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cis-2-Ethoxy-1-phenylsulfinylcyclopropane

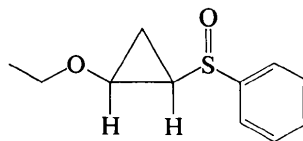
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Abstract. $C_{11}H_{14}O_2S$, $M_r = 210.3$, monoclinic, $P2_1/a$, $a = 13.479$ (4), $b = 7.159$ (1), $c = 11.482$ (4) Å, $\beta = 99.58$ (2)°, $V = 1092.5$ (5) Å³, $Z = 4$, $d_c = 1.28$ Mg m⁻³, $\mu = 2.357$ mm⁻¹. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1113 reflexions led to a final R of 0.097. The crystals decompose rapidly upon exposure to X-rays. The ethoxy and phenylsulfinyl groups are *cis* with respect to the cyclopropane ring. The cyclopropane and phenyl rings exhibit an interplanar angle of 23 (2)°.

Introduction. Heteroatom-substituted cyclopropanes are useful as synthetic intermediates and for the investigation of the characteristic features of cyclopropane ring systems and reactions. The reaction of phenylsulfinyldiazomethane with ethyl vinyl ether yields solid, m.p. 329–330 K, and liquid, b.p. 391–393 K (20 Pa), isomeric cyclopropane derivatives. The structures of the *cis*- and *trans*-2-ethoxy-1-phenylsulfinylcyclopropanes, as the solid and liquid products respectively, were based on an analysis of the proton–proton coupling constants for the ring H atoms (Bednar, Herzig, Schuster, Schuster & Wolschann, 1976). The structural assignments were greatly hampered by the fortuitous overlap of one of the ring protons with the methyl of the ethoxy group and a second with the methylene of the ethoxy group. On the basis of the fragmentary usable data in the NMR spectrum and judicious assumptions such as negligible effects of sulfur stereochemistry on proton–proton coupling constants, the solid compound was assigned the *cis* structure (I) (Ward, 1979).



Crystals of *cis*-2-ethoxy-1-phenylsulfinylcyclopropane decompose upon exposure to X-rays and three crystals were utilized during data collection. Data were collected on a Syntex $P2_1$ diffractometer by the $\theta:2\theta$ scanning technique using a variable scan speed with $Cu K\alpha$ radiation ($\lambda = 1.54178$ Å) and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflexions whose angles were measured by a centering routine associated with the Syntex diffractometer. Systematic absences were consistent with space group $P2_1/a$. 1459 independent reflexions were measured and Lorentz and polarization corrections were applied. No absorption corrections were made. Crystal deterioration was monitored by following the rate of decrease in the intensities of two reference reflexions. When the rate of decay in intensities began to deviate significantly from linearity, the crystal was changed. The reference reflexions were used to place the data on a common scale. 346 reflexions had intensities less than $3\sigma(I)$ and were excluded from the refinement. The direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) was used to calculate phases for the 300 $|E|$ values greater than 1.30. The phase set with the highest combined figure of merit was selected, and the E map calculated with these phases revealed the positions of all 14 nonhydrogen atoms. Alternate least-

squares refinements and difference Fourier calculations were used to locate H atom positions. Least-squares refinement with 1113 reflexions yielded a final *R* of 0.097 where $R = \sum |F_o| - |F_c| / \sum |F_o|$. The function minimized was $\sum (|F_o| - |F_c|)^2$ and all reflexions were assigned unit weights. H atom thermal parameters were refined isotropically.

A final difference map showed a peak of 0.75 e Å⁻³ associated with the S atom. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Atomic positional parameters are given in Table 1 while interatomic distances, valence angles and torsion angles are presented in Table 2.*

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1965) of *cis*-2-ethoxy-1-phenylsulfanyl cyclopropane. Although accuracy is limited by poor crystal quality and X-ray-induced decomposition, the bond lengths and angles agree reasonably well with values reported for other cyclopropane structures. The three cyclopropane bond lengths are not significantly different in the present structure; however, one short cyclo-

