

CRYSTAL STRUCTURE OF (*E*)-1,2-BIS(BUTYLSULFONYL)ETHYLENEJaroslav PODLAHA<sup>a</sup>, Jana PODLAHOVÁ<sup>a</sup> and Jindřich HAŠEK<sup>b</sup><sup>a</sup> Department of Chemistry, Charles University, 128 40 Prague 2 and<sup>b</sup> Institute of Macromolecular Chemistry,  
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The title compound is orthorhombic, space group *Pbca*,  $a = 8.523(1)$ ,  $b = 17.467(3)$ ,  $c = 9.449(1)$  Å\*,  $Z = 4$ ,  $R = 0.052$  for 878 observed reflections. The molecule is centrosymmetric with inversion at the middle of the double bond. The characteristic feature of the structure is an almost exactly planar O—S—C(H)=C'(H')—S'—O' moiety with the H···O' and H'···O distances of 2.55 Å, indicating much more weaker intramolecular hydrogen bonds than in the related ethylsulfonyl derivative studied earlier.

Systematic investigation of the kinetics and equilibria of *E*-*Z* isomerization of 1,2-disubstituted ethylenes<sup>1</sup> has been recently corroborated by determination of the structures of representative isomers in the gas phase<sup>2</sup> and in crystal<sup>3</sup>. In both phases, derivatives containing alkylsulfonyl groups are characterized by the *syn*-conformation of one oxygen atom of the SO<sub>2</sub> group relative to the double bond, resulting in a nearly planar H—C=C—S—O moiety in which the H...O distance is remarkably shorter than the sum of the van der Waals radii. For the case of (*E*)-1,2-bis(ethylsulfonyl)ethylene<sup>3</sup>, severe distortions of its overall molecular geometry were tentatively ascribed to electron delocalization within the two coplanar, fused rings of this type. The present paper deals with the crystal structure of the related butylsulfonyl derivative.

## EXPERIMENTAL

A polycrystalline sample, m.p. 147–148°C, was kindly provided by Dr J. Poláková. Single crystals were grown by cooling slowly a 10% solution in hot ethyl acetate. The density was determined by flotation in an aqueous ZnBr<sub>2</sub> solution. Crystal data, measurement and refinement details are summarized in Table I. Empirical absorption correction was applied<sup>4</sup> (410 reflections  $5^\circ \leq \theta \leq 58^\circ$ ,  $\Delta\psi = 10^\circ$ ). The structure was solved by direct methods (MULTAN 80, ref.<sup>5</sup>); coordinates, thermal parameters (anisotropic for non-hydrogen, isotropic for hydrogen atoms), scale factor and secondary isotropic extinction coefficient were refined simultaneously by full-matrix least squares (SHELX-76, ref.<sup>6</sup>). Scattering factors for neutral atoms were taken from ref.<sup>7</sup>. Molecular geometry was calculated by the PARST program<sup>8</sup>.

\* 1 Å = 10<sup>-10</sup> m.

TABLE I  
Crystal data, measurement and refinement details

Formula	$C_{10}H_{20}O_4S_2$	Scan mode	$\theta - 2\theta$
Molecular weight	268.39	Standard reflections	3 after every 97
Space group	<i>Pbca</i>	(variation)	(<2%)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.523(1), 17.467(3), 9.449(1)	Interval <i>h</i>	<0, 9>
$\alpha = \beta = \gamma$ (°)	90	Interval <i>k</i>	<0, 19>
Cell volume (Å <sup>3</sup> )	1 406.6(4)	Interval <i>l</i>	<0, 10>
<i>Z</i>	4	No. of reflections measured	965
<i>D<sub>m</sub></i> , <i>D<sub>x</sub></i> (g cm <sup>-3</sup> )	1.27(1), 1.267	No. of reflections used	878
Radiation	CuK $\alpha$ , $\lambda = 1.5418$ Å	( <i>I</i> < 1.96σ( <i>I</i> ))	
Absorption correction	Carried out, $\mu = 3.39$ mm <sup>-1</sup>	Resid. electr. density (e Å <sup>-3</sup> )	0.37, -0.23
<i>F</i> (000)	576	( <i>d</i> /σ) <sub>max</sub> for non-H atoms	0.194
Temperature (K)	295	Function minimized	$w( F_o  -  F_c )^2$
Crystal dimensions (mm <sup>3</sup> )	0.15 × 0.15 × 0.40	Weight	$\sigma^{-2}(F_o)$ , derived from
No. of reflections for lattice parameter determination	25 (8.5 < $\theta$ < 15°)	Second. extinction correction	$\sigma(F_o)/F_o = 1/2\sigma_2(I)/I$ and $\sigma_2(I) = (\sigma_1^2(I) + 0.06I^2)^{1/2}$
Diffractionmeter	Syntex P2 <sub>1</sub>	<i>R</i> , <i>wR</i>	Type I, $g = 1.6(1) \cdot 10^{-6}$ 0.052, 0.057

