and S atoms are listed in Table 1.* Bond lengths, bond angles and selected torsion angles are given in Table 2. The C(2)—C(3) bond of 1.346 (5) Å is comparable to the C=C bond of 1.362 (25) Å in thiophenes (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The S(3)—C(2) bond of 1.719 (4) Å is longer than the C=S bond of 1.683 (1) Å in the substituted thione 4-phenylthiazole-2(3*H*)-thione (Nalini & Desiraju, 1989) and is comparable to the S(1)—C(1) and S(2)—C(1) bonds of 1.715 (4) and 1.710 (3) Å respectively, but is significantly shorter than the S(1)—C(2) and S(2)—C(3) bonds of 1.764 (3) and 1.753 (3) Å respectively. The short S(3)—C(2) bond can be viewed as a single bond with the S atom carrying a negative charge so that C(2) is positive relative to S(3). The comparable and short S(1)—C(1) and S(2)—C(1) bonds can be viewed as a positive charge in the pentatomic ring close to C(1) so that C(1) is positive relative to the S(1) and S(2) atoms. The pentatomic ring system is nearly planar and the torsion angles involving the five ring atoms are close to 0 and 180°. All the features of the pentatomic

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes and a complete list of bonding interactions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54586 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

heterocyclic system in this compound agree very well with those in 5-methyl-2-piperidino-1,3-dithiolium-4-thiolate (Cheung *et al.*, 1991). The C(1)—N bridging distance between the two ring systems is 1.321 (4) Å. The morpholinyl ring has a chair conformation with N and O deviating −0.560 (2) and +0.670 (2) Å respectively from the plane through C(7), C(8), C(9) and C(10). The C_{sp^3}—N_{sp^3} bonds are 1.468 (4) and 1.472 (4) Å, the C_{sp^3}—C_{sp^3} bonds are 1.511 (4) and 1.512 (4) Å, while the C_{sp^3}—O bonds are 1.432 (4) and 1.419 (4) Å, and all six bond angles are close to 109.5°.

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Structure of an Intermediate Methylated Product in the Synthesis of Drimanes

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Abstract. 5-Methoxymethyl-1,1,4a-trimethyl-6-[(phenylthio)methyl]-1,5,8,8a-tetrahydro-4(4a*H*)-naphthalenone, $C_{22}H_{28}O_2S$, m.p. = 382 K, M_r = 356.53, monoclinic, $P2_1/c$, a = 11.810 (1), b = 8.929 (2), c = 18.716 (1) Å, β = 92.773 (8)°, V = 1971.32 Å^3, Z = 4, D_x = 1.201 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ(Mo $K\alpha$) = 0.137 mm^{-1}, $F(000)$ = 768, T = 291 K, final R = 0.055, wR = 0.074 using 2674 reflections. The bicyclic skeleton of the molecule is *cis* fused. An intermolecular C—H⋯O interaction [C(20)—H(20)⋯O(1′) 3.306 (3) Å] was observed.

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Introduction. Drimanes, both *cis* (Hirai, Nozoe & Tsuda, 1967) and *trans* (Kubo, Lee, Pettei, Pilikiewicz & Nakanishi, 1976; Ma & Kubo, 1977) fused, are known to be biologically active naturally occurring compounds. In an attempt to develop a new Diels–Alder strategy towards the synthesis of drimanes, the angular methylation of a crucial intermediate was of interest. The stereochemistry of the ring fusion in the methylated product could not be established unambiguously from spectroscopic studies. In order to assign the detailed stereochemistry, structural confirmation was essential. As the above synthesized angular methylated product was a liquid, an SPh group was introduced which yielded the title compound (1) as a crystalline product. The crystal structure was analyzed using X-ray diffraction techniques.

