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The Structure of Spiro[2(1*H*)-naphthalenone-1,3′-naphtho[1,2-*e*][1,3,4]oxadithiin]

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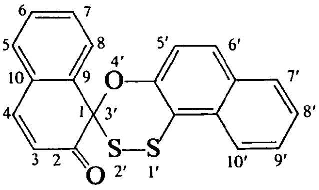
Abstract. $C_{20}H_{12}O_2S_2$, $M_r = 348\cdot1$, monoclinic, $P2_1/c$; $a = 9\cdot105$ (8), $b = 6\cdot476$ (6), $c = 27\cdot645$ (19) Å, $\beta = 106\cdot50$ (1)°, $Z = 4$, $D_c = 1\cdot48$, $D_m = 1\cdot47$ (1) g cm^{-3}, μ(Cu $K\alpha$) = 18·4 cm^{-1}. The crystal structure of the specimen examined is disordered, the molecules lying in separate columns parallel to y but statistically 0·23:1·0 are mirrored in $y = \frac{1}{4}$ (or $\frac{3}{4}$). Individual molecules can easily be resolved from the disordered pairs and are shown to have the structure assigned to them many years ago [Stevenson & Smiles (1930). *J. Chem. Soc.* pp. 1740–1745].

Introduction. The title compound was first prepared and its molecular structure (I) (showing chemical numbering) correctly assigned over forty years ago (Stevenson & Smiles, 1930).



(I)

It has recently been reinvestigated by Praefcke and coworkers (1976) as part of a series of studies on sulfur heterocycles. Spectroscopic data support the structural assignment and this is now positively confirmed by X-ray crystal structure analysis.

Orange crystals of (I) were kindly supplied by Professor Praefcke, Technical University of Berlin. Preliminary X-ray photographs showed systematic absences for space group $P2_1/c$ and pronounced streaking in the z^* direction (except in the $h0l$ zone).

The crystal used for data collection was a prism of dimensions *ca* 0·2 × 0·2 × 0·3 mm. It was mounted about the y axis, parallel to its longest dimension. The cell parameters and their standard deviations were obtained from diffractometer angular settings of twelve well-centered reflections using Cu $K\alpha$ radiation. Intensities were collected on a computer-controlled Picker four-circle diffractometer equipped with a pulse-height analyzer using Ni-filtered Cu $K\alpha$ radiation. Scanning was in the θ–2θ mode at 2° min^{-1}. Backgrounds were determined for 30 s at each end of the scan range of 2° adjusted for α splitting. The take-off angle was 3·0°. During the course of data collection there was a random deviation of ≤5% from the mean in the intensity of the standard reflection, recorded every 30 reflections. Counting statistics and a Bernstein factor (Abrahams & Bernstein, 1965) of 0·01 were used to calculate $\sigma(I)$. Of the 2605 independent reflections measured, 2438 were considered significant on the criterion $|F_o| > \sigma(F_o)$. Absorption corrections were not applied.

The crystal structure was determined by direct methods from the 460 reflexions having $|E| > 1\cdot30$, using the program *MULTAN* (Germain, Main & Woolfson, 1971). The best E map showed the structure to be disordered with the molecules partially mirrored in $y = \frac{1}{4}$. Refinement was by *ORXFLS*-3 (Busing,

Table 1. *Atomic coordinates and isotropic temperature factors*

(*a*) Non-hydrogen atomic coordinates (×10^4) of the major component

	x	y	z
S(1)	8028 (2)	5518 (2)	1090 (1)
S(2)	6542 (2)	5542 (3)	1516 (1)
O(1)	8551 (4)	1583 (7)	1397 (1)
O(2)	5495 (5)	1467 (10)	900 (2)
C(1)	7996 (5)	2646 (8)	949 (2)
C(2)	6345 (7)	2156 (10)	668 (3)
C(3)	5882 (6)	2523 (9)	128 (2)
C(4)	6926 (7)	2650 (9)	−127 (2)
C(5)	8543 (6)	2577 (7)	114 (2)
C(6)	9618 (7)	2532 (8)	−165 (2)
C(7)	11163 (7)	2447 (8)	69 (2)
C(8)	11710 (6)	2374 (9)	586 (2)
C(9)	10662 (5)	2400 (8)	882 (2)
C(10)	9111 (5)	2501 (7)	645 (2)
C(11)	7387 (6)	3593 (9)	1957 (2)
C(12)	8152 (6)	1935 (9)	1842 (2)
C(13)	8756 (7)	407 (10)	2203 (2)
C(14)	8503 (7)	443 (10)	2664 (2)
C(15)	7679 (6)	2109 (9)	2800 (2)
C(16)	7408 (7)	2185 (10)	3273 (2)
C(17)	6591 (7)	3815 (10)	3395 (2)
C(18)	6075 (7)	5433 (11)	3057 (2)
C(19)	6349 (7)	5380 (11)	2586 (2)
C(20)	7140 (5)	3731 (9)	2449 (2)

