

Structure of (*Z*)- and (*E*)-1,2-Bis(ethylsulfonyl)ethylene

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Abstract. (*Z*)-C₆H₁₂O₄S₂, $M_r = 212.29$, $P2_1/c$, $a = 5.4681$ (9), $b = 13.131$ (3), $c = 13.318$ (3) Å, $\beta = 96.91$ (2)°, $V = 949.3$ (3) Å³, $Z = 4$, $D_m = 1.453$ (2), $D_x = 1.486$ (1) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.507$ mm⁻¹, $F(000) = 448$, $T = 296$ K, $R = 0.059$ for 1518 unique observed reflections. (*E*)-C₆H₁₂O₄S₂, $M_r = 212.29$, $P2_1/c$, $a = 8.597$ (2), $b = 5.813$ (2), $c = 9.628$ (1) Å, $\beta = 97.62$ (1)°, $V = 476.8$ (2) Å³, $Z = 2$, $D_m = 1.466$ (2), $D_x = 1.478$ (1) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.507$ mm⁻¹, $F(000) = 224$, $T = 296$ K, $R = 0.053$ for 1136 unique observed reflections. The structure of the *Z* isomer is normal except that the conformations of the two sulfonyl groups are different, apparently due to minimization of the intramolecular repulsion of O atoms. The molecular structure of the *E* isomer is anomalous. Considerable differences from the usual values of the bond lengths and angles found for this isomer have been tentatively ascribed to electron delocalization within the approximately planar, centrosymmetric moiety of eight atoms around the olefinic bond where two five-membered rings are 'closed' by a short intramolecular hydrogen bond of the S=O...H-C= type.

Introduction. The *Z* and *E* isomers of 1,2-bis(ethylsulfonyl)ethylene were synthesized as part of a systematic study of the isomerization and conformation equilibria of 1,2-disubstituted ethylenes (Procházka, Vondrák & Poláková, 1983). The crystal-structure determination for both isomers was carried out in order to ascertain which of several possible, energetically close conformations is preferred for each isomer in the solid state.

Experimental. The crystals of the *Z* isomer were grown by liquid diffusion of hexane into a saturated solution in

acetone. The *E* isomer was crystallized by vapour diffusion of pentane into a solution in ethyl acetate; the selection of a crystal of the *E* isomer suitable for measurements involved considerable difficulty because of a remarkable tendency for the crystals to aggregate along the *b* axis. The density was determined by flotation in tetrachloromethane/hexane. The measurement and refinement data are summarized in Table 1.

Structure solution and refinement: both structures solved by heavy-atom method; F magnitudes used in full-matrix least-squares refinement; all H atoms found from ΔF synthesis; scale factor, positions and anisotropic temperature factors of non-H atoms refined; for *E* isomer, positions and isotropic temperature parameters of H atoms refined simultaneously; for *Z* isomer, H atoms assigned final isotropic temperature parameters of their bonding partners; scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); programs used: *TLS* (Sklenář

Table 1. Measurement and refinement data

	<i>Z</i> isomer	<i>E</i> isomer
Crystal dimensions (mm)	0.15 × 0.25 × 0.65	0.1 × 0.4 × 1.0
No. of reflections for lattice-parameter determination	31 ($6 < \theta < 24^\circ$)	35 ($5 < \theta < 22^\circ$)
Diffractometer	Hilger & Watts	
Scan mode	$\omega-2\theta$	
Maximum value of $(\sin \theta/\lambda)(\text{Å}^{-1})$	0.66	0.70
Standard reflections (variation)	Two after every 30 (3%)	
Absorption correction	None, $\mu = 0.507$ mm ⁻¹	
hE	$\langle 0,7 \rangle$	$\langle 0,12 \rangle$
kE	$\langle 0,17 \rangle$	$\langle 0,8 \rangle$
lE	$\langle -17,17 \rangle$	$\langle -12,13 \rangle$
No. of reflections measured	2299	1384
No. of reflections used	1518	1136
[$I > 1.96\sigma_1(I)$]		
Residual electron density ($e \text{ Å}^{-3}$)	0.38, -0.27	0.18, -0.32
$(\Delta/\sigma)_{\text{max}}$ for non-H atoms	0.07	0.08
for H atoms	0.19	0.38
Function minimized	$w(F_o - F_c)^2$	
Weight	$\sigma^{-2}(F_o)$, derived from $\sigma(F_o)/F_o = 1/2\sigma_z(I)$ and $\sigma_z(I) = \{\sigma_z^2(I) + (0.06 I)^2\}^{1/2}$	
R, wR	0.059, 0.071	0.053, 0.072

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& Petříček, 1973) and ORTEP (Johnson, 1965); ICL 4-72 computer.*

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes' details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42671 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

