

Discussion. Fractional coordinates are given in Table 1,* bond distances are in Fig. 1, bond angles are in Table 2, and the unit cell is shown in Fig. 2. The naphthalene ring system is nearly planar. It exhibits little structural distortion from the two fused three-membered rings, as all ten of its non-H atoms lie within 0.036 (2) Å of a common plane. The O atoms O1 and O2 lie 1.189 (1) and 1.184 (1) Å, respectively, out of this best plane. The deviation of the ring system from strict planarity consists of a bowing, such that the two six-membered rings, which are individually planar, form an angle of 2.6 (1)°, with the O atoms lying on the outside of the bow. The planes defined by the epoxy groups form angles with the best plane of the carbon ring system of 105.60 (6) and 106.34 (7)° for O1 and O2, respectively. The two planes of the epoxy groups intersect at an angle of 65.21 (11)°. The epoxy groups are asymmetric, with the C—O bonds nearest the center of the molecule [average 1.453 (2) Å], longer than

those toward the outside [average 1.427 (2) Å]. The angles at oxygen are both 60.7 (1)°. The geometry of the epoxy group is similar to that of syn-3,4-dimethoxy-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (Klein & Stevens, 1984).

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* Lists of structure factors, anisotropic thermal parameters, isotropic thermal parameters, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53029 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 9-Bromo-2,3-dihydro-8-methoxy-5,5-dimethyl-5H-benzo[b]pyrano-[3,4-b][1,4]dithiine

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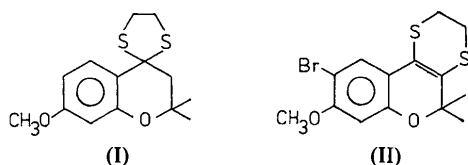
Abstract. C₁₄H₁₅BrO₂S₂. *M_r* = 359.31, monoclinic, *P*2₁/*c*, *a* = 8.607 (2), *b* = 16.120 (2), *c* = 12.597 (2) Å, β = 120.65 (1)°, *V* = 1503.5 (9) Å³, *Z* = 4, *D_x* =

1.59 Mg m⁻³, λ(Cu Kα) = 1.54184 Å, μ = 6.28 mm⁻¹, *F*(000) = 728, *T* = 296 (1) K, *R* = 0.058, *wR* = 0.083 for 2385 unique observed reflections. The 1,3-biplanar pyran ring assumes an almost perfect skew conformation, whereas the dithiine ring exhibits a state transitional between ⁴*E* envelope and ⁴*S*₅ skew forms.

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Introduction. Systematic synthetic studies of benzo-pyrans (Timár, Hosztafi, Jászberényi, Kövér & Batta, 1988; Timár & Jászberényi, 1988) have led to attempts to transform 4-spirodithiolane derivatives to 4-*gem*-difluorochromans, as reported recently by Sondej & Katzenellenbogen (1986). However, spectroscopic (^1H , ^{13}C NMR, MS and IR) investigations suggest that instead of forming the expected *gem*-difluorochromans, a known (Karmas, 1967) 1,3-dithiolane \rightarrow 2,3-dihydro-1,4-dithiine rearrangement takes place. To substantiate the novel, stable flourine-free structure, an X-ray diffraction analysis of the product (II), obtained from treatment of 7-methoxy-2,2-dimethyl-4-chroman ethylene thio-ketal (I) with 1,3-dibromo-5,5-dimethylhydantoin and pyridinium poly(hydrogen fluoride) has been carried out.



Experimental. A crystal, $0.20 \times 0.25 \times 0.40$ mm, was mounted on a CAD-4 diffractometer, graphite-monochromated $\text{Cu K}\alpha$ radiation. Cell constants were refined by a least-squares fit for 25 centred reflections with $23 \leq \theta \leq 40^\circ$. Systematic absences $0k0: k = 2n + 1$, $h0l: l = 2n + 1$. Data were collected by $\omega/2\theta$ scan in the range $0.017 \leq (\sin \theta)/\lambda \leq 0.626 \text{ \AA}^{-1}$ with h 0 to 10, k 0 to 20 and l -15 to 15. Of 2805 unique non-zero and non-systematically absent reflections, 2385 with $I > 4.0\sigma(I)$ were taken as observed. Three standard reflections (139, 632, 491) were monitored every hour but no intensity variations were recorded. The phase problem was solved by the *MULTAN*82 program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) using 249 normalized structure factors with $E \leq 1.75$. An E map computed from one of 16 phase combinations ($\text{ABSFOM} = 1.08$, $\text{RESID} = 11.64$, $\text{PSIZERO} = 1.379$) gave the positions of eight non-H atoms. The missing 11 atoms were located from weighted Fourier maps. Full-matrix least-squares refinement minimized $\sum w(\Delta F)^2$ for 233 parameters with $w = 4F_o^2/\sigma(F_o^2)^2$. At the end of the isotropic refinement an empirical absorption correction was included by use of the program *DIFABS* (Walker & Stuart, 1983). The minimum and maximum transmission coefficients were 0.365 and 1.209. The refinement was terminated at $R = 0.058$, $wR = 0.083$, $R_{\text{tot}} = 0.067$, $S = 3.22$. Maximum and minimum heights in the final difference synthesis were $\pm 0.68 (1) \text{ e \AA}^3$, $(\Delta/\sigma)_{\text{max}} = 0.22$. Positions of H atoms were generated from assumed geometries:

Table 1. *Final fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for non-H atoms*

Estimated standard deviations are in parentheses and are 1 \AA^2 for B_{eq} values. $B_{\text{eq}} = 4/3\text{trace}(\text{BG})$, where G is the direct metric tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B (\text{\AA}^2)$
Br	0.43537 (7)	0.00566 (3)	0.11237 (4)	4.34 (1)
S(1)	1.0382 (1)	-0.11456 (7)	0.52861 (9)	3.09 (2)
S(4)	1.0684 (1)	-0.22669 (9)	0.7676 (1)	4.16 (2)
O(6)	0.5646 (3)	-0.1431 (1)	0.5868 (2)	2.35 (5)
O(13)	0.1706 (4)	-0.0161 (2)	0.1964 (3)	4.53 (7)
C(2)	1.1831 (6)	-0.2025 (4)	0.6036 (4)	4.9 (1)
C(3)	1.2339 (6)	-0.2185 (4)	0.7228 (5)	5.8 (1)
C(4a)	0.8698 (4)	-0.1844 (2)	0.6446 (3)	2.42 (7)
C(5)	0.7000 (4)	-0.2080 (2)	0.6463 (3)	2.43 (8)
C(6a)	0.5372 (4)	-0.1130 (2)	0.4772 (3)	2.02 (7)
C(7)	0.3674 (4)	-0.0823 (2)	0.3955 (3)	2.51 (8)
C(8)	0.3328 (5)	-0.0463 (2)	0.2852 (3)	3.08 (7)
C(9)	0.4731 (5)	-0.0426 (2)	0.2610 (3)	2.78 (8)
C(10b)	0.8565 (4)	-0.1398 (2)	0.5489 (3)	2.28 (7)
C(10a)	0.6773 (4)	-0.1093 (2)	0.4533 (2)	2.14 (7)
C(10)	0.6436 (4)	-0.0728 (2)	0.3440 (3)	2.40 (8)
C(11)	0.6256 (5)	-0.2892 (2)	0.5792 (4)	3.33 (9)
C(12)	0.7291 (5)	-0.2105 (3)	0.7768 (3)	3.4 (1)
C(14)	0.0228 (6)	-0.0232 (3)	0.2159 (5)	4.8 (1)

Table 2. *Bond distances (\AA) and bond angles ($^\circ$) with their e.s.d.'s in parentheses*

Br—C(9)	1.896 (4)	C(5)—C(11)	1.512 (6)
S(1)—C(2)	1.805 (6)	C(5)—C(12)	1.532 (5)
S(1)—C(10b)	1.756 (2)	C(6a)—C(7)	1.381 (4)
S(4)—C(3)	1.784 (3)	C(6a)—C(10a)	1.385 (3)
S(4)—C(4a)	1.758 (3)	C(7)—C(8)	1.390 (5)
O(6)—C(5)	1.457 (4)	C(8)—C(9)	1.389 (3)
O(5)—C(6a)	1.366 (4)	C(9)—C(10)	1.386 (4)
O(13)—C(8)	1.359 (4)	C(10b)—C(10a)	1.476 (4)
O(13)—C(14)	1.418 (3)	C(10a)—C(10)	1.385 (5)
C(2)—C(3)	1.358 (8)		
C(4a)—C(5)	1.521 (3)		
C(4a)—C(10b)	1.357 (5)		
C(2)—S(1)—C(10b)	99.9 (3)	O(6)—C(6a)—C(10a)	121.0 (5)
C(3)—S(4)—C(4a)	105.5 (4)	C(7)—C(6a)—C(10a)	122.1 (5)
C(5)—O(6)—C(6a)	117.1 (4)	C(6a)—C(7)—C(8)	120.0 (5)
C(8)—O(13)—C(14)	117.6 (6)	O(13)—C(8)—C(7)	125.4 (6)
S(1)—C(2)—C(3)	118.3 (7)	O(13)—C(8)—C(9)	116.5 (5)
S(4)—C(3)—C(2)	120.3 (7)	C(7)—C(8)—C(9)	118.1 (6)
S(4)—C(4a)—C(5)	113.6 (4)	Br—C(9)—C(8)	120.3 (5)
S(4)—C(4a)—C(10b)	126.3 (5)	Br—C(9)—C(10)	118.1 (5)
C(5)—C(4a)—C(10b)	119.9 (5)	C(8)—C(9)—C(10)	121.6 (6)
O(6)—C(5)—C(4a)	109.6 (5)	S(1)—C(10b)—C(4a)	125.0 (4)
O(6)—C(5)—C(11)	109.6 (5)	S(1)—C(10b)—C(10a)	116.2 (4)
O(6)—C(5)—C(12)	102.8 (5)	C(4a)—C(10b)—C(10a)	118.8 (5)
C(4a)—C(5)—C(11)	110.2 (5)	C(6a)—C(10a)—C(10b)	118.1 (5)
C(4a)—C(5)—C(12)	112.9 (5)	C(6a)—C(10a)—C(10)	118.0 (5)
C(11)—C(5)—C(12)	111.6 (5)	C(10b)—C(10a)—C(10)	123.7 (5)
O(6)—C(6a)—C(7)	116.9 (5)	C(9)—C(10)—C(10a)	120.2 (5)