Table 1 (*cont.*)

(*b*) Non-hydrogen atomic coordinates ($\times 10^3$) and isotropic temperature factors for non-sulfur atoms, of the minor-site component

	x	y	z	B (Å^2)
S(1′)	799 (1)	−50 (1)	109 (0)	
S(2′)	651 (1)	−51 (1)	151 (0)	
O(1′)	861 (2)	335 (3)	143 (1)	3·4
O(2′)	546 (3)	356 (5)	91 (1)	6·1
C(2′)	636 (2)	292 (3)	68 (1)	3·4
C(11′)	733 (3)	132 (4)	196 (1)	2·0
C(12′)	815 (3)	300 (4)	185 (1)	2·6
C(13′)	877 (4)	454 (5)	221 (1)	4·5
C(14′)	851 (3)	453 (4)	268 (1)	4·7
C(15′)	772 (3)	286 (4)	280 (1)	3·2
C(16′)	735 (2)	276 (3)	328 (1)	3·1
C(17′)	662 (3)	112 (5)	339 (1)	3·8
C(18′)	607 (3)	−60 (5)	305 (1)	3·9
C(19′)	641 (3)	−33 (5)	257 (1)	4·1
C(20′)	715 (2)	122 (4)	245 (1)	2·3

(*c*) Hydrogen atomic coordinates ($\times 10^3$) and, for the major component, isotropic temperature factors

	x	y	z	B (Å^2)
H(3)	469	269	−7	5·0
H(4)	654	282	−53	5·0
H(6)	922	257	−57	5·0
H(7)	1195	244	−15	5·0
H(8)	1292	230	77	5·0
H(9)	1107	234	129	5·0
H(13)	943	−81	211	5·0
H(14)	892	−78	293	5·0
H(16)	783	98	354	5·0
H(17)	636	383	375	5·0
H(18)	547	671	316	5·0
H(19)	595	662	233	5·0
H(13′)	945	574	212	
H(14′)	890	577	294	
H(16′)	765	401	354	
H(17′)	644	106	375	
H(18′)	549	−192	315	
H(19′)	600	−150	229	

Martin & Levy, 1971) using $[\sigma(F_o)]^{-2}$ as weights and Hartree–Fock scattering factors (Cromer & Mann, 1968) with appropriate corrections for anomalous dispersion applied for S. Nine non-hydrogen atoms lie so close to $y = \frac{1}{4}$ that they and their images could not be separately resolved. Those atoms whose positions could be refined had average occupancies in the ratio 1·00:0·23. Accordingly the unresolved atoms were given weight 1·23. Two cycles of refinement using anisotropic temperature factors for all resolved atoms, isotropic otherwise, lowered the conventional R value to 0·10. A difference map revealed all major-site hydrogen atoms, which, with B = 5·0 Å^2, were kept fixed; R fell to 0·092.* Minor-site hydrogen atom positions were calculated for the determination of intermolecular contacts using C—H = 1·07 Å but were not included in F_c. All hydrogen positions were idealized before being included in the list of atomic coordinates, Table 1. If the disordering were perfect the disordered image of an atom at x,y,z should come exactly at $x, \frac{1}{2}-y, z$. The fact (see Table 1) that this is only approximately so shows the disordering to be somewhat imperfect.

Discussion. An unresolved molecular pair is illustrated in Fig. 1. Because of the unequal occupancy of the two molecular images no problems were encountered in resolving a single molecule (see Fig. 2, showing the crystallographic numbering of atoms). It is clear that the structure assigned by Stevenson & Smiles (1930) is correct. Bond lengths and angles are given in Fig. 3.

Ring *C* and its attached bonds C(5)—C(4) and C(10)—C(1) form a coplanar group as does the double-bond system about C(3)—C(4). However, the two systems are not coplanar, there being a 7° dihedral angle about C(4)—C(5). Thus O(2) is significantly out of the plane of ring *C* as can be seen from a side view of the molecule (Fig. 1). Rings *D* and *E* are mutually coplanar. Ring *A* has an envelope conformation with S(1) at the flap, all the other atoms of the ring being coplanar with the *DE* system. [If the flap of the envelope were bent in the opposite direction, H(9) would clash severely with atoms C(11) and C(12).] The spiro planes C(2)C(1)C(10) and O(1)C(1)S(1) are at 90 (1)°. The arrangement of bonds around the spiro-carbon atom C(1) is such that the bond C(1)—S(1)

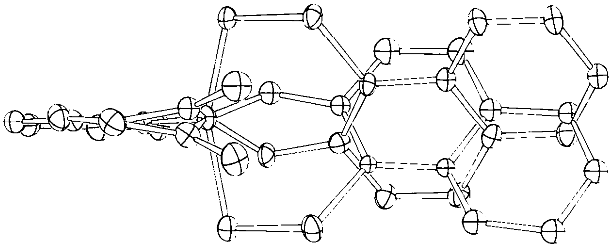


Fig. 1. A composite view of the disordered molecular pair.

