

Dispiro[fluorene-9,5'-[1,2,3,4]tetra- thiane-6',9''-fluorene]

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The tetrathiane ring of the title compound, $C_{26}H_{16}S_4$, has a chair conformation and the molecule has approximate C_2 symmetry. Each of the two fluorene ring systems is virtually planar, with the ring planes intersecting at an angle of $67.58(5)^\circ$. This novel compound has been formed as a side product from the treatment of 9*H*-fluorene-9-thione with methyl *N*-[(benzylidene)phenyl]glycinate in the presence of LiBr and 1,6-diazabicyclo[5.4.0]undecane.

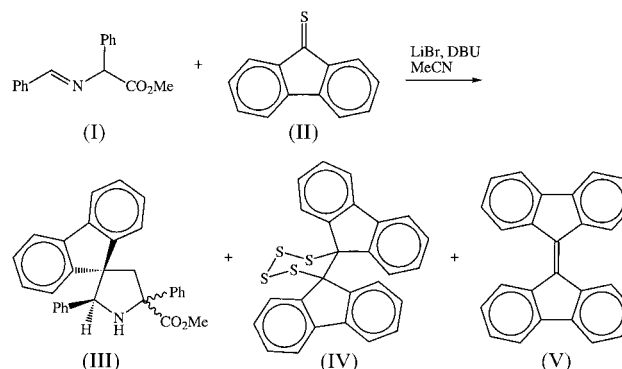
Comment

For many years we have been investigating reactions involving compounds containing C=S groups, for example, thioketones and 1,3-thiazole-5(4*H*)-thiones (Heimgartner, 1986, 1991; Mloston & Heimgartner, 2000). The focus of our studies is on 1,3-dipolar cycloadditions which lead to new sulfur heterocycles. Among the 1,3-dipoles that have been used are nitrile ylides (Büchel *et al.*, 1984), nitrile imines (Linden *et al.*, 1999), azides (Mloston & Heimgartner, 1995; Mloston *et al.*, 1996), diazo compounds (Kägi *et al.*, 1996; Kelmendi *et al.*, 2000), carbonyl ylides (Meier *et al.*, 1997) and thiocarbonyl ylides (Mloston & Heimgartner, 2000). In some cases, such as with azides and diazo compounds under forced conditions, elemental sulfur was formed ('twofold extrusion'; Guzic & Sanfilippo, 1988), which led to the formation of products containing more than one S atom per molecule. As an example, reactions of reactive thiocarbonyl compounds, such as thiobenzophenone or 9*H*-fluorene-9-thione, with phenyl azide yielded the corresponding *N*-phenylimines and 1,2,4-trithiolanes (Mloston & Heimgartner, 1995; *cf.* Fabian & Senning, 1998). The intermediate formation of a thiosulfine (thiocarbonyl-*S*-sulfide) *via* sulfur transfer and a subsequent 1,3-dipolar cycloaddition is proposed as the reaction mechanism. Thiosulfines, which can also be generated by thiation of thiocarbonyl compounds with S_8 , can dimerize to give 1,2,4,5-tetrathianes (Franeek, 1991*a,b*; Huisgen & Rapp, 1997; Huisgen *et al.*, 1997; *cf.* Senning, 1994).

Cyclic polysulfides are a highly interesting class of sulfur heterocycles (*cf.* Block *et al.*, 1988; Sato *et al.*, 2001). Among them, several 1,2,3,4-tetrathianes have been prepared by

reacting 1,2-dithiols with dichlorodisulfane (S_2Cl_2 ; Fehér & Degen, 1967; Fehér *et al.*, 1972*a,b*; Kustos & Stendel, 1995). Different approaches have been developed by heating alkenes with polysulfides (Krespan & Brasen, 1962), with sulfur (S_8) and catalysts (Chernyshev *et al.*, 1984; Nekhaev *et al.*, 1991) or by treatment of thiiranes with catalytic amounts of tris(4-bromophenyl)aminium hexachloroantimonate, an aminium radical salt, in dichloromethane, the latter reaction occurring *via* an SET mechanism (Kamata *et al.*, 1990).

