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Structure of Fluorene-9-spiro-6′-(3′,6′-dihydro-3′,3′,5′-triphenyl-1′,2′,4′-oxathiazine), a δ-Sultene, $C_{33}H_{23}NOS$

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Abstract. $M_r = 481\cdot61$, monoclinic, $P2_1$, $a = 7\cdot799\ (5)$, $b = 10\cdot556\ (2)$, $c = 15\cdot291\ (9)$ Å, $\beta = 103\cdot59\ (4)$°, $V = 1223\cdot7$ Å^3, $Z = 2$, $D_x = 1\cdot31$ g m^{-3}, Mo $K\alpha$ (graphite crystal monochromator), $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot62$ cm^{-1}, $F(000) = 504$, $T = 290$ K, final conventional $R = 0\cdot107$, $wR = 0\cdot111$ for 2006 unique reflections and 264 variables, using idealized phenyl groups with calculated hydrogen atoms. The structure determination was hampered by the poor crystal quality and a chemical transformation during X-ray irradiation. The title compound was prepared by a new [3,3]-cycloaddition reaction of a sulfine (thioketone *S*-oxide) and a 2*H*-azirine. The molecule is a δ-sultene (3,6-dihydro-1,2,4-oxathiazine), which is an unusual cyclic sulfenate. The present analysis unambiguously shows that the compound has the six-membered ring sulfenate structure and not the expected rearranged five-membered sulfoxide structure.

Introduction. In our programme of the chemistry of sulfines (Zwanenburg, 1982) the reaction of diphenylsulfine and fluorene-9-spiro-2′-(3′-phenyl-2′*H*-azirine) in the presence of boron trifluoride–diethyl ether using diethyl ether as solvent was investigated. In a yield of 70% a product $C_{33}H_{23}NOS$ was isolated (Bonini, Maccagnani, Mazzanti & Zwanenburg, 1985), the structure of which could not be established unambiguously by the usual spectroscopic methods. Therefore the present analysis was undertaken.

Experimental. Crystals of the product (m.p. 532–533 K) obtained by recrystallization from a petroleum ether/diethyl ether/benzene mixture. Crystal approximately $0\cdot24 \times 0\cdot22 \times 0\cdot18$ mm used for measurements. Nonius CAD-4 single-crystal diffractometer. Unit-cell dimensions determined from angular settings of 25 reflections with $8 < \theta < 15°$. Space group $P2_1$ from systematic absences $0k0$, $k = 2n+1$ and structure determination. 5970 reflections (full sphere up to $\theta = 22°$) measured, ω–2θ scan technique, scan angle $1\cdot00°$, variable scan rate $\geq 1°$ min^{-1}. Intensity of primary beam checked throughout data collection by monitoring three standard reflections every 30 min. Final drift correction factors between 1·00 and 1·27, an indication that crystal quality became worse during data collection. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction, using ψ scans (North, Phillips & Mathews, 1968) applied (correction factors in the range 0·62 to 1·00). Laue symmetry-equivalent reflections averaged, $R_{\rm int} = 0\cdot077$, resulting in 2984 unique reflections of which 1875 considered observed with $I > 3\sigma(I)$. Lorentz and polarization corrections, data reduced to $|F_o|$ values. Structure solved using *MULTAN*80 (Main *et al.*, 1980) and *DIRDIF* (Beurskens *et al.*, 1982). *MULTAN* did not give a recognizable structure, but highest peak was used as sulfur atom and input to *DIRDIF*, which gave in two runs all non-hydrogen atoms. Isotropic least-squares refinement (*SHELX*76; Sheldrick, 1976) converged to $R = 0\cdot134$. Empirical absorption correction applied (Walker & Stuart, 1983). Refinement continued using idealized benzene rings, based on isotropically refined separate carbon atoms, with calculated hydrogen atoms. Positional parameters of atoms of central ring, positional and rotational parameters of fixed idealized benzene groups and anisotropic temperature-factor parameters of all non-hydrogen atoms refined. Calculated hydrogen atoms had fixed isotropic temperature factors of 0·07 Å^2. y parameter of S atom kept fixed throughout refinement. Final conventional agreement factors $R = 0\cdot107$ and $wR = 0\cdot111$ for 2006 'observed' reflections and 264 variables. Function minimized $\sum w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0\cdot0006 \times F_o^2]$ with $\sigma(F_o)$ from counting statistics. Max. Δ/σ in last least-squares cycle (full matrix) $< 0\cdot066$. Final

