

Während die P–N-Bindungsabstände im Mittel um rund 0,02 bis 0,03 Å kürzer sind als in den analogen Ringverbindungen, wo für $r[\text{P}–\text{N}(sp^2)]$ 1,645 (3) Å (*cis*-Isomeres) und 1,656 (4) Å (*trans*-Isomeres) gefunden wurden (Engelhardt & Hartl, 1975, 1976), ist der P–S-Bindungsabstand im Phenoxythiophosphoryldihydrazid um rund 0,03 Å und der P–O-Bindungsabstand um rund 0,01 Å länger. Einige intermolekulare S...H-Kontakte sind deutlich kürzer als die Summe der van-der-Waals-Radien von Wasserstoff und Schwefel nach Pauling (1973) von 3,05 Å: S...H(10)(\bar{x} , 2– y , 2– z) = 2,66 (3) Å; S...H(11)($x+1$, y , z) = 2,72 (3) Å. Intermolekulare N...H-Wasserstoffbrückenbindungen verknüpfen die Hydrazingruppen so, dass die azideren α -ständigen Wasserstoffatome als Elektronenpaar-Akzeptoren, die basischeren β -Stickstoffatome als Elektronenpaar-Donatoren fungieren: N(4)...H(1)(\bar{x} , 1– y , 2– z) = 2,07 (3) Å, mit N(4)...N(1)(\bar{x} , 1– y , 2– z) = 2,965 (4) Å; N(2)...H(9)(\bar{x} , 2– y , 2– z) = 2,20 (3) Å mit N(2)...N(3)(\bar{x} , 2– y , 2– z) = 3,124 (4) Å.

Die Wasserstoffbrücken vernetzen die Moleküle schichtartig parallel zur (001)-Ebene. Die Schichten sind durch in Richtung der *b*-Achse sich erstreckende Stapel von Phenylringen miteinander verzahnt.

Wir danken den Herren Kollegen des Instituts für Kristallographie der Freien Universität Berlin für ihre Unterstützung bei den Messungen und für die Bereitstellung einiger Rechenprogramme. Dem Fonds der Chemischen Industrie gilt unser Dank für finanzielle Unterstützung.

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Acta Cryst. (1979). **B35**, 3119–3122

(±)-3-Bis(phenylsulfinyl)methyl-1,2-dimethylcyclopropene

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(Received 21 June 1979; accepted 4 September 1979)

Abstract. C₁₈H₁₈O₂S₂, $M_r = 330.47$, orthorhombic, *Pbca*, $a = 20.711$ (9), $b = 15.761$ (7), $c = 10.740$ (3) Å, $V = 3506$ (2) Å³, $Z = 8$, $d_c = 1.252$ Mg m⁻³, $\mu =$

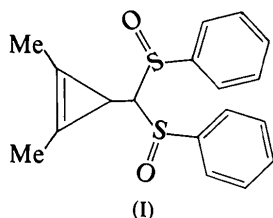
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2.73 mm⁻¹. Full-matrix least-squares refinement (non-hydrogen atoms anisotropic, H atoms isotropic) based on 2535 reflexions led to a final *R* of 0.078. The geometries around the two S atoms are pyramidal (tetrahedral when the lone pair is considered) and the molecules exhibit *R,R* and *S,S* stereochemistries which

is consistent with the diastereoisomeric (\pm) formulation.

Introduction. Sulfinyl carbenes are a new and largely unstudied class of organic reactive intermediates (Venier, Barager & Ward, 1975). In a study of their reactions with alkynes, adducts with a stoichiometry of two molecules of sulfinyl carbene to one molecule of acetylene were isolated (Venier & Beckhaus, 1978). On the basis of proton and ^{13}C NMR, the unusual and unexpected structure (I) was proposed. Structure (I) can be formulated as two diastereoisomers: a (\pm) and a *meso* form. On the basis of proton NMR, the stereochemistry was predicted to be that of the (\pm) isomer. Lacking precedence for this assignment, the structure and stereochemistry were confirmed by a single-crystal X-ray diffraction investigation.