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34750 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ($\times 10^4$, for H $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	3271 (6)	6668 (15)	8703 (8)
C(2)	3649 (7)	8078 (17)	7876 (10)
C(3)	3980 (7)	8271 (15)	9175 (8)
S(4)	3810 (2)	4407 (4)	8870 (2)
O(5)	3616 (5)	3591 (11)	10023 (6)
C(6)	2899 (7)	3367 (15)	7774 (8)
C(7)	2096 (7)	2301 (16)	8047 (9)
C(8)	1436 (7)	1511 (18)	7218 (12)
C(9)	1558 (8)	1575 (18)	6037 (11)
C(10)	2333 (8)	2579 (17)	5750 (9)
C(11)	3040 (8)	3416 (16)	6601 (11)
O(12)	4314 (4)	7475 (10)	7232 (5)
C(13)	4978 (8)	9041 (18)	6995 (11)
C(14)	5717 (8)	8335 (18)	6317 (11)
H(1)	250 (5)	669 (9)	883 (5)
H(2)	314 (8)	908 (12)	741 (7)
H(3a)	363 (6)	914 (11)	950 (6)
H(3b)	466 (4)	766 (9)	942 (5)
H(7)	202 (9)	212 (16)	896 (10)
H(8)	79 (7)	80 (14)	746 (8)
H(9)	105 (11)	84 (20)	537 (12)
H(10)	240 (10)	273 (19)	483 (11)
H(11)	362 (6)	427 (12)	641 (7)
H(13a)	453 (9)	1011 (18)	650 (11)
H(13b)	536 (14)	961 (30)	782 (16)
H(14a)	625 (18)	744 (37)	685 (21)
H(14b)	611 (17)	949 (34)	601 (19)
H(14c)	534 (9)	756 (18)	557 (9)

Table 2. Bond lengths (Å), valence angles (°) and torsion angles (°)

C—H lengths range from 0.90 to 1.08 Å and average 1.06 Å.

C(1)—C(2)	1.53 (2)	C(8)—C(9)	1.39 (2)
C(2)—C(3)	1.49 (2)	C(9)—C(10)	1.35 (2)
C(3)—C(1)	1.53 (2)	C(10)—C(11)	1.38 (2)
C(1)—S(4)	1.77 (1)	C(6)—C(11)	1.39 (2)
S(4)—O(5)	1.509 (8)	C(2)—O(12)	1.33 (2)
S(4)—C(6)	1.77 (2)	O(12)—C(13)	1.49 (1)
C(6)—C(7)	1.40 (2)	C(13)—C(14)	1.45 (2)
C(7)—C(8)	1.32 (2)		
C(1)C(2)C(3)	61.1 (7)	C(6)C(7)C(8)	122 (1)
C(2)C(3)C(1)	60.7 (7)	C(7)C(8)C(9)	121 (1)
C(3)C(1)C(2)	58.2 (7)	C(8)C(9)C(10)	118 (1)
C(2)C(1)S(4)	119.8 (7)	C(9)C(10)C(11)	122 (1)
C(3)C(1)S(4)	115.1 (6)	C(10)C(11)C(6)	119 (1)
C(1)S(4)O(5)	108.7 (5)	C(11)C(6)C(7)	117.7 (9)
C(1)S(4)C(6)	94.8 (4)	C(1)C(2)O(12)	117.2 (9)
O(5)S(4)C(6)	105.1 (4)	C(3)C(2)O(12)	118.1 (8)
S(4)C(6)C(7)	122.7 (7)	C(2)O(12)C(13)	109.9 (8)
S(4)C(6)C(11)	119.2 (7)	O(12)C(13)C(14)	109 (1)
O(5)—S(4)—6—11	-162.4 (8)	14—13—O(12)—2	178.4 (8)
O(5)—S(4)—6—7	10 (1)	13—O(12)—2—1	-150.5 (9)
1—S(4)—6—7	-101 (1)	13—O(12)—2—3	-81 (1)
1—S(4)—6—11	87 (1)	O(12)—2—1—S(4)	6 (1)
O(12)—2—3—1	-107 (1)	2—1—S(4)—5	158.5 (8)
2—1—S(4)—6	-94 (1)	2—3—1—S(4)	111 (1)
3—1—S(4)—O(5)	92 (1)	3—1—S(4)—6	-160 (1)