## RESULTS AND DISCUSSION

The atomic coordinates of non-hydrogen atoms are presented in Table II and bond distances and angles in Table III. Fig. 1 depicts a perspective view of the molecule; the crystal packing is obvious from Fig. 2.\*

The crystal structure consists of discrete molecules arranged at van der Waals or longer distances. The packing is very loose since there are only three inter-

TABLE II

Atomic coordinates ( $\cdot 10^4$ ) of non-H atoms with estimated standard deviations in parentheses  $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$

Atom	$x/a$	$y/b$	$z/c$	$U_{eq}(\cdot 10^3), \text{\AA}^2$
S(1)	2 198.9(8)	177.3(4)	3 872.6(7)	51.7(4)
O(1)	3 028(3)	- 513(1)	3 513(3)	74(1)
O(2)	1 465(2)	605(1)	2 744(2)	67(1)
C(1)	736(3)	- 86(2)	5 106(3)	48(1)
C(2)	3 461(3)	778(2)	4 849(3)	58(1)
C(3)	2 747(5)	1 516(2)	5 316(4)	70(1)
C(4)	3 993(7)	2 024(3)	6 024(7)	106(2)
C(5)	3 408(11)	2 784(4)	6 395(10)	137(3)

TABLE III

Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with estimated standard deviations in parentheses. Symmetry code:  $-x, -y, 1-z$

S(1)-O(1)	1.438(3)	O(1)-S(1)-O(2)	118.2(1)
S(1)-O(2)	1.444(2)	O(1)-S(1)-C(1)	106.5(1)
S(1)-C(1)	1.767(3)	O(1)-S(1)-C(2)	108.8(1)
S(1)-C(2)	1.763(3)	O(2)-S(1)-C(1)	108.4(1)
		O(2)-S(1)-C(2)	110.0(1)
		C(1)-S(1)-C(2)	103.9(1)
C(1)-C(1)'	1.306(4)	S(1)-C(1)-C(1)'	121.1(2)
C(2)-C(3)	1.493(5)	S(1)-C(2)-C(3)	114.8(2)
C(3)-C(4)	1.537(7)	C(2)-C(3)-C(4)	110.2(3)
C(4)-C(5)	1.461(9)	C(3)-C(4)-C(5)	113.1(5)

\* Tables of structure factors, anisotropic thermal parameters and hydrogen atom coordinates are available from the authors on request.

molecular C...C contacts at the usual level of 3.7 to 4.0 Å and no intermolecular C...O and O...O contacts below 3.4 and 3.7 Å respectively. Analogously to the ethyl derivative<sup>3</sup>, the characteristic feature of the molecular structure is an almost