(1)
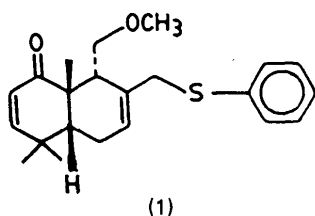
Experimental. Transparent crystals were obtained from a petroleum ether and chloroform solution of the title compound (Gore, Desai, Moyelvaganan, Padmakumar & Bhat, 1991). Intensity data were collected from a crystal, $0.13 \times 0.27 \times 0.34$ mm, using an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation. The cell constants were refined using 25 reflections in the range $9 \le \theta \le 16°$. A total of 2890 unique reflections ($R_{int} = 0.009$) were scanned. $\omega/2\theta$ mode, in the range $0 \le \theta \le 23.5°$ with $h_{max} = 13$, $k_{max} = 10$ and $l_{min/max} = \mp 21$. Three standard reflections checked at every 3600 s interval indicated no significant variation in intensity. Data were corrected for Lp factors, neglecting the effects due to absorption and extinction. The structure was determined by the multisolution direct-methods package *MULTAN88* (Debaerdemaeker, Germain, Main, Refaat, Tate & Woolfson, 1988) using the Sayre equation tangent formula for phase refinements. With an assigned weight of 0.60 for negative quartets, all non-H atoms were located from the E map corresponding to the seventh phase set (RESID = 17.27, CFOM = 2.758). H atoms were located from difference Fourier maps. The structure refinement was by the least-squares method based on F values. In the final refinement, non-H atoms were refined anisotropically and H atoms isotropically; 338 parameters refined using 2674 observed reflections with $F_o \ge 3.0\sigma(|F_o|)$. Final $R = 0.055$ and $wR =$

Table 1. *Atomic coordinates ($\times 10^5$ for S; $\times 10^4$ for remaining non-H atoms) and equivalent isotropic temperature factors ($Å^2 \times 10^3$) with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	U_{eq}
S	59211 (6)	25838 (8)	93205 (4)	48 (1)
O(1)	2312 (2)	4024 (2)	7047 (1)	67 (2)
O(2)	4484 (2)	2243 (2)	6774 (1)	48 (2)
C(1)	1744 (2)	−448 (3)	7623 (2)	45 (3)
C(2)	1725 (2)	143 (4)	6876 (2)	55 (3)
C(3)	1944 (3)	1557 (4)	6689 (2)	56 (3)
C(4)	2323 (2)	2704 (3)	7203 (2)	45 (3)
C(4a)	2712 (2)	2171 (3)	7953 (1)	35 (2)
C(5)	4010 (2)	1799 (3)	7978 (1)	33 (2)
C(6)	4347 (2)	900 (3)	8637 (1)	37 (2)
C(7)	3603 (2)	234 (3)	9039 (1)	44 (2)
C(8a)	1952 (2)	841 (3)	8174 (1)	39 (2)
C(8)	2341 (2)	292 (4)	8914 (1)	47 (3)
C(9)	2574 (3)	−1783 (3)	7693 (2)	58 (4)
C(10)	550 (3)	−1100 (5)	7734 (3)	73 (4)
C(11)	2556 (3)	3464 (3)	8485 (2)	53 (3)
C(12)	4478 (2)	1112 (3)	7307 (1)	39 (2)
C(13)	4796 (4)	1680 (4)	6110 (2)	62 (4)
C(14)	5590 (2)	846 (3)	8859 (2)	43 (3)
C(15)	7386 (2)	2485 (3)	9549 (1)	38 (2)
C(16)	7805 (3)	3552 (3)	10037 (2)	51 (3)
C(17)	8953 (3)	3559 (4)	10241 (2)	67 (4)
C(18)	9665 (3)	2536 (4)	9964 (2)	70 (4)
C(19)	9257 (3)	1477 (4)	9484 (2)	58 (3)
C(20)	8116 (2)	1442 (3)	9276 (1)	45 (3)

0.074, where $w = 1.000/[\sigma^2(F) + 0.0234F^2]$, $(\Delta/\sigma)_{max} = 0.065$. In final difference map $(\Delta\rho)_{max} = 0.269$ and $(\Delta\rho)_{min} = -0.389$ e Å^{-3}. *SHELX76* (Sheldrick, 1976) was used for the structure refinements and a CYBER-180 for all the computations. Scattering factors were those imbedded in *SHELX76*.

