HASSEL, O., RØMMING, C. & TUFTE, T. (1961). *Acta Chem. Scand.* **15**, 967–974.

LEMIEUX, R. U. & MORGAN, A. R. (1965). *Can. J. Chem.* **43**, 2190–2198.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. C. (1968). *Acta Cryst.* A**24**, 351–359.

OSBORN, R. S. (1972). PhD Thesis, Univ. of London.

PRITZKOW, H. (1975). *Acta Cryst.* B**31**, 1505–1506.

RØMMING, C. (1972). *Acta Chem. Scand.* **26**, 1555–1560.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

STOUT, G. H. & JENSEN, L. H. (1968). *X-Ray Structure Determination, A Practical Guide*, pp. 454–458. New York: Macmillan.

STRØMME, K. O. (1959). *Acta Chem. Scand.* **13**, 268–274.

X-ray Analysis of 3,4-Dihydro-2H-[1]benzothieno[3,2-b]pyran-2-spiro-2'(3'H)- (1-benzothiophen)-3'-one

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Abstract. $C_{18}H_{12}O_2S_2$, $M_r = 324.4$, $D_x = 1.443$ Mg m^{-3}, monoclinic, $P2_1/c$, $Z = 4$, $a = 9.722$ (4), $b = 12.982$ (16), $c = 11.991$ (6) Å, $\beta = 99.40$ (4)°, $U = 1493.1$ Å^3, μ(Mo $K\alpha$) = 0.307 mm^{-1}. Final $R = 0.050$ for 1695 independent reflexions. The dimer is spiro-fused and contains benzothiophene moieties that are almost planar, together with a central dihydropyran ring that adopts a half-chair conformation.

Introduction. An X-ray analysis of the title compound was undertaken to determine the constitution of the molecule. As previously reported (Cox, MacKenzie & Thomson, 1981), it is formed by reaction of 3-bromothiochroman-4-one with sodium acetate in acetic acid. Data were obtained for a yellow, needle-shaped crystal from a Nicolet *P3* automated diffractometer using monochromatized Mo $K\alpha$ radiation. Integrated relative intensities for 2366 independent reflexions with $2\theta < 50°$ were measured as θ–2θ scans; 1695 reflexions had $I > 2.5\sigma(I)$.

The crystal structure was elucidated by direct phasing using the program *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All H atoms were located (near calculated positions) on electron density maps calculated at intermediate stages of structure refinement. In the final cycles of full-matrix

least-squares refinement the positional parameters for all atoms, anisotropic thermal parameters for the C and O atoms and isotropic thermal parameters for the H atoms were varied. A unit weighting scheme was used and convergence was reached at $R = 0.050$.

Discussion. The molecular structure and the packing of the molecules in the unit cell are shown in Figs. 1 and 2. The atomic coordinates are listed in Table 1 and the bond lengths, valency angles and torsion angles are in Tables 2–4.*

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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 36234 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
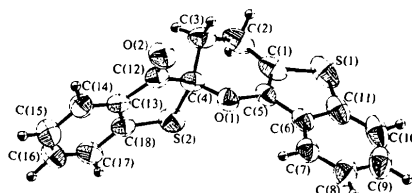

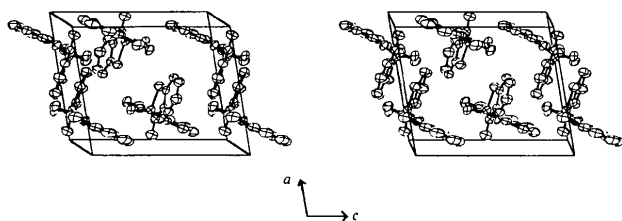Fig. 1. The atomic arrangement in the molecule.

$C_{18}H_{12}O_2S_2$

Fig. 2. A stereoscopic view of the molecular packing.

Table 1. *Fractional atomic coordinates* $(\times 10^4, \times 10^3$ *for* H) *with e.s.d.'s and equivalent values of the anisotropic temperature factor coefficient* $(\times 10^3)$

