1990; accepted 25 June 1991)

**Abstract.** (1) (3a*S*,6*S*,6a*R*,8*S*,9*S*,9a*R*,9b*S*)-2',2',2'',-2''-Tetrafluoro-3-methylene-2-oxo-2,3,3a,4,5,6,6a,7,-8,9,9a,9b-dodecahydrodispiro[azuleno[4,5-*b*]furan-6,1':9,1''-biscyclopropan]-8-yl acetate, C<sub>19</sub>H<sub>20</sub>F<sub>4</sub>O<sub>4</sub>,  $M_r = 388.4$ , monoclinic,  $P2_1$ ,  $a = 9.912$  (3),  $b = 8.415$  (2),  $c = 11.096$  (3) Å,  $\beta = 99.98$  (2)°,  $V = 911.5$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.41$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 10.52$  cm<sup>-1</sup>,  $F(000) = 404$ ,  $T = 293$  K,  $R = 0.064$ ,  $wR = 0.073$  for 1182 observed reflections [ $F > 3\sigma(F)$ ]. (2) (3*S*,3a*S*,6*S*,6a*R*,8*S*,9*S*,9a*R*,9b*S*)-2',2',2'',2''',2''''-Hexafluoro-3-methylene-2-oxo-2,3,3a,4,5,6,6a,7,8,9,9a,9b-dodecahydro-trispiro[azuleno[4,5-*b*]furan-6,1':6,1''':9,1''''-triscyclopropan]-8-yl acetate, C<sub>20</sub>H<sub>20</sub>F<sub>6</sub>O<sub>4</sub>,  $M_r = 438$ , monoclinic,  $P2_1$ ,  $a = 10.348$  (3),  $b = 8.388$  (2),  $c = 11.093$  (3) Å,  $\beta = 97.64$  (2)°,  $V = 954.3$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.53$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu =$

12.34 cm<sup>-1</sup>,  $F(000) = 452$ ,  $T = 293$  K,  $R = 0.033$ ,  $wR = 0.037$  for 1264 observed reflections [ $F > 3\sigma(F)$ ]. The chiral centers formed during the difluorocarbination of zaluzanin D were determined relative to the 7*S* chiral center as has been found in zaluzanins and most of the guaianolides isolated so far. The asymmetry of difluorocyclopropane ring can be proposed as  $\delta_1 + = [(\delta_2 -) + (\delta_3 -)]$  rather than  $[\delta + = 2\delta -]$  as described before [Allen (1980). *Acta Cryst.* **B36**, 81–96]. Molecular packing in the crystals is due entirely to van der Waals interactions.

**Experimental.** Title compounds were synthesized as previously described by Salazar & Díaz (1978).

(1). Colorless crystals 0.04 × 0.22 × 0.52 mm from acetone-isopropyl ether. Intensity data from Nicolet P3/F diffractometer, Ni-filtered Cu radiation. Lattice parameters from 25 centered reflections (8.11 < 2θ < 29.20°), 1326 measured intensities with 3 < 2θ < 110°, 1240 unique,  $R_{\text{int}} = 0.28$ . 58 unobserved [ $F <$

\* Contribution No. 1071 of the Instituto de Química, UNAM.  
 † Author to whom correspondence should be addressed.