3-Bis(phenylsulfinyl)methyl-1,2-dimethylcyclopropene is difficult to crystallize and a few usable crystals were obtained by the very slow evaporation of a saturated toluene solution. The crystals decompose upon exposure to X-rays and three crystals were used in unit-cell determination and data collection. Dimensions of all crystals were 0.1–0.3 mm. Intensity data were collected on a Syntex $P2_1$ diffractometer system by the $\theta:2\theta$ scanning technique using a variable scan speed with Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) 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 $Pbca$. 2843 independent reflexions were measured, and Lorentz and polarization corrections were applied. Several standard reflexions were monitored and the crystal was changed when the intensities decayed by approximately 15%. The initial intensities of the standard reflexions and several common recollected intensities were used to scale the data sets together. A linear correction, based upon the decrease in intensities of the standard reflexions, was applied to all intensities. 300 reflexions with $I < 3\sigma(I)$ were excluded from the refinements. No absorption corrections were made. The direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) was used to calculate phases for the 300 $|E|$ values greater than 1.6. The phase set with the highest combined figure of merit was selected, and the E map calculated

with these phases revealed the positions of 19 non-hydrogen atoms. Alternate least-squares refinement and difference Fourier calculations yielded the coordinates of the remaining atoms. Least-squares refinement yielded a final R of 0.078 where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)^2$ was determined from counting statistics. The R value for all 2843 reflexions was 0.086; however, no attempt was made to correct the intensities which measured less than $3\sigma(I)$ because of crystal decomposition but were computed to be greater than $3\sigma(I)$. H atom thermal parameters were refined isotropically.

A final difference map showed peaks of about 0.7 e \AA^{-3} associated with the S atoms in positions where lone pairs would be expected. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Atomic positional parameters are given in Table 1 while interatomic distances and

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

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	462 (3)	678 (4)	1250 (6)
C(2)	-125 (3)	978 (4)	-950 (6)
C(3)	434 (2)	1145 (3)	-19 (4)
C(4)	748 (2)	2017 (3)	76 (4)
C(5)	906 (4)	194 (4)	-2069 (7)
C(6)	-848 (3)	1050 (5)	-1141 (7)
S(7)	515 (1)	2568 (1)	1517 (1)
O(8)	466 (2)	1911 (3)	2532 (3)
C(9)	-297 (2)	2809 (3)	1065 (5)
C(10)	-421 (3)	3462 (4)	237 (5)
C(11)	-1043 (3)	3662 (4)	-47 (6)
C(12)	-1533 (3)	3228 (4)	434 (7)
C(13)	-1425 (3)	2573 (5)	1228 (7)
C(14)	-793 (3)	2355 (4)	1561 (6)
S(7')	1619 (1)	1884 (1)	-27 (1)
O(8')	1839 (2)	1401 (2)	1083 (4)
C(9')	1876 (2)	2967 (3)	187 (5)
C(10')	1795 (3)	3539 (4)	-771 (5)
C(11')	2059 (3)	4342 (4)	-600 (7)
C(12')	2385 (3)	4529 (4)	520 (8)
C(13')	2453 (3)	3951 (5)	1440 (7)
C(14')	2202 (2)	3162 (4)	1279 (5)
H(3)	66 (1)	75 (1)	66 (2)
H(4)	59 (2)	238 (2)	-71 (3)
H(5a)	116 (3)	52 (4)	-279 (6)
H(5b)	62 (5)	-29 (6)	-251 (10)
H(5c)	126 (2)	-9 (2)	-148 (3)
H(6a)	-102 (1)	46 (2)	-152 (3)
H(6b)	-99 (6)	155 (9)	-176 (13)
H(6c)	-112 (6)	109 (9)	-29 (13)
H(10)	1 (3)	377 (3)	-5 (5)
H(11)	-112 (3)	401 (3)	-91 (5)
H(12)	-202 (3)	340 (4)	19 (6)
H(13)	-173 (2)	224 (3)	164 (5)
H(14)	-67 (2)	190 (3)	220 (5)
H(10')	148 (3)	343 (3)	-164 (5)
H(11')	202 (3)	467 (4)	-143 (5)
H(12')	259 (3)	515 (4)	65 (6)
H(13')	271 (3)	396 (4)	238 (6)
H(14')	230 (2)	278 (3)	199 (5)