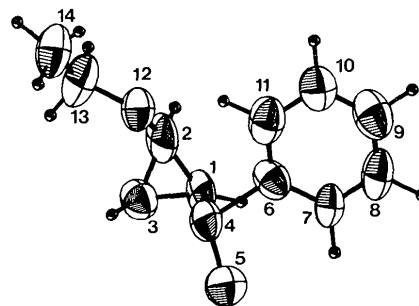


Fig. 1. *ORTEP* drawing of *cis*-2-ethoxy-1-phenylsulfanyl cyclopropane. Thermal ellipsoids are presented at the 50% probability level while H atoms are represented by spheres of arbitrary radius.

propane bond, 1.49 (2) Å, and the small opposite angle, 58.2 (7)°, are common features in cyclopropane compounds such as *trans*-2,*trans*-3-dimethylcyclopropanecarboxylic acid (Luhan & McPhail, 1972), 1-chloro-1-phenylsulfonyl-2,3-dimethylcyclopropane (Saenger & Schwalbe, 1971) and methyl 1-carbamoylcyclopropane-1-carboxylate (de Jong & Schenk, 1973). The cyclopropane ring and the plane of the phenyl ring make an angle of 23 (2)°. The sulfanyl O atom is twisted slightly out of the plane of the phenyl ring as indicated by the O(5)S(4)C(6)C(7) torsion angle of 10 (1)°. The C(1)—S(4) bond is almost perpendicular to the phenyl ring, C(1)S(4)C(6)C(11) =

87 (1)°. The ethoxy side chain exhibits an extended conformation with a C(14)C(13)O(12)C(2) torsion angle of 178.4 (8)°.

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rel-(2*S*,3*S*)-3-Hydroxy-7-methoxy-3',4'-methylenedioxyflavan

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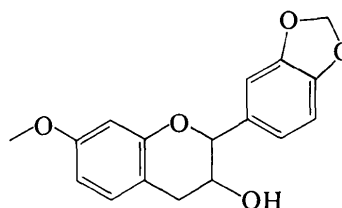
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Abstract. C₁₇H₁₆O₅, *M_r* = 300.33, monoclinic, *P*2₁, *a* = 12.634 (2), *b* = 11.491 (3), *c* = 4.881 (1) Å, β = 99.64 (1)°, *V* = 698.6 (3) Å³, *Z* = 2, *d_c* = 1.427, *d_o* = 1.42 Mg m⁻³, μ = 0.828 mm⁻¹. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1082 reflexions led to a final *R* of 0.045. The two ring systems exhibit an interplanar angle of 19.2 (7)°. An intermolecular hydrogen bond is formed between the hydroxyl H and the methoxy O atom of adjacent molecules.

Introduction. Extracts of the bulbs of *Hippeastrum añáñuca* (Amaryllidaceae) exhibited cytotoxic activity in the *in vitro* KB cell assay (Pacheco, Silva, Steglich & Watson, 1978). The alkaloids lycorine (Gopalakrishna, Watson, Pacheco & Silva, 1976), 17-epihomolycorine (Gopalakrishna, Watson, Silva & Pacheco, 1978), maritidine (Zabel, Watson, Pacheco & Silva, 1979) and hippeastidine (Watson, Taira, Silva & Pacheco, 1977) were isolated and identified by spectroscopic and single-crystal X-ray diffraction techniques. A white crystalline nonalkaloidal compound, m.p. 411–412 K, was also isolated and proved to be the new procyanidin 3-hydroxy-7-methoxy-3',4'-methylenedioxyflavan (I). Procyanidins occur in many fruit-bearing plants as oligomers where the yield is highly dependent upon the

state of fruit maturity. The occurrence of procyanidins in the bulbs of Amaryllidaceae has not been reported previously.



(I)

A crystal of dimensions 0.15 × 0.25 × 0.35 mm was used to collect intensity data on a Syntex *P*2₁ diffractometer system by the θ:2θ scanning technique using a variable scan speed with Cu Kα radiation (λ = 1.54178 Å) and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 medium-angle reflexions whose angles were measured by a centering routine associated with the Syntex diffractometer. Systematic absences were consistent with space group *P*2₁. 1102 independent reflexions were measured for 2θ < 120° and 1082 had intensities greater than 3σ(*I*). Lorentz and polarization corrections were applied, but no