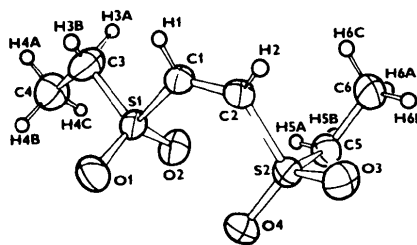


Fig. 1. A perspective view of a molecule of the Z isomer.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for both isomers

$$B_{eq} = \frac{1}{3}(\sum_i \sum_j \beta_{ij} a_i \cdot a_j).$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Z isomer				
S(1)	696 (2)	2330 (1)	1251 (1)	2.63 (2)
O(1)	-522 (6)	2709 (3)	2061 (3)	3.87 (9)
O(2)	-331 (6)	1460 (2)	711 (3)	3.68 (9)
C(1)	3800 (7)	2081 (3)	1734 (3)	2.7 (1)
C(3)	1027 (10)	3311 (4)	359 (5)	4.5 (2)
C(4)	-1454 (11)	3615 (5)	-191 (5)	4.6 (2)
S(2)	3149 (2)	146 (1)	2493 (1)	2.48 (2)
O(3)	4762 (6)	-338 (3)	3282 (2)	3.74 (8)
O(4)	728 (5)	417 (3)	2696 (3)	3.53 (7)
C(2)	4746 (7)	1256 (3)	2171 (4)	2.7 (1)
C(5)	2949 (9)	-609 (4)	1397 (4)	3.2 (1)
C(6)	5454 (11)	-886 (4)	1095 (5)	4.2 (2)

E isomer				
S(1)	1815.1 (6)	773.8 (9)	1287.8 (5)	2.75 (1)
O(1)	1358 (3)	405 (4)	2766 (2)	4.62 (5)
O(2)	2909 (3)	-788 (3)	547 (3)	4.56 (5)
C(1)	73 (3)	733 (4)	509 (2)	2.82 (4)
C(2)	2495 (3)	3626 (4)	1019 (2)	2.95 (5)
C(3)	3973 (4)	4009 (5)	1687 (3)	4.16 (6)

Table 3. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Symmetry code: (i) $-x, -y, -z$.

Z isomer		E isomer	
C(1)—C(2)	1.307 (6)	C(1)—C(1')	1.292 (3)
C(1)—S(1)	1.772 (4)	C(1)—S(1)	1.584 (3)
C(2)—S(2)	1.778 (4)		
S(1)—O(1)	1.424 (4)	S(1)—O(1)	1.541 (2)
S(1)—O(2)	1.429 (3)	S(1)—O(2)	1.548 (3)
S(2)—O(3)	1.436 (3)		
S(2)—O(4)	1.428 (3)		
S(1)—C(3)	1.776 (6)	S(1)—C(2)	1.788 (2)
S(2)—C(5)	1.757 (5)		
C(3)—C(4)	1.516 (8)	C(2)—C(3)	1.364 (4)
C(5)—C(6)	1.516 (8)		
S(1)—C(1)—C(2)	128.7 (3)	S(1)—C(1)—C(1')	111.1 (2)
S(2)—C(2)—C(1)	127.4 (3)		
O(1)—S(1)—O(2)	118.0 (2)	O(1)—S(1)—O(2)	126.1 (1)
O(3)—S(2)—O(4)	118.3 (2)		
C(1)—S(1)—O(1)	107.7 (2)	C(1)—S(1)—O(1)	95.4 (1)
C(1)—S(1)—O(2)	109.7 (2)	C(1)—S(1)—O(2)	111.6 (1)
C(2)—S(2)—O(3)	105.3 (2)		
C(2)—S(2)—O(4)	109.6 (2)		
C(3)—S(1)—O(1)	110.4 (3)	C(2)—S(1)—O(1)	113.0 (1)
C(3)—S(1)—O(2)	108.0 (3)	C(2)—S(1)—O(2)	104.3 (1)
C(5)—S(2)—O(3)	109.2 (2)		
C(5)—S(2)—O(4)	109.3 (2)		
C(1)—S(1)—C(3)	101.9 (2)	C(1)—S(1)—C(2)	104.6 (1)
C(2)—S(2)—C(5)	104.2 (2)		
S(1)—C(3)—C(4)	110.9 (4)	S(1)—C(2)—C(3)	112.6 (2)
S(2)—C(5)—C(6)	112.8 (4)		

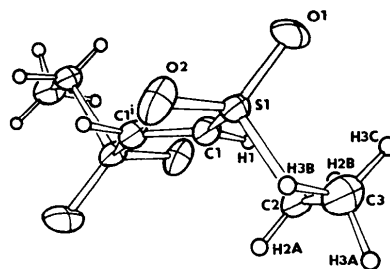


Fig. 2. A perspective view of a molecule of the E isomer.