Table 2. *Interatomic distances (Å) and angles (°)*

C(1)–C(2)	1.343 (9)	C(1)–C(5)	1.484 (10)
C(2)–C(3)	1.552 (8)	C(2)–C(6)	1.516 (9)
C(1)–C(3)	1.514 (8)	C(3)–C(4)	1.524 (6)
C(4)–S(7)	1.840 (5)	C(4)–S(7')	1.817 (5)
S(7)–O(8)	1.508 (4)	S(7')–O(8')	1.487 (4)
S(7)–C(9)	1.791 (5)	S(7')–C(9')	1.802 (5)
C(9)–C(10)	1.385 (7)	C(9')–C(10')	1.378 (7)
C(10)–C(11)	1.361 (8)	C(10')–C(11')	1.391 (8)
C(11)–C(12)	1.329 (9)	C(11')–C(12')	1.410 (11)
C(12)–C(13)	1.359 (10)	C(12')–C(13')	1.351 (11)
C(13)–C(14)	1.400 (8)	C(13')–C(14')	1.358 (9)
C(14)–C(9)	1.359 (7)	C(14')–C(9')	1.388 (7)
C(1)C(2)C(3)	62.6 (3)	C(3)C(1)C(5)	142.3 (5)
C(2)C(3)C(1)	51.9 (3)	C(2)C(1)C(5)	152.1 (5)
C(3)C(1)C(2)	65.5 (4)	C(1)C(2)C(6)	152.6 (5)
C(1)C(3)C(4)	118.8 (4)	C(3)C(2)C(6)	144.3 (5)
C(2)C(3)C(4)	121.0 (4)	S(7)C(4)S(7')	111.5 (3)
C(3)C(4)S(7)	111.8 (3)	C(3)C(4)S(7')	108.4 (3)
C(4)S(7)C(9)	96.8 (2)	C(4)S(7')C(9')	100.2 (2)
C(4)S(7)O(8)	107.5 (2)	C(4)S(7')O(8')	108.3 (2)
O(8)S(7)C(9)	106.1 (2)	O(8')S(7')C(9')	107.0 (2)
S(7)C(9)C(10)	120.3 (4)	S(7')C(9')C(10')	119.2 (4)
S(7)C(9)C(14)	119.4 (4)	S(7')C(9')C(14')	117.5 (4)
C(9)C(10)C(11)	119.5 (4)	C(9')C(10')C(11')	116.7 (4)
C(10)C(11)C(12)	121.1 (5)	C(10')C(11')C(12')	119.4 (5)
C(11)C(12)C(13)	120.6 (5)	C(11')C(12')C(13')	122.2 (6)
C(12)C(13)C(14)	120.1 (5)	C(12')C(13')C(14')	119.0 (5)
C(13)C(14)C(9)	118.5 (4)	C(13')C(14')C(9')	119.8 (4)
C(14)C(9)C(10)	120.2 (4)	C(14')C(9')C(10')	123.0 (4)

Table 3. *Torsion angles (°)*

Standard deviations are approximately 1°.