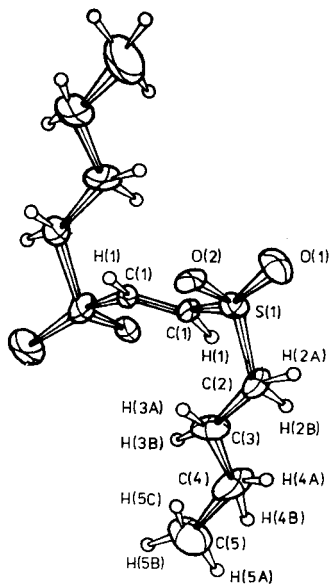


FIG. 1

Perspective view of the molecule with atom numbering

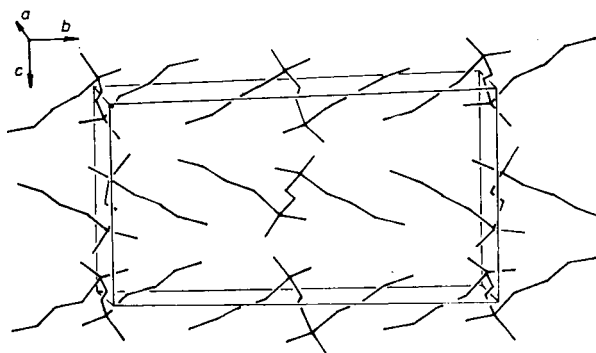
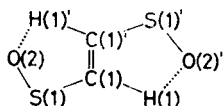


FIG. 2

Perspective view of the unit cell contents

exactly planar (within 0.03 Å) moiety composed of eight atoms,



with the H...O distances of 2.55(2) Å (the van der Waals radii sum is 2.70 Å) and the C—H...O angles of 106(2)°. For comparison, the values for the ethylsulfonyl derivative are 0.125 Å, 2.26 Å and 98° respectively. There are no further resemblances between the two derivatives, however. In contrast to *(E)*-1,2-bis(ethylsulfonyl)ethylene, all the bond distances and angles in the butyl derivative are normal, lying inside the 3σ limit of the mean values for a large number of related structures<sup>9,10</sup>. The apparent shortening of the C(4)—C(5) bond can be undoubtedly accounted for the high thermal motion of the atoms involved. The conformation of the butyl group is fully extended with torsional angles of ±174.4(6) and ∓175(1)° around the C(2)—C(3) and C(3)—C(4) bonds respectively. The corresponding S(1)C(2)C(3)C(4)—C(5) plane (within 0.14 Å) bisects the olefinic plane at a dihedral angle of 93.9°. As can be seen from Fig. 2, this molecular conformation facilitates remarkably the crystal packing.

In conclusion, the coplanar arrangement of the abovementioned eight-membered bicyclic system appears to be the general feature of *(E)*-1,2-bis(alkylsulfonyl)ethylenes. Its influence on the overall molecular geometry is, however, dramatically different for the ethyl and the butyl derivative. It would be possible — although insufficiently found by that time — to speculate whether this is merely a consequence of the varying H...O distance<sup>11–13</sup>. Clearly, the problem requires to investigate further members of this interesting alkylsulfonyl series.

#### REFERENCES

1. Procházka M., Vondrák T., Poláková J.: *Collect. Czech. Chem. Commun.* **48**, 286 (1983) and references therein.
2. Vajda E., Hargittai L., Hnyk D.: *J. Mol. Struct.* **162**, 75 (1987).
3. Podlaha J., Podlahová J., Kratochvíl B., Tulsani N. B., Khawaja A. M., Malý K.: *Acta Crystallogr. C* **42**, 491 (1986).
4. Flack H. D.: *Acta Crystallogr. A* **30**, 569 (1974).
5. Main P., Fiske S. J., Hull S. E., Lessinger L., Germain G., Declercq J. P., Woolfson M. M.: *MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. University of York, England, and Louvain, Belgium, 1980.
6. Sheldrick G. M.: *SHELX-76. Program for Crystal Structure Determination*. University of Cambridge, England, 1976.
7. *International Tables for X-ray Crystallography*, Vol. IV. Kynoch Press, Birmingham 1974.
8. Nardelli H.: *PARST. A System of Computer Routines for Calculating Molecular Parameters from Results of Crystal Structure Analysis*. University of Parma, Italy, 1982.

9. *Cambridge Structural Database* (1987 release). University Chemical Laboratory, Cambridge, England.
10. Allen F. H., Kennard O., Watson D.G., Brammer L., Orpen A. G., Taylor R.: *J. Chem. Soc., Perkin Trans. 2* 1987, S1.
11. Luk K. S., Sammes M. P., Harlow R. L.: *J. Chem. Soc., Perkin Trans.* 1980, 1166.
12. Kusa A., Polynova T. N., Porai-Koshits M. A., Kovac J., Végh D.: *Zh. Strukt. Khim.* 20, 561 (1979).
13. Tran Qui D., Vicat J., Fillion H.: *Acta Crystallogr. B* 32, 1228 (1976).

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