their positions were refined with fixed isotropic temperature factors ($B_{\text{H}} = B_{\text{IC}} + 1 \text{ \AA}^2$) except those bound to C(2) and C(3). These four H positions were only taken into account in structure-factor calculations, and not in the refinement. Data were not corrected for extinction. Scattering factors were taken from *SDP-Plus* (Enraf-Nonius, 1983) run on a PDP 11/34 minicomputer with local modifications.

Discussion. Atomic coordinates of non-H atoms are listed in Table 1.* The bond lengths and angles for non-H atoms are given in Table 2. The molecular geometry depicted in Fig. 1 confirms the results of spectroscopic studies.

The phenyl ring, which is coplanar with the methoxy group, exhibits endocyclic bond angles in the range 118–122°, whereas the bond lengths forming the ring are close to the standard value [mean C_{ph}—C_{ph} distance 1.386 (3) Å]. The 1,3-biplanar pyran ring, made up of different C—C and C—O single and multiple bonds, assumes an almost perfect skew conformation. The corresponding puckering parameters (Cremer & Pople, 1975) are: $Q = 0.379$ (4) Å, $\varphi = 216.0$ (7)° and $\theta = 115.2$ (6)° [starting from O(6) through C(5), etc. in a clockwise direction]. Atom C(5) has an almost perfect tetrahedral configuration [mean bond angle 109.5 (3.5)°] with C(11) and C(12) methyl groups in pseudo-axial and pseudo-equatorial positions, respectively.

The rather distorted dithiine ring exhibits a state transitional between ⁴E-envelope and ⁴S₅-skew forms. This phenomenon can be attributed to the vigorous thermal motions of C(2) and C(3), presumably influenced by the presence of the two bulky S atoms. As the conformational disorder of the dithiine ring could not be resolved, its puckering cannot be discussed in detail. However, the unusually short C(2)—C(3) single bond of 1.358 (8) Å is evidence of this disorder. A similar phenomenon was found in both polymorphs of 2-phenyl-5,6-tetramethylenepyrimidine-4(3H)-thione (Kálmán, Argay, Lázár, Rudisch & Bernáth, 1985).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53061 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

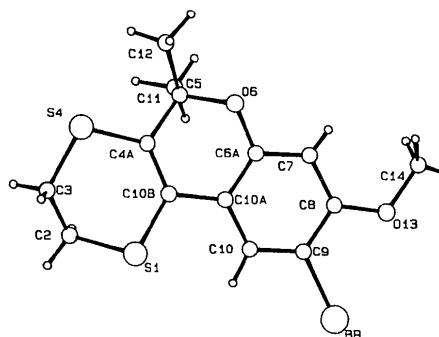


Fig. 1. Perspective view of the molecule showing atomic numbering. The H atoms are shown but not labelled.

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Structure of 3-(4-Methoxyphenyl)-4-phenyl-4H-1,2,4-triazole

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Abstract. C₁₅H₁₃N₃O, $M_r = 251.29$, triclinic, $P\bar{1}$, $a = 9.294$ (1), $b = 11.394$ (4), $c = 13.375$ (2) Å, $\alpha = 103.60$ (2), $\beta = 96.82$ (1), $\gamma = 107.47$ (2)°, $V =$

1285 Å^3 , $Z = 4$, $D_x = 1.30 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ Å}$, $\mu = 0.92 \text{ cm}^{-1}$, $F(000) = 528$, $T = 295 \text{ K}$, final $R = 0.045$ for 2311 observed [$F_o \geq 5\sigma(F_o)$] reflections. There are two molecules in the asymmetric unit. The triazole rings are planar with the

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