5–1–2–3	176	6–2–1–3	–170
1–2–3–4	104	2–1–3–4	–108
5–1–3–4	75	6–2–3–4	–84
1–3–4–7	168	1–3–4–7'	–69
2–3–4–7	107	2–3–4–7'	–130
3–4–7–8	37	3–4–7'–8'	–65
3–4–7–9	–73	3–4–7'–9'	–177
8–7–4–7'	–85	8'–7'–4–7	58
7–4–7'–9'	–54	7'–4–7–9	166
4–7–9–10	–77	4–7'–9'–10'	–74
4–7–9–14	105	4–7'–9'–14'	112
9–10–11–12	–2	9'–10'–11'–12'	–1
10–11–12–13	0	10'–11'–12'–13'	0
11–12–13–14	1	11'–12'–13'–14'	0
12–13–14–9	–1	12'–13'–14'–9'	0
13–14–9–10	–1	13'–14'–9'–10'	1
14–9–10–11	2	14'–9'–10'–11'	0
5–1–2–6	6		

angles are shown in Table 2. Table 3 contains selected torsion angles.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34742 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

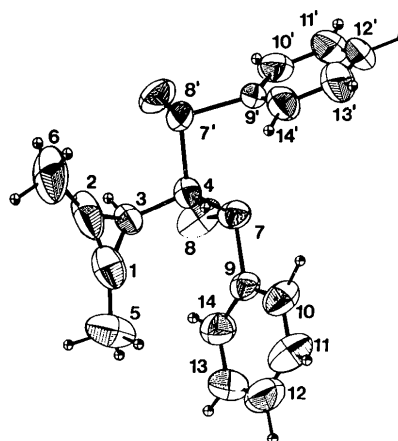


Fig. 1. ORTEP drawing of the title compound. Thermal ellipsoids are presented at the 50% probability level while H atoms are represented by spheres of arbitrary radius.

Discussion. Fig. 1 is an ORTEP drawing (Johnson, 1965) of the title compound. The C=C distance in the cyclopropene ring is 1.343 (9) Å which is comparable to the 1.338 Å reported for diphenylcyclopropene-thione (Reed & Schaefer, 1972). The C(1)–C(3) and C(2)–C(3) distances of 1.514 (8) and 1.552 (8) Å may be significantly different; however, the inequality is probably due to crystal deterioration, scaling errors and absorption. The C(5) and C(6) methyl groups lie out of the plane of the cyclopropene ring by 0.05 (1) and 0.12 (1) Å and exhibit a C(5)C(1)C(2)C(6) torsion angle of 6 (1)°. The S=O groups and their associated phenyl rings are coplanar with the two planar SOPh systems exhibiting an interplanar angle of 57 (1)°. The planar S(7) system makes an angle of 100 (1)° with the cyclopropene ring while the S(7') system makes an angle of 84 (1)°. The angles about the S atoms and the assumed position of the lone pair of electrons indicate an approximate tetrahedral geometry with both S atoms exhibiting identical stereochemistries (*R,R* or *S,S*), which is consistent with the (±) formulation.

The S=O distances of 1.508 (4) and 1.487 (4) Å yield an average value of 1.497 (11) Å which can be compared with the average of 1.490 (3) Å for (*S,S*)-1,2-bis(phenylsulfinyl)ethane (Pelizzi, Coghi, Michelon & Bonivento, 1976) and *meso*-1,2-bis(phenylsulfinyl)ethane (Pelizzi, Michelon & Bonivento, 1976). The average C(*sp*²)–S and C(*sp*³)–S lengths of 1.797 (6) Å and 1.828 (11) Å, respectively, may be compared with the average values of 1.798 (6) and 1.821 (5) Å for the (*S,S*)- and *meso*-1,2-bis(phenylsulfinyl)ethane compounds.

We thank the Robert A. Welch Foundation and the TCU Research Foundation for their financial support. This is FASTBIOS contribution No. 59.

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Acta Cryst. (1979). **B35**, 3122–3124

cis-2-Ethoxy-1-phenylsulfinylcyclopropane

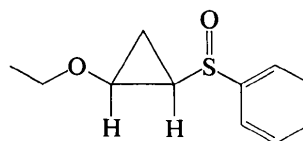
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(Received 11 July 1979; accepted 6 September 1979)

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-