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Tetra(3,4-thienylene), $(C_4H_2S)_4$

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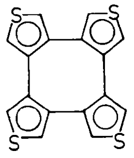
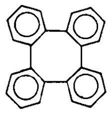
Abstract. M_r = 328·5, monoclinic, $P2/c$, a = 9·956 (2), b = 15·670 (2), c = 13·700 (2) Å, β = 91·80 (2)°, V = 2131·6 (10) Å^3, Z = 6, D_x = 1·54 Mg m^{-3}, Mo $K\alpha$, λ = 0·71073 Å, μ = 0·627 mm^{-1}, $F(000)$ = 1008, T = 295 K, R = 0·037 for 3341 observed reflections [$I > 3\sigma(I)$]. The eight-membered ring has a tub conformation with bond angles of 126·0 (4)° and torsional angles of 58 (2)°. The bonds in the eight-membered ring [1·436 (3) and 1·469 (5) Å] have only little alternating nature. The bonding character of this ring is closer to an octamethylene–cyclooctane rather than to a cyclooctatetraene system. The thiophene rings are tilted outwards from the eight-membered ring by 3·7 (8)°. Two neighbouring thiophene rings are twisted by an angle of 53·7 (14)°.

Introduction. According to molecular models tetra(3,4-thienylene) (cycloocta[1,2-*c*:3,4-*c*′:5,6-*c*″:7,8-*c*‴]tetrathiophene) (1) should have a tub-shaped structure (Kauffmann, Greving, Kriegesmann, Mitschker & Woltermann, 1978). The corresponding benzo derivative tetrabenzo[*a,c,e,g*]cyclooctatetraene (2) does have this conformation and deviates strongly from a planar arrangement (Irngartinger & Reibel, 1981). Cyclooctatetraene (COT) with four attached five-membered rings of perfluorocyclopentene also has a boat conformation (Cobbledick & Einstein, 1977). On the other hand, the corresponding cyclooctatetraene derivative with four four-membered rings of perfluorocyclobutene is completely planar (Einstein, Willis, Cullen & Soulen, 1981). We determined the structure of (1) to see how far the eight-membered ring system deviates from a planar arrangement if four five-membered rings of thiophene are attached to it.



(1)



(2)

Experimental. Crystal: yellow needle 0·2 × 0·4 × 0·6 mm, grown from nitromethane solution. Enraf–Nonius CAD-4 diffractometer. Cell dimensions from 2θ angles of 25 reflections (16 < 2θ < 38°). 4997 data up to $\sin\theta/\lambda$ = 0·64 Å^{-1} (excluding systematic absences). $0 \leq h \leq 13$, $0 \leq k \leq 19$, $-18 \leq l \leq 17$. 3 standard reflections ($2\bar{6}\bar{6}$, $\bar{2}8\bar{5}$, $\bar{3}\bar{4}\bar{5}$), max. variation 1·00 to 1·01. 4724 unique reflections ($R_{\rm int}$ = 0·023). Empirical absorption correction: ψ scan with 9 reflections, variation of correction factor 0·95 to 1·00. 3341 intensities with $I > 3\sigma(I)$. Structure solution by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Structure refined by full-matrix least squares on F^2 with anisotropic thermal parameters for S and C atoms. The positions of the H atoms were calculated according to geometrical requirements. The H atoms were refined isotropically. 319 variables, R = 0·037 for 3341 observed reflections, wR = 0·047, $w = 4F^2/\sigma^2(F^2) + (0{\cdot}03F^2)^2$, S = 1·96;* Δ/σ < 0·17, largest $\Delta\rho$ peak 0·34 e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974); *SDP* programs (Frenz, 1978) used on PDP 11/44.

Discussion. Final atomic coordinates are given in Table 1, the atomic numbering scheme and a stereoscopic drawing in Figs. 1 and 2 respectively. One molecule lies on a general position, a second on a crystallographic twofold axis. Chemically equivalent bond lengths and angles agree within experimental accuracy. The average values together with the deviations are given in Table 2. The differences between the bond lengths a [1·436 (3)] and b [1·469 (5) Å] in the eight-membered ring of (1) are three times smaller than in (2) (Table 2). In the thiophene rings the bond c [1·364 (6) Å] has high and bond a low double-bond character. Therefore the bonds in the eight-membered ring of (1) have only little alternating nature. This ring has a strong octamethylene–cyclooctane and only a small cyclooctatetraene character. Since the bond angles in the five-membered thiophene rings are smaller than 120° [γ = 111·6 (3)°], the bond angles within the eight-membered ring can be significantly larger [α = 126·0 (4)°]. Therefore, the puckering of this ring in (1) is reduced compared to (2). The torsion angles a—b—a' are 58·1 (15) and 66·1 (17)° in (1) and (2) respectively. The COT ring in the derivative with four perfluorocyclopentene rings attached to it has a conformation

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, some torsion angles and a full list of bond lengths and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42156 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and thermal parameters of* (1)