Discussion. The atomic coordinates for non-H atoms are listed in Table 1 and the bond distances along with the bond angles in Table 2.* Fig. 1 represents the perspective view of the molecule (Motherwell & Clegg, 1978).

The bicyclic skeleton of the molecule is *cis* fused with torsion angle C(11)—C(4a)—C(8a)—H(8a) = 53.3 (2)°. Ring *A* has an approximate sofa conformation, with C(4a) 0.536 (2) Å out of the least-squares plane [with maximum deviation ±0.075 (3) Å] passing through the remaining five atoms. In ring *B*, the orientation of the CH₂OCH₃ group [attached to C(5)] is opposite to the orientation of the methyl carbon, C(11), attached to C(4a). However, both C(4a) and C(5) are on the same side, by −0.737 (2) and −0.260 (2) Å respectively, of the mean plane passing through the atoms C(6), C(7), C(8) and C(8a) [with maximum deviation 0.083 (3) Å from the

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

C(14)—S	1.810 (3)	C(11)—C(4a)	1.541 (4)
C(15)—S	1.764 (3)	C(6)—C(5)	1.508 (3)
C(4)—O(1)	1.214 (3)	C(12)—C(5)	1.524 (4)
C(12)—O(2)	1.420 (3)	C(7)—C(6)	1.325 (4)
C(13)—O(2)	1.406 (4)	C(14)—C(6)	1.507 (4)
C(2)—C(1)	1.493 (4)	C(8)—C(7)	1.498 (4)
C(8a)—C(1)	1.557 (4)	C(8)—C(8a)	1.520 (4)
C(9)—C(1)	1.545 (4)	C(16)—C(15)	1.394 (4)
C(10)—C(1)	1.549 (4)	C(20)—C(15)	1.383 (4)
C(3)—C(2)	1.339 (5)	C(17)—C(16)	1.391 (5)
C(4)—C(3)	1.461 (5)	C(18)—C(17)	1.361 (5)
C(4a)—C(4)	1.532 (4)	C(19)—C(18)	1.375 (5)
C(5)—C(4a)	1.567 (3)	C(20)—C(19)	1.384 (4)
C(8a)—C(4a)	1.556 (3)		