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difference Fourier map showed peaks as high as $1\cdot1\,\text{e}\,\text{Å}^{-3}$ clustered around the central ring. Atomic scattering factors from *SHELX*. Anisotropic refinement without restraints gives a slightly better R value of 0·099 ($wR = 0\cdot104$), with 2006 reflections and 393 parameters, but leads to unacceptable interatomic distances and angles.

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses*

$U_{\text{eq}} = \frac{1}{3}$ trace $\mathbf{U}$.

	x	y	z	U_{eq}(Å^2)
S(1)	0·3291 (6)	0·3297	0·1996 (2)	0·048 (3)
O(1)	0·157 (1)	0·410 (1)	0·1395 (6)	0·052 (5)
N(1)	0·139 (2)	0·365 (1)	0·3229 (9)	0·055 (7)
C(1)	0·209 (2)	0·262 (1)	0·2747 (8)	0·041 (7)
C(2)	0·091 (2)	0·475 (2)	0·2866 (8)	0·046 (7)
C(3)	0·101 (2)	0·510 (1)	0·1912 (9)	0·043 (7)
C(4)	0·199 (1)	0·628 (1)	0·1804 (7)	0·050 (7)
C(5)	0·374 (1)	0·656 (1)	0·2219 (7)	0·059 (7)
C(6)	0·449 (1)	0·770 (1)	0·2031 (7)	0·084 (9)
C(7)	0·348 (1)	0·856 (1)	0·1427 (7)	0·072 (8)
C(8)	0·173 (1)	0·827 (1)	0·1011 (7)	0·077 (8)
C(9)	0·099 (1)	0·713 (1)	0·1200 (7)	0·055 (8)
C(10)	−0·076 (2)	0·6622 (9)	0·0920 (7)	0·056 (8)
C(11)	−0·230 (2)	0·7118 (9)	0·0379 (7)	0·068 (8)
C(12)	−0·388 (2)	0·6441 (9)	0·0253 (7)	0·062 (8)
C(13)	−0·391 (2)	0·5267 (9)	0·0669 (7)	0·085 (9)
C(14)	−0·236 (2)	0·4770 (9)	0·1210 (7)	0·044 (6)
C(15)	−0·078 (2)	0·5448 (9)	0·1335 (7)	0·051 (7)
C(16)	0·003 (1)	0·5612 (9)	0·3362 (7)	0·032 (8)
C(17)	0·020 (1)	0·6923 (9)	0·3314 (7)	0·065 (9)
C(18)	−0·058 (1)	0·7711 (9)	0·3842 (7)	0·072 (9)
C(19)	−0·154 (1)	0·7186 (9)	0·4417 (7)	0·100 (10)
C(20)	−0·171 (1)	0·5875 (9)	0·4466 (7)	0·102 (12)
C(21)	−0·093 (1)	0·5087 (9)	0·3938 (7)	0·069 (8)
C(22)	0·053 (1)	0·185 (1)	0·2341 (5)	0·035 (6)
C(23)	−0·068 (1)	0·153 (1)	0·2844 (5)	0·063 (7)
C(24)	−0·218 (1)	0·083 (1)	0·2454 (5)	0·090 (10)
C(25)	−0·246 (1)	0·043 (1)	0·1561 (5)	0·093 (10)
C(26)	−0·124 (1)	0·075 (1)	0·1058 (5)	0·066 (8)
C(27)	0·025 (1)	0·145 (1)	0·1448 (5)	0·063 (8)
C(28)	0·349 (1)	0·1900 (9)	0·3439 (6)	0·059 (9)
C(29)	0·358 (1)	0·0580 (9)	0·3433 (6)	0·060 (8)
C(30)	0·494 (1)	−0·0046 (9)	0·4035 (6)	0·064 (9)
C(31)	0·620 (1)	0·0647 (9)	0·4644 (6)	0·069 (9)
C(32)	0·611 (1)	0·1967 (9)	0·4650 (6)	0·115 (12)
C(33)	0·476 (1)	0·2593 (9)	0·4048 (6)	0·065 (8)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