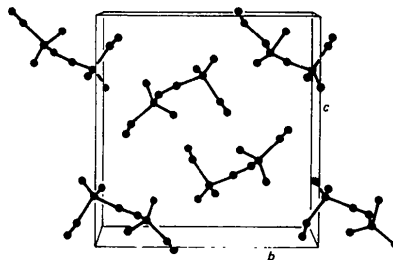


Fig. 3. The unit-cell content of the Z isomer.

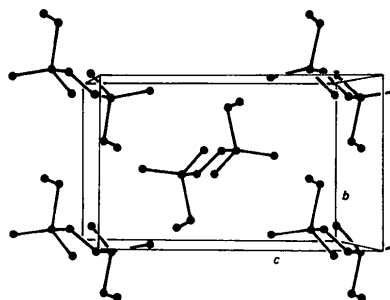


Fig. 4. The unit-cell content of the E isomer.

Discussion. The atomic coordinates are given in Table 2. Figs. 1 and 2 depict perspective views of the molecules with the atom numbering. The unit-cell contents are presented in Figs. 3 and 4. Important bond lengths and angles are compared in Table 3.

Both structures consist of isolated molecules packed at van der Waals or longer distances. There are no intermolecular H...O contacts shorter than 2.6 Å, which otherwise occur relatively commonly in sulfone structures (Luk, Sammes & Harlow, 1980).

In the molecule of the *Z* isomer, the bond distances and angles fall within the ranges which are normal for related structures. Table 4 compares the distances and angles of interest with average values extracted from the Cambridge Structural Database (1985) for the RSO_2R' molecules (R, R' are substituents bonded to S through a C atom).

Because of steric and electronic constraints on the *cis*-sulfone groups, the S(H)C=C(H)S plane is slightly distorted, and, more strikingly, the sulfone groups adopt different conformations relative to the olefinic plane.* Obviously, the repulsive energy of the O atoms is minimized in this arrangement where the shortest contact between the O atoms is 3.181 (6) Å for O(1) and O(4).

As can be seen from Table 4, the molecular geometry of the *E* isomer is anomalous in many respects. The most conspicuous feature of the structure is the nearly planar (within ± 0.125 Å) arrangement of the eight atoms around the C=C bond which includes an exceptionally short intramolecular contact of 2.26 (2) Å between H(1') and O(2), *i.e.* 0.44 Å less than the sum of the van der Waals radii. Planar OSC=CH moieties in unsaturated sulfones are known (Luk *et al.*, 1980; Tran Qui, Vicat & Fillion, 1976; Kusa, Polynova, Porai-Koshits, Kovac & Vegh, 1979) but none of them involve such a short intramolecular H...O contact. In accordance with generally accepted criteria (Taylor & Kennard, 1982, 1984; Pogorelyi & Vishnyakova, 1984), the geometry around O(2) and H(1') corresponds to hydrogen bonding which could be firm enough to mediate electron delocalization within two condensed rings formed by the eight approximately coplanar atoms. With this tentative concept of electron delocalization, the anomalous geometry within the rings can be easily understood (see Desiderato & Sass, 1967, for a similar case in sulfone structures). It is difficult to decide, however, whether this effect could also influence the terminal ethyl groups. More or less serious distortions of alkyl groups adjoining strongly electronegative substituents are known (Lotter, Klein, Rudiger & Scheer, 1977; Wilson, Wilson, Shoemaker, Wooldridge & Hodgson, 1982; Von Deuten, Knoechel,

* This can be seen from the distances of the O atoms from the mean S(1)C(1)H(1)C(2)H(2)S(2) plane which are O(1), -1.376 (4); O(2), 0.919 (4); O(3), -0.455 (3); and O(4), -0.767 (4) Å.

Table 4. Comparison of bond lengths (Å) and angles (°) with the mean values for other sulfone structures

Bond (angle)	<i>Z</i> isomer	<i>E</i> isomer	Mean value [No. of structures]
S—O	1.429 (3)	1.541 (2)	1.439 (18)
	1.428 (3)	1.548 (3)	[88]
	1.424 (4)		
	1.436 (3)		
S—C—	1.776 (6)	1.788 (2)	1.769 (29)
	1.757 (5)		[88]
S—C=	1.772 (4)	1.584 (3)	1.771 (30)
	1.778 (4)		[21]
C—C	1.516 (8)	1.364 (4)	1.49 (5)
	1.516 (8)		[9]
C=C	1.307 (6)	1.292 (3)	1.302 (17)
			[21]
O—S—O	118.0 (2)	126.1 (1)	118.0 (2)
	118.3 (2)		[88]

Kopf, Oehler & Rudolph, 1979; Mangia, Pellizi & Pellizi, 1973; Ohrt, Parthasarathy, Wolf & Truce, 1975), but the wide variety of compound types involved does not permit any unequivocal judgement about the origin of the distortions and their eventual relationship to electron-delocalization effects.

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