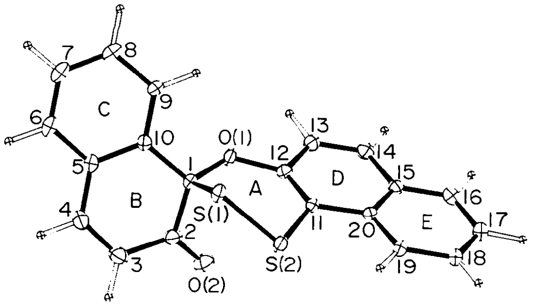


Fig. 2. *ORTEP* (Johnson, 1965) plot of a single molecule.

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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 33594 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

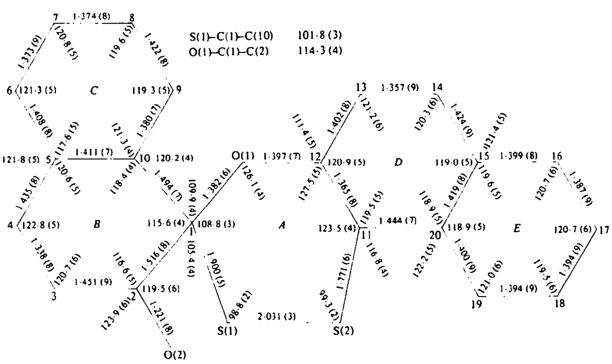
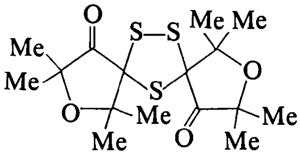


Fig. 3. Bond lengths (Å) and angles (°).

makes smaller angles with C(1)–C(2) and with C(1)–C(10) [mean 103·6 (3)°] than C(1)–O(1) makes with these bonds [mean 112·1 (4)], a trend we have also noted in a spiro-thiiran system (Nyburg & Wong-Ng, 1978).

S(1)–S(2) has a normal single-bond length as does S(2)–C(11) for S–C(sp^2). However, S(1)–C(1) is long at 1·900 (5) Å compared with a normal single-bond length of *ca* 1·81 Å. The –S–S– dihedral angle, 52 (1)° does not appear to fit the correlation curve with the S–S length given by Hordvik (1966); both the length and the dihedral angle are similar to those found in compound (II) (Cheng & Nyburg, 1975).



(II)

The molecules can be thought of as packed in columns parallel to the *y* axis (Fig. 4). Wherever this type of packing is present there is the potentiality for disorder in which any given molecule in a column is replaced by one having the 'wrong' equivalent position or the 'wrong' chirality. If no intra- or inter-column conflicts are generated, the structure can be expected to be completely disordered; conflicts of any kind will limit the extent and the nature of the disorder. In the crystals of (II) above, the molecules are packed in columns parallel to *y* in $P2_1$. However any molecule can be replaced by one mirrored about $y = \frac{1}{4}$ or $\frac{3}{4}$ without intra-column conflict. There is however inter-column conflict and this can only be relieved by the molecules in all the columns changing sense together. The consequent disorder is 100% $P2_1/m$. The present case is not so straightforward. If any molecule in a column changes sense (by being mirrored normal to the *y* axis) there is severe intra-column conflict with either the molecule above it in the column or that below it (but not both, see Fig. 5). The conflicting atoms are H(18) *x*,*y*,*z* and H(18') *x*', *y*' + 1, *z*' which would be only 0·87 Å apart. In the other direction along *y* there is virtually no conflict, the closest atoms being H(14) *x*,*y*,*z* and H(14') *x*', *y*' − 1, *z*', 2·24 Å apart. There is possibly some conflict between adjacent columns. If the molecule at $x, \frac{1}{2} - y, \frac{1}{2} + z$ in $P2_1/c$ is mirrored in $y = \frac{1}{4}$ H(4)···H(17) is 2·09 Å. Hence if a column shows disorder it can consist of only two distinct regions in which the molecules are of opposite chirality (one

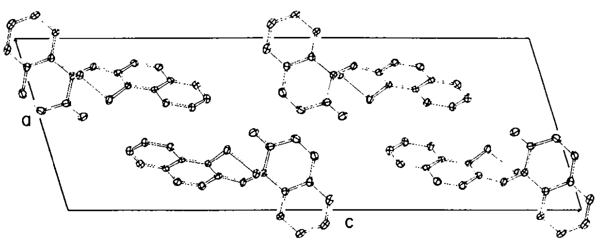


Fig. 4. Crystal structure in *y* projection.

