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1,5,8,12-Tetrathiaspiro[6.6]tridecane

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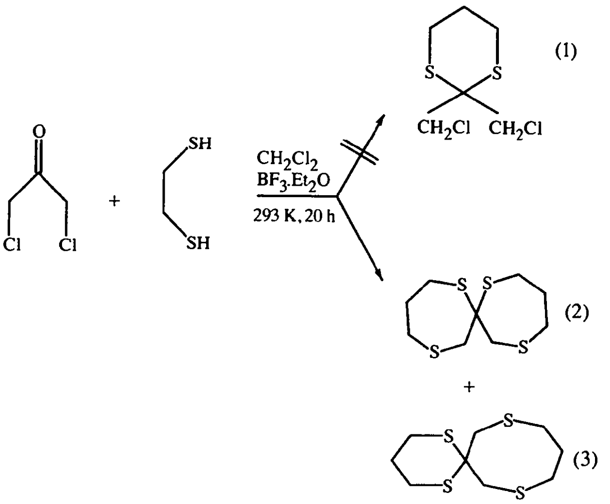
Abstract

The title compound, $C_9H_{16}S_4$, crystallizes in the space group $P\bar{1}$ with two molecules in the asymmetric unit. All seven-membered rings adopt a twist-chair (C_2 symmetry) conformation.

Comment

Our ongoing investigation of cyclopropene fatty acids as desaturase inhibitors in the biosynthesis of insect sex pheromones (Gosalbo *et al.*, 1994) led us to study alternative procedures to the previously reported preparations of these compounds (Baird *et al.*, 1992; Gensler *et al.*, 1970). We anticipated that cyclopropenone dithioacetal derivatives might be the appropriate precursor when submitted to reductive desulfuration. In this context, preparation of the dithioacetal (1) was required. However after the synthesis, unexpected formation of a mixture of 1,5,8,12-tetrathiaspiro[6.6]tridecane, (2), and 1,5,8,12-tetrathiaspiro[5.7]tridecane, (3), was found to have occurred.



Conformational analysis of seven-membered ring compounds is still a challenging problem because these compounds are flexible with many (conformational) possibilities. As shown in Fig. 1, the two crystallographically independent molecules of the title compound, (2), consist of two 1,4-dithiacycloheptane rings coupled together at the spiro-C atoms C7 or C7′. The molecules are similar and related by pseudo-symmetry operations. All four seven-membered rings adopt a twist-chair conformation with a pseudo-twofold axis running along C3 and the midpoint of C6—C7, and in the second ring, running along C7 and the midpoint of C10—C11. In the second molecule, the twofold axis runs along C7′ and the midpoints of bonds C3′—C4′ and C10′—C11′. The total puckering amplitude Q_T (Cremer & Pople, 1975) ranges from 1.062 (1) to 1.111 (1) Å. The conformational features agree with those reported previously for 1,4-dithiacycloheptane (Setzer *et al.*, 1981) and dioxepin (Ianelli *et al.*, 1989).

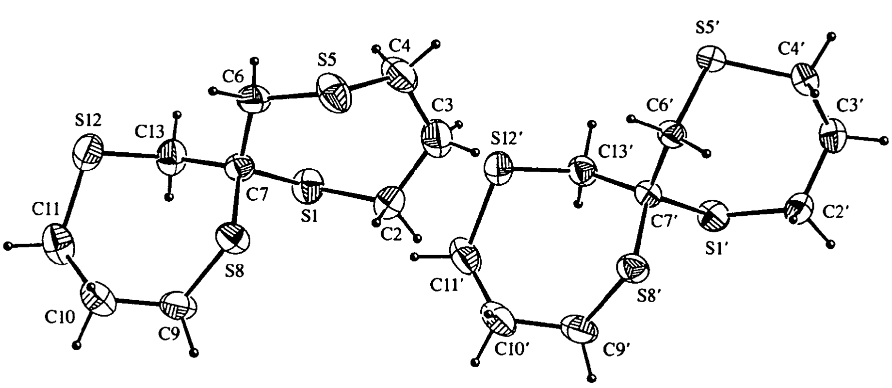


Fig. 1. The structure and labelling scheme for compound (2). Displacement ellipsoids are drawn at the 50% probability level.