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	U_{eq} (Å^2)
S(1)	7518 (2)	11010 (1)	5179 (2)	82 (1)
S(2)	5558 (1)	7502 (1)	4113 (1)	61 (1)
O(1)	8178 (3)	8204 (3)	4237 (3)	50 (2)
O(2)	9183 (4)	6330 (3)	5221 (3)	69 (2)
C(1)	7477 (5)	9677 (5)	5241 (5)	61 (3)
C(2)	6894 (7)	9061 (6)	6093 (5)	74 (4)
C(3)	7407 (6)	7965 (5)	6057 (5)	63 (3)
C(4)	7374 (5)	7589 (4)	4857 (4)	49 (3)
C(5)	8058 (5)	9247 (4)	4410 (4)	48 (2)
C(6)	8542 (5)	9969 (4)	3662 (5)	50 (3)
C(7)	9132 (5)	9793 (5)	2702 (5)	57 (3)
C(8)	9448 (6)	10603 (5)	2044 (6)	73 (4)
C(9)	9201 (7)	11610 (6)	2385 (8)	86 (5)
C(10)	8647 (6)	11803 (5)	3342 (7)	78 (4)
C(11)	8316 (5)	10975 (5)	3984 (5)	64 (3)
C(12)	8005 (5)	6489 (4)	4840 (4)	50 (3)
C(13)	6983 (5)	5736 (4)	4284 (4)	45 (2)
C(14)	7203 (6)	4692 (4)	4146 (5)	56 (3)
C(15)	6132 (6)	4099 (5)	3582 (5)	68 (3)
C(16)	4855 (6)	4549 (5)	3192 (5)	65 (3)
C(17)	4613 (5)	5567 (5)	3329 (5)	58 (3)
C(18)	5687 (5)	6183 (4)	3880 (4)	47 (2)
H(2A)	707 (6)	938 (4)	682 (3)	
H(2B)	587 (3)	911 (4)	599 (4)	
H(3A)	842 (3)	793 (5)	634 (5)	
H(3B)	686 (5)	750 (4)	644 (4)	
H(7)	929 (5)	909 (2)	250 (4)	
H(8)	993 (5)	1060 (4)	136 (3)	
H(9)	945 (7)	1218 (4)	189 (5)	
H(10)	847 (5)	1249 (3)	360 (4)	
H(14)	804 (4)	435 (4)	454 (5)	
H(15)	632 (6)	336 (2)	346 (5)	
H(16)	416 (4)	414 (3)	272 (4)	
H(17)	383 (5)	599 (4)	295 (5)	

Table 2. *Bond lengths* (Å) *with e.s.d.'s*

S(1)–C(1)	1·733 (6)	C(6)–C(7)	1·386 (8)
S(1)–C(11)	1·738 (6)	C(6)–C(11)	1·389 (8)
S(2)–C(4)	1·847 (5)	C(7)–C(8)	1·379 (9)
S(2)–C(18)	1·743 (5)	C(8)–C(9)	1·402 (10)
O(1)–C(4)	1·411 (6)	C(9)–C(10)	1·368 (12)
O(1)–C(5)	1·378 (6)	C(10)–C(11)	1·390 (9)
O(2)–C(12)	1·180 (6)	C(12)–C(13)	1·473 (7)
C(1)–C(2)	1·481 (9)	C(13)–C(14)	1·386 (7)
C(1)–C(5)	1·344 (7)	C(13)–C(18)	1·400 (6)
C(2)–C(3)	1·511 (10)	C(14)–C(15)	1·380 (8)
C(3)–C(4)	1·515 (7)	C(15)–C(16)	1·383 (8)
C(4)–C(12)	1·556 (7)	C(16)–C(17)	1·357 (9)
C(5)–C(6)	1·429 (7)	C(17)–C(18)	1·393 (7)
C(2)–H(2A)	0·955 (42)	C(9)–H(9)	1·007 (55)
C(2)–H(2B)	0·985 (29)	C(10)–H(10)	0·971 (36)
C(3)–H(3A)	0·986 (32)	C(14)–H(14)	0·980 (47)
C(3)–H(3B)	0·970 (48)	C(15)–H(15)	0·997 (34)
C(7)–H(7)	0·963 (32)	C(16)–H(16)	0·969 (42)
C(8)–H(8)	1·008 (44)	C(17)–H(17)	0·984 (48)