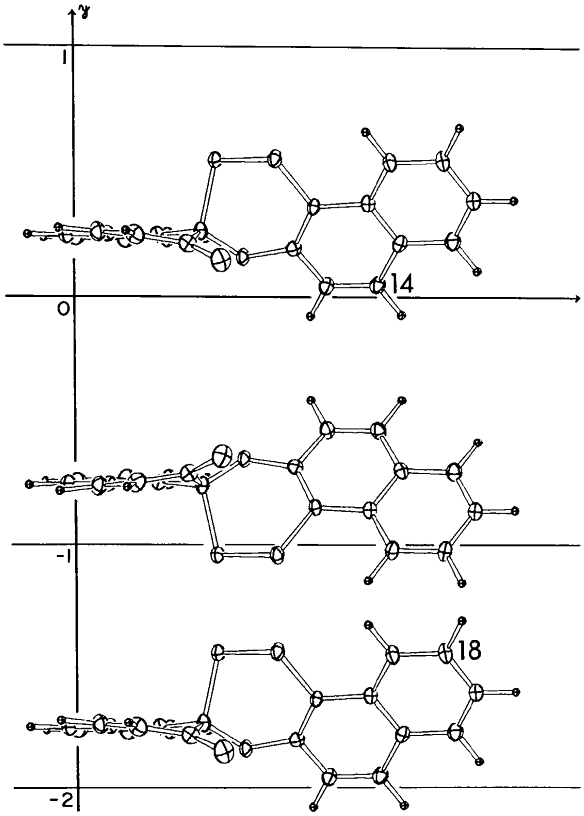


Fig. 5. A column of molecules along *y*. The central molecule has been mirrored about $y = -\frac{3}{4}$ and shows no conflict with the upper molecule. The lower molecule is in the same orientation as the upper and conflicts so badly with the central molecule that it cannot pack this way.

reversal of chirality per column) unless there are vacancies.

If all y columns suffered equally from disorder (disorder ratio 1·0:1·0) the space group would be $P2_1/m$.

The disorder ratio of 1·0:0·23 in this specimen can be explained if a fraction p of the columns along the y axis is free from disorder while the remaining $1-p$ contain just one change in chirality. [These latter columns will thus, on average, contribute $\frac{1}{2}(1-p)$ to the ordered structure.] Hence p should be about two-thirds (this gives a disorder ratio of 1·0:0·25). Why some columns are free from disorder and others not, is not clear.

Helpful discussions with Professor Praefcke and financial assistance from the National Research Council of Canada are both gratefully acknowledged.

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The Structure of Spiro[2(1*H*)-naphthalenone-1,2'-naphtho[1,2-*d*][1,3]oxathiole]

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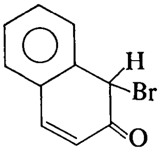
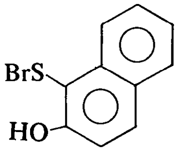
Abstract. $C_{20}H_{12}O_2S$, M_r = 316·38, triclinic, $P\bar{1}$; cell dimensions (chosen such that $b > a > c$, α and β obtuse): a = 9·042 (2), b = 10·636 (3), c = 8·309 (3) Å, α = 93·88 (6), β = 108·52 (9), γ = 99·41 (6)°, Z = 2, D_c = 1·42 g cm^{-3} (D_m not determined), μ(Cu $K\alpha$) = 2·25 cm^{-1}. X-ray analysis of the title compound confirms the molecular structure assigned many years ago [Stevenson & Smiles (1930). *J. Chem. Soc.* pp. 1740–1745]. The molecule consists of a non-planar 1,3-oxathiole ring fused to a naphthalene nucleus on one side and spiro-fused to a 2(1*H*)-naphthalenone on the other. The S—C(sp^2) bond length, 1·764 (2) Å, is comparable to that found in other five-ring hetero-sulfur systems, but S—C(sp^3) at 1·874 (2) Å is significantly longer.

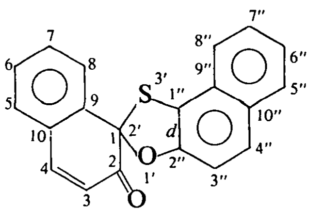
Introduction. Stevenson & Smiles (1930) ascribed to the product of the reaction of 1-bromothio-2-naphthol (II) with 1-bromo-2-naphthol (I, written in the keto-methylene form) the title compound (III, showing chemical numbering):



(I)



(II)



(III)

Praefcke (1976) and co-workers have recently re-investigated this and related reactions. X-ray analysis of compound (III) reported here confirms the original structure assignment.