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Experimental

1,3-Dichloropropanone (3.5 g, 26 mmol) was reacted with 1,3-propanedithiol (4.3 g, 40 mmol) in the presence of $BF_3.OEt_2$ (0.1 g, 1.1 mmol) in anhydrous CH_2Cl_2 (90 ml) for 20 h. After the usual work-up, the formation of (1) was not observed (see scheme). Thin-layer chromatography (TLC) analysis of the residue revealed the presence of two compounds which were isolated by column chromatography on Al_2O_3, eluting with a 4:1 hexane–diethyl ether mixture. The major compound (m.p. 377–378 K, 2.27 g, 42% yield) exhibited spectral features in agreement with structure (2). ^{1}H NMR: δ 2.7–3.4 (complex, 12H, S—CH_2) and 1.8–2.4 (complex, 4H, S—CH_2—CH_2). ^{13}C NMR: δ 66.1 (C7), 48.3 (C6, C13), 34.4 (C2, C9), 32.0 (C4, C11), 28.5 (C3, C10). GC–MS: m/z 252 (M^+, 4%), 146 (33%), 106 (100%). Analysis calculated for $C_9H_{16}S_4$: C 42.82, H 6.39, S 50.79%; found: C 42.42, H 6.49, S 50.64%. The minor compound (m.p. 370–371 K, 0.59 g, 11% yield) exhibited spectral features in agreement with the previously reported structure of (3) (Arya, 1972).

Crystal data

$C_9H_{16}S_4$
M_r = 252.47
Triclinic
$P\bar{1}$
a = 10.446 (1) Å
b = 11.045 (1) Å
c = 11.316 (1) Å
α = 64.24 (1)°
β = 79.20 (1)°
γ = 85.35 (1)°
V = 1155.02 (18) Å^3
Z = 4
D_x = 1.452 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 15.33–19.44°
μ = 0.78 mm^{-1}
T = 294 (2) K
Prism
0.82 × 0.67 × 0.55 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.569, $T_{\max}$ = 0.675
6979 measured reflections
6979 independent reflections

6226 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 30.41°
$h = 0 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: 0.5%

Refinement

Refinement on F^2
$R(F)$ = 0.029
$wR(F^2)$ = 0.088
S = 1.122
6979 reflections
235 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 0.2769P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.006
$\Delta\rho_{\max}$ = 0.805 e Å^{-3}
$\Delta\rho_{\min}$ = −0.554 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C2	1.8107 (19)	S1′—C2′	1.8053 (17)
S1—C7	1.8467 (14)	S1′—C7′	1.8296 (12)
S5—C4	1.8053 (19)	S5′—C4′	1.8100 (17)
S5—C6	1.8041 (17)	S5′—C6′	1.8022 (14)
S8—C7	1.8223 (13)	S8′—C7′	1.8292 (13)
S8—C9	1.8103 (17)	S8′—C9′	1.8104 (16)
C2—S1—C7	104.34 (7)	C2′—S1′—C7′	104.65 (6)
C4—S5—C6	100.95 (8)	C4′—S5′—C6′	101.08 (7)
C7—S8—C9	104.58 (7)	C7′—S8′—C9′	103.92 (7)
C11—S12—C13	99.93 (8)	C11′—S12′—C13′	99.64 (7)
S1—C2—C3	116.12 (13)	S1′—C2′—C3′	114.15 (11)
S5—C4—C3	115.66 (14)	S5′—C4′—C3′	116.70 (12)
S5—C6—C7	118.30 (10)	S5′—C6′—C7′	115.65 (9)
S1—C7—S8	113.23 (7)	S1′—C7′—S8′	112.22 (6)
S1—C7—C6	113.24 (10)	S1′—C7′—C6′	114.44 (9)

All H atoms were included at calculated positions and refined using a riding model, each with an isotropic displacement parameter equal to $1.2U_{eq}$ of the attached C atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1997). Software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1520). Services for accessing these data are described at the back of the journal.

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