Table 3. *Valency angles* (°) *with e.s.d.'s*

C(11)–S(1)–C(1)	91·5 (3)	C(2)–C(1)–S(1)	125·7 (5)
C(5)–C(1)–S(1)	111·6 (4)	C(6)–C(11)–S(1)	111·5 (4)
C(10)–C(11)–S(1)	127·7 (5)	C(18)–S(2)–C(4)	92·8 (2)
O(1)–C(4)–S(2)	110·4 (3)	C(3)–C(4)–S(2)	110·4 (3)
C(12)–C(4)–S(2)	106·6 (3)	C(13)–C(18)–S(2)	115·9 (4)
C(17)–C(18)–S(2)	124·9 (4)	C(5)–O(1)–C(4)	114·1 (4)
C(3)–C(4)–O(1)	113·0 (4)	C(12)–C(4)–O(1)	105·0 (4)
C(1)–C(5)–O(1)	125·2 (5)	C(6)–C(5)–O(1)	120·4 (4)
C(4)–C(12)–O(2)	121·0 (5)	C(13)–C(12)–O(2)	126·8 (5)
C(5)–C(1)–C(2)	122·8 (5)	C(3)–C(2)–C(1)	108·9 (5)
C(6)–C(5)–C(1)	114·5 (5)	C(4)–C(3)–C(2)	112·0 (5)
C(12)–C(4)–C(3)	111·2 (4)	C(13)–C(12)–C(4)	112·1 (4)
C(7)–C(6)–C(5)	129·5 (5)	C(11)–C(6)–C(5)	111·0 (5)
C(11)–C(6)–C(7)	119·4 (5)	C(8)–C(7)–C(6)	120·7 (5)
C(10)–C(11)–C(6)	120·8 (6)	C(9)–C(8)–C(7)	118·6 (6)
C(10)–C(9)–C(8)	121·7 (7)	C(11)–C(10)–C(9)	118·8 (6)
C(14)–C(13)–C(12)	126·6 (4)	C(18)–C(13)–C(12)	112·6 (4)
C(18)–C(13)–C(14)	120·8 (4)	C(15)–C(14)–C(13)	119·0 (5)
C(17)–C(18)–C(13)	119·3 (5)	C(16)–C(15)–C(14)	119·6 (6)
C(17)–C(16)–C(15)	122·3 (5)	C(18)–C(17)–C(16)	119·0 (5)

The dihydrobenzothiophenone and benzothiophene ring systems are almost planar (Table 5) and the dihedral angle between these moieties is 83°. The central dihydropyran ring adopts a half-chair conformation with $\Delta C_2(1-5) = 1·57°$. The tetrahedral angles around the spiro carbon vary from 105·0 (4)–113·0 (4)° and similar distortions have been found for

spiro junctions in other thioxa-heterocycles (Cheng & Nyburg, 1978; Wong-Ng & Nyburg, 1978). The spiro planes S(2)C(4)C(12) and C(3)C(4)O(1) are inclined at 92·3°. The C(4)–C(12) bond distance of 1·556 (7) Å is significantly longer than the other $C(sp^3)–C(sp^2)$ bond length at C(1)–C(2) which is 1·481 (9) Å. This long bond may be a consequence of intramolecular non-bonded interactions around the spiran junction.

In-plane bending at the aromatic ring fusions is present as C(5)–C(6)–C(7) and C(10)–C(11)–S(1) are 129·5 (5) and 127·7 (5)° respectively and C(12)–C(13)–C(14) and C(17)–C(18)–S(2) are 126·6 (4) and 124·9 (4)° respectively. This angular deviation from trigonal values is also found in 3-formylbenzothiophene (Pascard & Pascard-Billy, 1972). The $S–C(sp^2)$ bond lengths range from 1·733 (6)–