Recently, we became interested in the reaction of azomethine ylides with C=S compounds (Mloston *et al.*, 1998; Gebert, 2001; Gebert *et al.*, 2001). Among the different known routes for synthesizing reactive azomethine ylides, we followed a protocol that starts with *N*-benzylidene- α -amino acid esters in the presence of LiBr and 1,6-diazabicyclo[5.4.0]undecane (DBU) as the base (Grigg & Sridharan, 1993; Kanemasa & Tsuge, 1993; Barr *et al.*, 1995). In the case of methyl *N*-[(benzylidene)phenyl]glycinate, (I), and 9*H*-fluorene-9-thione, (II), the reaction at room temperature was terminated after two minutes. In addition to the two diastereoisomeric cycloadducts of type (III), which were isolated in 82% yield (*cis/trans* ratio 2.4:1) (Gebert *et al.*, 2001), small amounts of 9*H*-fluorene-9-one, dispiro[fluorene-9,5'-[1,2,3,4]tetrathiane-6',9''-fluorene], (IV), and olefin (V) were isolated after chromatography. Whereas 9*H*-fluorene-9-one and the olefin (V) are well known side products in reactions involving (II), the tetrathiane (IV) has never been observed before. The latter was obtained in 1–3% yield after crystallization and, as part of the full characterization of this compound, its low-temperature crystal structure has been determined.



The molecule of compound (IV) has approximate C_2 symmetry, with an r.m.s. deviation of the related atoms of 0.14 Å. The C_2 axis is not parallel to any of the unit-cell axes. The 1,2,3,4-tetrathiane ring has a slightly distorted chair conformation, with puckering parameters (Cremer & Pople, 1975) of $Q = 0.927(1)$ Å, $\theta = 13.4(1)^\circ$ and $\varphi = 85.3(4)^\circ$ for the atom sequence S1, S2, S3, S4, C14 and C1. Ideally, θ would be equal to 0° for a perfect chair and the distortions can be attributed to the heteroatomic nature of the ring. Each of the two fluorene ring systems is nearly planar, although the phenyl rings are inclined very slightly from the plane to form a flat dish-shaped moiety. In the fluorene group defined by atoms C1–C13, the r.m.s. deviation of these atoms from their mean

plane is 0.034 Å, with a maximum deviation of 0.060 (2) Å for C3. The angle between the two phenyl ring planes is 3.91 (18)°. In the second fluorene moiety, the r.m.s. deviation of atoms C14–C26 from their mean plane is 0.060 Å, with a maximum deviation of 0.104 (2) Å for C17, and the angle between the two phenyl ring planes is 6.49 (15)°. The mean planes of the two fluorene ring systems intersect at an angle of 67.58 (5)°.

Atoms C3 and H3 have short intramolecular contacts with S2 and S4, while atoms C25 and H25 have similar contacts with S1 and S3 (Table 2). These contacts are only 0.06–0.15 Å shorter than the sum of the van der Waals radii of the respective atoms and it may be inappropriate to describe them as weak hydrogen-bonding interactions because the C–H...S angles are less than 120°. Distortions in the conformation of the molecule suggest that the contacts probably cause repulsive interactions and that the lack of sufficient conformational flexibility in the molecule prevents these atoms from being able to increase their interatomic separation any further. The C3–H3 bond nestles neatly between S2 and S4 of the 1,2,3,4-tetrathiane ring and is virtually equidistant from these S atoms. In this position and in the absence of steric strain, C3 and H3 would come too close to S2 and S4. The repulsive interactions cause the fluorene ring to be tipped back slightly on its C2–C1–C13 pivot, so that the plane defined by S1, C1 and C14 does not intersect the C7–C8 bond at its midpoint, but at a point much closer to C7. The distances of C7 and C8 from this plane are 0.451 (10) and 1.003 (10) Å, respectively. The interactions of C25 and H24 with S1 and S3 cause the second fluorene moiety to be tipped in a similar manner, with C21 and C20 being 0.435 (10) and 1.019 (10) Å, respectively, from the plane defined by C1, C14 and S4.

The Cambridge Structural Database (CSD, October 2000 release; Allen & Kennard, 1993) cites three structures containing 1,2,3,4-tetrathiane rings, these being simply substituted derivatives, namely 1,1-dimethylsila-4,5,6,7-tetra-thiabicyclo[4.3.0]nonane (Chernyshev *et al.*, 1984), *trans*-5,6-diphenyl-1,2,3,4-tetrathiane (Kamata *et al.*, 1990) and 1,2,3,4-