|			
C(15)—S—C(14)	105.0 (1)	C(12)—C(5)—C(4a)	117.0 (2)
C(13)—O(2)—C(12)	112.2 (2)	C(12)—C(5)—C(6)	111.5 (2)
C(8a)—C(1)—C(2)	110.7 (2)	C(7)—C(6)—C(5)	123.1 (2)
C(9)—C(1)—C(2)	109.5 (3)	C(14)—C(6)—C(5)	117.3 (2)
C(9)—C(1)—C(8a)	115.7 (2)	C(14)—C(6)—C(7)	119.5 (2)
C(10)—C(1)—C(2)	106.6 (3)	C(8)—C(7)—C(6)	125.3 (2)
C(10)—C(1)—C(8a)	107.7 (2)	C(4a)—C(8a)—C(1)	117.6 (2)
C(10)—C(1)—C(9)	106.1 (3)	C(8)—C(8a)—C(1)	113.4 (2)
C(3)—C(2)—C(1)	125.8 (3)	C(8)—C(8a)—C(4a)	109.6 (2)
C(4)—C(3)—C(2)	123.0 (3)	C(8a)—C(8)—C(7)	114.1 (2)
C(3)—C(4)—O(1)	121.5 (3)	C(5)—C(12)—O(2)	107.9 (2)
C(4a)—C(4)—O(1)	121.5 (3)	C(6)—C(14)—S	106.8 (2)
C(4a)—C(4)—C(3)	117.1 (2)	C(16)—C(15)—S	115.9 (2)
C(5)—C(4a)—C(4)	110.1 (2)	C(20)—C(15)—S	124.5 (2)
C(8a)—C(4a)—C(4)	109.2 (2)	C(20)—C(15)—C(16)	119.6 (3)
C(8a)—C(4a)—C(5)	114.0 (2)	C(17)—C(16)—C(15)	119.5 (3)
C(11)—C(4a)—C(4)	108.6 (2)	C(18)—C(17)—C(16)	120.3 (3)
C(11)—C(4a)—C(5)	106.7 (2)	C(19)—C(18)—C(17)	120.4 (3)
C(11)—C(4a)—C(8a)	108.2 (2)	C(20)—C(19)—C(18)	120.3 (3)
C(6)—C(5)—C(4a)	110.9 (2)	C(19)—C(20)—C(15)	119.8 (3)
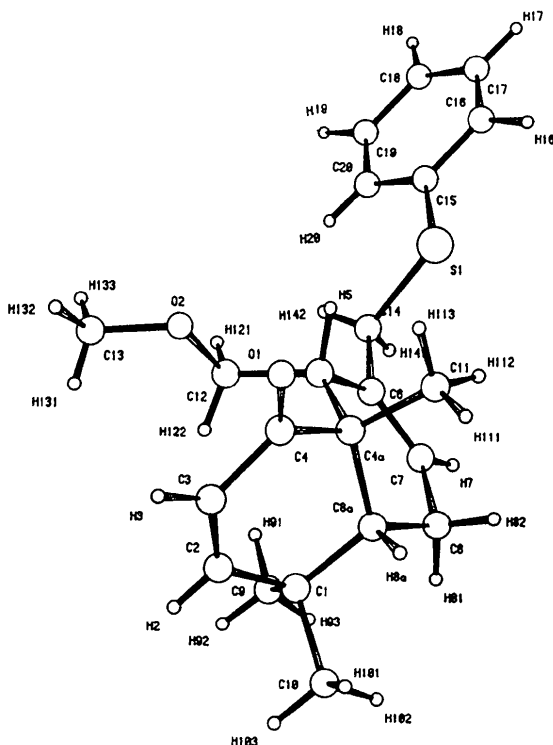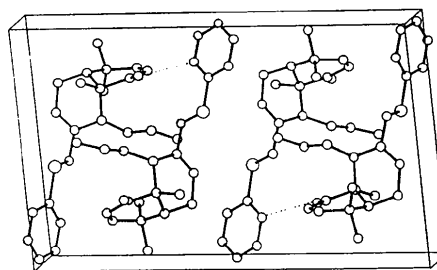
Fig. 2. Unit-cell packing diagram.

least-squares plane]. Ring *B* is in a distorted half-chair conformation. The dihedral angle between the mean planes passing through rings *A* and *B* is 69.0 (3)°. The atom C(14), to which the SPh group is attached, is in the plane [with deviation 0.023 (2) Å] passing through ring *B*. For the S atom, C(sp^3)—S and C(sp^2)—S bonds are localized with respective bond lengths, 1.810 (3) and 1.764 (3) Å. The C(sp^3)—C(sp^3) bond lengths range from 1.461 (5) to 1.567 (3) with an average 1.525 (4) Å. Remaining bond lengths and angles are close to normal values.

Fig. 2 shows the crystal packing diagram; the dotted lines indicate intermolecular C—H···O interactions (Taylor & Kennard, 1982; Das, Sinha, Narkhede & Manisekharan, 1990). The distance between C(20) and O(1^i) [(i) $1 - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$] is 3.306 (3) with H(20)···O(1^i) distance 2.41 (5) Å and C—H···O angle 169.9 (10)°. The closest intermolecular C···S distance is between C(13) and S^i, 3.720 (2) Å, with the C(13)—H(132)···S angle 119.2 (8)°.

Fig. 1. Perspective view of the molecule.

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