Table 4. *Torsion angles* (°) *with e.s.d.'s*

C(11)—S(1)—C(1)—C(2)	−179·5 (5)	C(11)—S(1)—C(1)—C(5)	0·9 (4)
C(1)—S(1)—C(11)—C(6)	−0·4 (4)	C(1)—S(1)—C(11)—C(10)	176·0 (6)
C(18)—S(2)—C(4)—O(1)	114·9 (3)	C(18)—S(2)—C(4)—C(3)	−119·5 (4)
C(18)—S(2)—C(4)—C(12)	1·4 (3)	C(4)—S(2)—C(18)—C(13)	−0·9 (4)
C(4)—S(2)—C(18)—C(17)	179·4 (5)	C(5)—O(1)—C(4)—S(2)	82·8 (4)
C(5)—O(1)—C(4)—C(3)	−41·4 (5)	C(5)—O(1)—C(4)—C(12)	−162·7 (4)
C(4)—O(1)—C(5)—C(1)	13·0 (7)	C(4)—O(1)—C(5)—C(6)	−165·6 (4)
S(1)—C(1)—C(2)—C(3)	−164·5 (4)	C(5)—C(1)—C(2)—C(3)	15·1 (8)
S(1)—C(1)—C(5)—O(1)	−179·9 (4)	S(1)—C(1)—C(5)—C(6)	−1·3 (6)
C(2)—C(1)—C(5)—O(1)	0·5 (8)	C(2)—C(1)—C(5)—C(6)	179·1 (5)
C(1)—C(2)—C(3)—C(4)	−42·1 (7)	C(2)—C(3)—C(4)—S(2)	−66·0 (5)
C(2)—C(3)—C(4)—O(1)	58·2 (6)	C(2)—C(3)—C(4)—C(12)	175·9 (5)
S(2)—C(4)—C(12)—O(2)	176·9 (4)	S(2)—C(4)—C(12)—C(13)	−1·6 (5)
O(1)—C(4)—C(12)—O(2)	59·8 (6)	O(1)—C(4)—C(12)—C(13)	−118·7 (4)
C(3)—C(4)—C(12)—O(2)	−62·7 (6)	C(3)—C(4)—C(12)—C(13)	118·8 (5)
O(1)—C(5)—C(6)—C(7)	1·6 (8)	O(1)—C(5)—C(6)—C(11)	179·7 (4)
C(1)—C(5)—C(6)—C(7)	−177·1 (5)	C(1)—C(5)—C(6)—C(11)	1·0 (7)
C(5)—C(6)—C(7)—C(8)	175·5 (6)	C(11)—C(6)—C(7)—C(8)	−2·4 (8)
C(5)—C(6)—C(11)—S(1)	−0·2 (6)	C(5)—C(6)—C(11)—C(10)	−176·9 (5)
C(7)—C(6)—C(11)—S(1)	178·0 (4)	C(7)—C(6)—C(11)—C(10)	1·4 (8)
C(6)—C(7)—C(8)—C(9)	2·0 (9)	C(7)—C(8)—C(9)—C(10)	−0·6 (11)
C(8)—C(9)—C(10)—C(11)	−0·4 (11)	C(9)—C(10)—C(11)—S(1)	−176·1 (5)
C(9)—C(10)—C(11)—C(6)	−0·0 (10)	O(2)—C(12)—C(13)—C(14)	2·8 (9)
O(2)—C(12)—C(13)—C(18)	−177·3 (5)	C(4)—C(12)—C(13)—C(14)	−178·8 (5)
C(4)—C(12)—C(13)—C(18)	1·1 (6)	C(12)—C(13)—C(14)—C(15)	−178·8 (5)
C(18)—C(13)—C(14)—C(15)	1·3 (8)	C(12)—C(13)—C(18)—S(2)	0·0 (5)
C(12)—C(13)—C(18)—C(17)	179·8 (4)	C(14)—C(13)—C(18)—S(2)	179·9 (4)
C(14)—C(13)—C(18)—C(17)	−0·3 (7)	C(13)—C(14)—C(15)—C(16)	−1·6 (9)
C(14)—C(15)—C(16)—C(17)	0·9 (9)	C(15)—C(16)—C(17)—C(18)	0·1 (9)
C(16)—C(17)—C(18)—S(2)	179·3 (4)	C(16)—C(17)—C(18)—C(13)	−0·4 (8)

Table 5. *Displacements* (Å) *of atoms from various planes* (*average e.s.d.* 0·01 Å)

Atoms in italics were not included in the derivation of the plane.

(i) C(1) 0·04, C(5) 0·00, C(6) −0·03, C(7) −0·02, C(8) 0·04, C(9), 0·04, C(10) 0·00, C(11) −0·04, S(1) 0·00, *O(1)* 0·02, *C(2)* 0·10, *C(3)* −0·27, *C(4)* 0·37

(ii) C(4) −0·03, C(12) −0·01, C(13) −0·01, C(14) −0·02, C(15) 0·01, C(16) 0·01, C(17) 0·00, C(18) 0·00, S(2) 0·00, O(2) 0·02, *O(1)* 1·16, *C(3)* −1·28, *C(2)* 1·27, *C(1)* 0·09, *C(5)* 1·17

(iii) O(1) 0·00, C(1) 0·00, C(2) 0·00, C(5) 0·00, *C(3)* −0·38, *C(4)* 0·30

1·743 (5) Å and the S—C(sp^3) bond length is 1·847 (5) Å; these values are similar to those found in other five-ring hetero-sulphur systems. There are no intermolecular contacts less than the sum of the appropriate van der Waals radii for the non-H atoms. The S(1)···S(2)(1 − x, −y, 1 − z) contact of

3·772 (2) Å is similar to the S···S contact of 3·77 Å found in *trans-Δ²,²′*-bis(4,4-dimethylthiolan-3-one) (Ammon & Hermann, 1978).

References

Ammon, H. L. & Hermann, H. (1978). *J. Org. Chem.* **43**, 4581–4586.

Cheng, P. T. & Nyburg, S. C. (1978). *Acta Cryst.* B**34**, 2907–2910.

Cox, P. J., MacKenzie, N. E. & Thomson, R. H. (1981). *Tetrahedron Lett.* **22**, 2221–2224.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. & Woolfson, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Pascard, R. & Pascard-Billy, C. (1972). *Acta Cryst.* B**28**, 1926–1935.

Wong-Ng, W. K. & Nyburg, S. C. (1978). *Acta Cryst.* B**34**. 2910–2912.