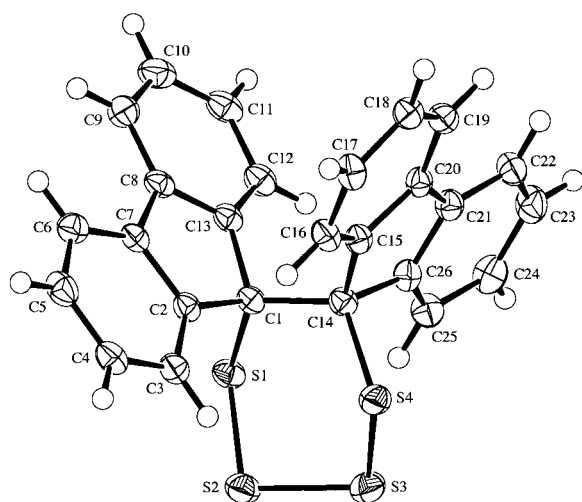


Figure 1

View of the molecule of the title compound, (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

tetrathiadecalin (Fehér *et al.*, 1972a). In each case, the tetra-thiane ring adopts a slightly distorted chair conformation and the bond lengths and angles around the ring are in close agreement with those observed for compound (IV) (Table 1). For all four compounds, the intra-ring angles involving S atoms are several degrees smaller than the ideal tetrahedral angle, with the S–S–S angles being the smallest, while those involving C atoms are slightly larger than the ideal tetrahedral angle. Such distortions are consistent with the ring strain introduced by the presence of two elements with significantly different covalent radii in the ring.

Experimental

The title compound, (IV), was obtained in 1–3% yield by reacting methyl *N*-[(benzylidene)phenyl]glycinate, (I) (253 mg, 1.0 mmol), with 9*H*-fluorene-9-thione, (II) (394 mg, 2.0 mmol), in a mixture of acetonitrile (5 ml) and toluene (1 ml) for 2 min at room temperature. After chromatography (silica gel, hexane/ethyl acetate 30:1) and crystallization from chloroform/hexane, (IV) was isolated as colourless prisms (m.p. 445–449 K). Suitable single crystals of (IV) were obtained by recrystallization from chloroform/hexane.

Crystal data

$C_{26}H_{16}S_4$	$D_x = 1.484 \text{ Mg m}^{-3}$
$M_r = 456.65$	Mo $K\alpha$ radiation
Orthorhombic, <i>Pbcn</i>	Cell parameters from 22 reflections
$a = 13.510$ (3) Å	$\theta = 15.0$ – 20.0°
$b = 18.014$ (7) Å	$\mu = 0.48 \text{ mm}^{-1}$
$c = 16.795$ (5) Å	$T = 173$ (1) K
$V = 4087$ (2) Å ³	Prism, colourless
$Z = 8$	$0.45 \times 0.25 \times 0.25 \text{ mm}$

Data collection

Rigaku AFC-5R diffractometer	$R_{\text{int}} = 0.038$
ω - 2θ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: ψ scan	$h = -1 \rightarrow 17$
(North <i>et al.</i> , 1968) $T_{\text{min}} =$	$k = -1 \rightarrow 23$
0.833, $T_{\text{max}} = 0.888$	$l = -21 \rightarrow 0$
5956 measured reflections	3 standard reflections every 150
4685 independent reflections	reflections intensity decay: none
3074 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 +$
$wR(F^2) = 0.116$	$1.1375P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4685 reflections	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
271 parameters	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

S1–C1	1.863 (3)	C1–C2	1.530 (3)
S1–S2	2.0534 (11)	C1–C13	1.534 (4)
S2–S3	2.0585 (13)	C1–C14	1.576 (3)
S3–S4	2.0546 (11)	C14–C15	1.538 (4)
S4–C14	1.867 (3)	C14–C26	1.532 (4)
C1–S1–S2	104.77 (9)	S3–S4–C14	105.04 (9)
S1–S2–S3	100.06 (4)	S1–C1–C14	113.28 (17)
S2–S3–S4	100.43 (4)	S4–C14–C1	114.43 (18)

Table 2

Intramolecular contact geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C3—H3···S2	0.95	2.92	3.436 (3)	115
C3—H3···S4	0.95	2.85	3.396 (3)	118
C25—H25···S1	0.95	2.87	3.405 (3)	117
C25—H25···S3	0.95	2.89	3.429 (3)	117