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}(Å^2 × 10^4)
S(1)	0·67581 (7)	0·09829 (5)	0·58908 (5)	513 (3)
S(2)	0·04524 (7)	0·11490 (5)	0·62010 (5)	497 (3)
S(3)	0·24206 (7)	0·10163 (4)	0·18606 (4)	473 (3)
S(4)	0·42424 (8)	0·43457 (4)	0·40891 (6)	528 (4)
S(5)	0·05854 (9)	0·34530 (5)	0·02528 (6)	641 (4)
S(6)	0·31617 (7)	0·65971 (5)	0·25089 (6)	602 (4)
C(1)	0·50644 (22)	0·20308 (14)	0·51178 (15)	315 (10)
C(2)	0·42886 (23)	0·13588 (14)	0·55299 (15)	325 (10)
C(3)	0·28192 (23)	0·13245 (14)	0·55477 (16)	330 (11)
C(4)	0·19074 (22)	0·13187 (13)	0·47098 (15)	312 (10)
C(5)	0·23100 (22)	0·13616 (13)	0·36820 (15)	306 (10)
C(6)	0·31055 (20)	0·20232 (14)	0·32618 (15)	301 (10)
C(7)	0·36514 (21)	0·27813 (14)	0·37622 (15)	312 (10)
C(8)	0·45276 (21)	0·27896 (14)	0·46151 (15)	312 (10)
C(9)	0·64144 (24)	0·19079 (16)	0·52770 (17)	399 (12)
C(10)	0·50971 (26)	0·07571 (16)	0·59739 (17)	426 (12)
C(11)	0·21425 (25)	0·12434 (16)	0·63931 (17)	409 (12)
C(12)	0·06104 (24)	0·12216 (16)	0·49668 (17)	407 (12)
C(13)	0·18693 (24)	0·07875 (15)	0·30030 (17)	386 (12)
C(14)	0·32264 (23)	0·19103 (16)	0·22847 (17)	394 (12)
C(15)	0·34277 (24)	0·35832 (15)	0·34071 (18)	403 (12)
C(16)	0·49212 (26)	0·35906 (16)	0·48586 (18)	436 (13)
C(17)	0·02125 (23)	0·39775 (15)	0·19923 (17)	388 (12)
C(18)	0·09797 (23)	0·46297 (15)	0·15279 (17)	378 (11)
C(19)	0·15114 (23)	0·54112 (15)	0·19946 (16)	373 (11)
C(20)	0·07335 (22)	0·60583 (15)	0·24584 (17)	360 (11)
C(21)	−0·00487 (27)	0·33033 (17)	0·13791 (21)	516 (14)
C(22)	0·12524 (28)	0·44120 (18)	0·05909 (19)	515 (14)
C(23)	0·28427 (25)	0·56333 (17)	0·19823 (20)	484 (13)
C(24)	0·15136 (25)	0·67269 (16)	0·27662 (19)	455 (13)

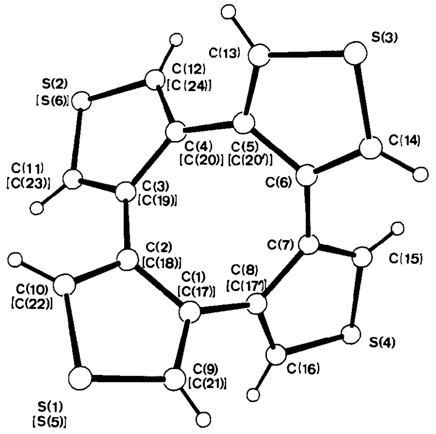


Fig. 1. Projection of the title compound (1) with the atomic numbering scheme of both independent molecules. The atom names of the second molecule are in square brackets.

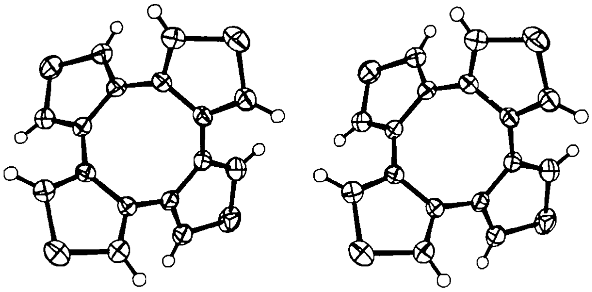
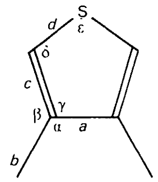


Fig. 2. Stereoscopic view of the first molecule of (1).

Table 2. *Average bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

The scatter is given in parentheses. The standard deviations of the individual values are: 0·002–0·004 Å, 0·1–0·2° and 0·2–0·4°, respectively. The values of (2) are taken from Irngartinger & Reibel (1981).



	(1)	(2)	(1)	(2)
a	1·436 (3)	1·400 (2)	α 126·0 (4)	122·5 (3)
b	1·469 (5)	1·494 (4)	β 122·3 (4)	118·6 (3)
c	1·364 (6)	—	γ 111·6 (3)	118·8 (2)
d	1·704 (5)	—	δ 112·6 (3)	—
			ε 91·5 (2)	—
b—a—b'	1·4 (6)	1·0 (6)		
a—b—a'	58·1 (15)	66·1 (17)		
c—b—c'	49·4 (15)	—		

comparable to (1) (Cobbledick & Einstein, 1977). Because of the considerable deviation of the atoms in the central ring of (1) from the geometry expected for sp^2-hybridized C atoms the thiophene rings are tilted outwards by 3·7 (8)° from a plane passing through both C atoms common to the central ring and thiophene and the corresponding neighbouring atoms within the eight-membered ring [*e.g.* for the first thiophene ring: C(1), C(2), C(3), C(8)]. This is also the reason for the difference of both torsion angles *a—b—a'* and *c—b—c'*, 58·1 (15) and 49·4 (15)°. The angle between the plane of two neighbouring thiophene rings is 53·7 (14)°.

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