S(1)–O(1)	1·666 (11)	N(1)–C(1)	1·486 (17)
N(1)–C(2)	1·303 (18)	C(2)–C(3)	1·524 (19)
C(2)–C(16)	1·460 (19)	C(9)–C(10)	1·434 (16)
S(1)–C(1)	1·793 (16)	O(1)–C(3)	1·448 (16)
C(1)–C(22)	1·472 (19)	C(1)–C(28)	1·532 (16)
C(3)–C(4)	1·494 (17)	C(3)–C(15)	1·514 (20)

O(1)–S(1)–C(1)	94·7 (6)	C(2)–C(3)–C(15)	111·7 (12)
S(1)–C(1)–N(1)	109·5 (10)	C(4)–C(9)–C(10)	107·4 (4)
S(1)–C(1)–C(28)	104·2 (10)	C(3)–C(15)–C(14)	128·1 (6)
N(1)–C(2)–C(3)	123·4 (13)	C(9)–C(10)–C(15)	108·3 (4)
O(1)–C(3)–C(2)	115·7 (11)	C(1)–C(22)–C(23)	119·9 (6)
O(1)–C(3)–C(15)	102·6 (10)	C(1)–C(28)–C(33)	118·7 (6)
C(8)–C(9)–C(10)	132·5 (4)	C(1)–N(1)–C(2)	122·8 (13)
C(3)–C(4)–C(9)	113·0 (7)	N(1)–C(1)–C(22)	104·5 (11)
C(9)–C(10)–C(11)	131·6 (4)	C(22)–C(1)–C(28)	113·7 (11)
C(2)–C(16)–C(21)	117·8 (7)	C(3)–C(2)–C(16)	118·7 (13)
C(1)–C(28)–C(29)	121·2 (6)	C(2)–C(3)–C(4)	116·9 (11)
S(1)··O(1)–C(3)	112·1 (8)	C(4)–C(3)–C(15)	99·2 (9)
S(1)–C(1)–C(22)	117·0 (8)	C(3)–C(4)–C(5)	127·0 (7)
N(1)–C(1)–C(28)	107·7 (9)	C(3)–C(15)–C(10)	111·8 (6)
N(1)–C(2)–C(16)	117·4 (12)	C(2)–C(16)–C(17)	122·1 (7)
O(1)–C(3)–C(4)	108·6 (11)	C(1)–C(22)–C(27)	120·1 (6)

Discussion. Final positional and thermal parameters are given in Table 1.* Molecular geometry data are collected in Table 2. Fixed idealized phenyl-ring and hydrogen-atom values are not included. A stereoview of the molecule in minimum overlap position, showing the molecular configuration, is given in Fig. 1. The crystallographic atomic numbering scheme is given in Fig. 2.

The structure analysis shows that the product is a substituted 3,6-dihydro-1,2,4-oxathiazine (a δ-sultene). Its formation involves ring expansion of azirine (*cf.* Leonard & Zwanenburg, 1967; Bader & Hansen, 1978), resulting in a 1,3-cyclization across the C—S—O bonds in the sulfine. This type of reaction has not been observed previously.

The structure shows no unusual features. The S—O bond length compares well with that (1·661 Å) reported (Schaumann, Ehlers & Behrens, 1978) for a five-membered-ring sulfenate (γ-sultene).

The crystal-structure determination was hampered by the poor crystal quality and the slow decomposition of the product owing to a chemical transformation (conversion into a sulfoxide) (Bonini *et al.*, 1985) during the data collection, which affected the conformation of the sulfur-containing ring.

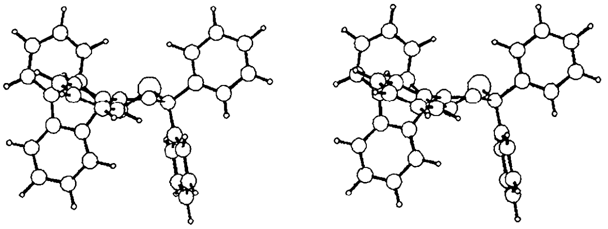

Fig. 1. Stereoview of the molecule in minimum overlap position.