Data collection: *MSC/AFSC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFSC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1515). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
- Barr, D. A., Dorrity, M. J., Grigg, R., Hargreaves, S., Malone, J. F., Montgomery, J., Redpath, J., Stevenson, P. & Thornton-Pett, M. (1995). *Tetrahedron*, **51**, 273–394.
- Block, E., Iyer, R., Grisoni, S., Saha, C., Belman, S. & Lossing, F. P. (1988). *J. Am. Chem. Soc.* **110**, 7813–7827.
- Büchel, T., Prewo, R., Bieri, J. H. & Heimgartner, H. (1984). *Helv. Chim. Acta*, **67**, 534–549.
- Chernyshev, E. A., Kuz'min, O. V., Lebedev, A. V., Gusev, A. I., Kirillova, N. I., Komalenkova, N. G., Nametkin, N. S. & Tyurin, V. D. (1984). *Bull. Acad. Sci. USSR Div. Chem. Sci.* **33**, 585–588.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Fabian, J. & Senning, A. (1998). *Sulfur Rep.* **21**, 1–42.
- Fehér, F. & Degen, B. (1967). *Angew. Chem.* **79**, 689–690.
- Fehér, F., Klaeren, A. & Linke, K.-H. (1972a). *Acta Cryst.* **B28**, 534–537.
- Fehér, F., Langer, M. & Volkert, R. (1972b). *Z. Naturforsch. Teil B*, **27**, 1006–1007.
- Franek, W. (1991a). *Sulfur Rep.* **10**, 193–232.
- Franek, W. (1991b). *Sulfur Rep.* **10**, 233–278.
- Gebert, A. (2001). PhD thesis, University of Zürich, Switzerland.
- Gebert, A., Linden, A. & Heimgartner, H. (2001). *Heterocycles*, **54**, 691–704.
- Grigg, R. & Sridharan, V. (1993). *Adv. Cycloaddition*, **3**, 161–204.
- Guziec, F. S. & Sanfilippo, L. J. (1988). *Tetrahedron*, **44**, 6241–6285.
- Heimgartner, H. (1986). *Croat. Chem. Acta*, **59**, 237–265.
- Heimgartner, H. (1991). *Phosphorus Sulfur Silicon*, **58**, 281–293.
- Huisgen, R. & Rapp, J. (1997). *Heterocycles*, **45**, 507–525.
- Huisgen, R., Rapp, J. & Huber, H. (1997). *Liebigs Ann. Recl.*, pp. 1517–1523.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kägi, M., Linden, A., Mloston, G. & Heimgartner, H. (1996). *Helv. Chim. Acta*, **79**, 855–874.
- Kamata, M., Murayama, K., Suzuki, T. & Miyashi, T. (1990). *J. Chem. Soc. Chem. Commun.* pp. 827–829.
- Kanemasa, S. & Tsuge, O. (1993). *Adv. Cycloaddition*, **3**, 99–159.
- Kelmendi, B., Mloston, G. & Heimgartner, H. (2000). *Heterocycles*, **52**, 475–482.
- Krespan, C. G. & Brasen, W. R. (1962). *J. Org. Chem.* **27**, 3995–4000.
- Kustos, M. & Stendel, R. (1995). *J. Org. Chem.* **60**, 8056–8061.
- Linden, A., Awad, E. M. A. H. & Heimgartner, H. (1999). *Acta Cryst.* **C55**, 1877–1881.
- Meier, K.-R., Linden, A., Mloston, G. & Heimgartner, H. (1997). *Helv. Chim. Acta*, **80**, 1190–1204.
- Mloston, G. & Heimgartner, H. (1995). *Helv. Chim. Acta*, **78**, 1298–1310.
- Mloston, G. & Heimgartner, H. (2000). *Pol. J. Chem.* **74**, 1503–1532.
- Mloston, G., Linden, A. & Heimgartner, H. (1998). *Helv. Chim. Acta*, **81**, 558–569.
- Mloston, G., Romanski, J. & Heimgartner, H. (1996). *Pol. J. Chem.* **70**, 437–445.
- Molecular Structure Corporation (1991). *MSC/AFSC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA. (Current address: MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.)
- Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10b. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
- Nekhaev, A. I., Kolobkov, B. I., Toshev, M. T., Dustov, K. B. & Aleksandrov, G. G. (1991). *Bull. Acad. Sci. USSR Div. Chem. Sci.* **40**, 827–830.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sato, R., Ohyama, T., Kawagoe, T., Baba, M., Nakajo, S., Kimura, T. & Ogawa, S. (2001). *Heterocycles*, **55**, 145–154.
- Senning, A. (1994). *Main Group Chem. News*, **2**, 33–36.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.