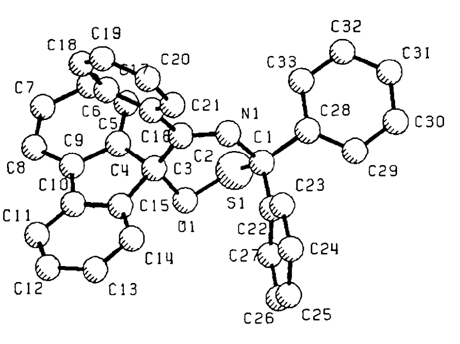

Fig. 2. Crystallographic atomic numbering scheme. (Molecule in minimum overlap position.)

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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 42135 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 3,6-Bis(4-methoxyphenyl)-1,4,2,5-dithiadiazine, $C_{16}H_{14}N_2O_2S_2$

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Abstract. $M_r = 330{\cdot}42$, orthorhombic, $P2_12_12$, $a = 11{\cdot}260\,(2)$, $b = 17{\cdot}086\,(3)$, $c = 3{\cdot}948\,(1)$ Å, $V = 759{\cdot}6$ Å^3, $Z = 2$, $D_x = 1{\cdot}45$ g cm^{-3}, Mo $K\alpha$(graphite crystal monochromator), $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}53$ cm^{-1}, $F(000) = 344$, $T = 290$ K, final conventional $R = 0{\cdot}027$, $wR = 0{\cdot}024$ for 839 unique reflections and 121 variables. The title compound was prepared by a new reaction of aminosulfines (thioamide *S*-oxides) and triethyloxonium tetrafluoroborate. The molecule contains the cyclic 1,4,2,5-dithiadiazine system, which is a new heterocycle. The molecule is in the boat conformation. The benzene substituent has a dihedral angle of 31·1 (1)° with the CCSN moiety of the dithiadiazine ring.

Introduction. In exploring the chemistry of sulfines (thioketone *S*-oxides; Zwanenburg, 1982), benzenethioamide *S*-oxides, ArC(=SO)NH_2, were treated with triethyloxonium tetrafluoroborate. The resulting iminium salts gave upon reaction with pyridine instead of the expected α-imino sulfoxides novel heterocyclic systems, *viz* 1,4,2,5-dithiadiazines (Lenz & Zwanenburg, 1984). On the basis of the molecular formula and spectroscopic data the arrangement of the N and S atoms in the six-membered heterocyclic ring could not be established unambiguously. Therefore, the present analysis was undertaken.

Experimental. Crystals obtained by recrystallization from toluene/petroleum ether. Crystal approximately 0·25 × 0·07 × 0·07 mm used for measurements. Nonius CAD-4 single-crystal diffractometer. Unit-cell dimensions determined from angular settings of 25 reflections with $20 < \theta < 22°$. Space group $P2_12_12$ from systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$. 6914 reflections (full sphere up to $\theta = 27{\cdot}5°$) measured, ω–2θ scan technique, scan angle 1·00°, variable scan rate $\geq 1°$ min^{-1}. Intensity of primary beam checked throughout data collection by monitoring three standard reflections every 30 min. Final drift correction factors between 1·00 and 1·04. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction using ψ scans (North, Phillips & Mathews, 1968) applied (min. transmission 96%, av. 99%). Symmetry-equivalent reflections averaged, $R_{\text{int}} = 0{\cdot}033$, 1731 unique reflections of which 840 considered observed with $I > 3\sigma(I)$. Lorentz and polarization corrections, data reduced to $|F_o|$ values. Structure solved using *MULTAN* (Main *et al.*, 1980). Solution was straightforward, using default parameters. Isotropic least-squares refinement (*SHELX76*; Sheldrick, 1976) converged to $R = 0{\cdot}063$. Empirical absorption correction applied (Walker & Stuart, 1983). H atoms located from difference Fourier map. Additional refinement

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