O(1) atom of this second molecule in turn is linked with a third molecule, producing a chain-like structure. The structural analysis thus confirms the *N*-oxide form of triazene and both intra- and intermolecular hydrogen bonds.

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References

Behera, B. & Zacharias, P. S. (1971). *Spectrochim. Acta Part A*, **27**, 2273–2275.

Chakraborti, D. & Majumdar, A. K. (1977). *J. Indian Chem. Soc.* **54**, 258–264.

Chakraborty, A., Behera, H. & Zacharias, P. S. (1968). *Inorg. Chim. Acta*, **2**, 85–88.

Datta, R. L. & Sharma, R. (1983). *J. Indian Chem. Soc.* **60**, 325–327.

Dwivedi, G. L. & Srivastava, R. C. (1971). *Acta Cryst.* B**27**, 2316–2324.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Mitsuhashi, T., Osamura, Y. & Simamura, O. (1965). *Tetrahedron Lett.* pp. 2593–2596.

Purohit, D. N. (1967). *Talanta*, **14**, 353–359.

Rajshekharan, M. V., Varughese, K. I. & Monoharan, P. T. (1979). *Inorg. Chem.* **18**, 2221–2226.

Sarkar, S. B., Khalil, Md., Saha, S. C. & Talapatra, S. K. (1983). *Acta Cryst.* C**39**, 1075–1076.

Seal, A. & Roy, S. (1981). *Indian J. Phys.* **55**A, 414–416.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Vickery, B. L., Bright, D. & Mallinson, P. R. (1973). *XRAY ARC* program system. Agricultural Research Council, London, England. *World List of Crystallographic Computer Programs. J. Appl. Cryst.* (1973), **6**, 309–346.

Acta Cryst. (1985). C**41**, 144–146

Absolute Configuration of (—)-Methyl 2-(4-Bromobenzylsulfinyl)benzoate, $C_{15}H_{13}BrO_3S$

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Abstract. $M_r = 353{\cdot}22$, monoclinic, $P2_1$, $a = 12{\cdot}081$ (2), $b = 5{\cdot}740$ (1), $c = 12{\cdot}956$ (2) Å, $\beta = 122{\cdot}48$ (2)°, $V = 757{\cdot}9$ (3) Å^3, $Z = 2$, $D_m = 1{\cdot}51$, $D_x = 1{\cdot}548$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71093$ Å, $\mu = 2{\cdot}76$ mm^{-1}, $F(000) = 356$, room temperature, $R = 0{\cdot}060$ for 3228 unique reflections and 181 parameters. The absolute configuration of the chiral S atom was established as *S*. The S—O bond with respect to the methoxycarbonyl group is in the *transoid* conformation. The conformation around the S—C(7) bond is *sc–sc*. An interaction occurs between the substituents of the *para*-substituted benzene ring. The methoxycarbonyl group is involved in two short intermolecular contacts.

Introduction. The problem of the effect of position isomerism of certain substituents in aromatic rings on optical properties of aromatic–aliphatic systems containing heteroatomic chirality centers separated from aromatic fragments of the molecule by methylene groups has been examined in our laboratory. The observed optical order in the group of isomeric bromobenzylsulfinylacetic acids (Janczewski, Księżopolski & Rak-Najda, 1981; Janczewski & Księżopolski, 1984) as well as in the group of isomeric methylbenzylsulfinylacetic acids (Janczewski & Janowski, 1978) suggested that a single methylene group does not isolate completely the chiral sulfoxide system from the effects caused by introduction of substituents on an aromatic ring. The observed optical and stereochemical relationships encouraged us to further studies in the group of isomeric 2-(bromobenzylsulfinyl)benzoic acids.

The unsubstituted 2-(benzylsulfinyl)benzoic acid (Janczewski, Majewski, Radkiewicz & Grzegórski, 1983) was assumed as a reference system having the standard type of configuration as well as being a standard for comparing the measured rotation values. Crystals of this compound were of poor quality; only (—)-methyl 2-(4-bromobenzylsulfinyl)benzoate (Janczewski, Jurczak & Majewski, 1984) crystals could be used for X-ray analysis. It was found on the basis of the Freudenberg optical shift rule and the comparison of ORD and CD spectra that the optically active 2-(benzylsulfinyl)- and 2-(4-bromobenzylsulfinyl)benzoic acids with the same direction of molar rotation have the same spatial structure. Therefore, the present determination of absolute configuration of (—)-2-(4-

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bromobenzylsulfinyl)benzoic acid enabled a univocal assignment of the spatial structure of the molecule used as standard.

Experimental. Crystals obtained by crystallization from ethanol solution, density measured by flotation in KI solution. Lattice parameters determined using Cu $K\alpha$ radiation and 15 reflections. Crystal dimensions $0{\cdot}43 \times 0{\cdot}56 \times 0{\cdot}75$ mm, Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $2\theta_{\max} = 60°$. Two standard reflections (131, $\bar{6}03$) monitored every 50 reflections, intensity variation $< \pm 3{\cdot}5\%$. 4359 reflections in four octants (hkl, $hk\bar{l}$, $\bar{h}\bar{k}\bar{l}$, $\bar{h}\bar{k}l$) measured (range $h \pm 16$, $k \pm 8$, $l \pm 17$), 3230 with $F \geq 3\sigma(F)$ considered observed. Semi-empirical absorption corrections based on ψ scan of four reflections, absorption factors 1·00 to 0·44. Structure solved by Patterson method and successive Fourier syntheses. Most H atoms found on difference map, positions of two H atoms of methyl group calculated assuming tetrahedral conformation around C. Molecular model refined with non-H atoms anisotropic; positional and thermal ($U_{\rm iso} = 0{\cdot}06$ Å^2) parameters of H atoms fixed. Full-matrix least squares minimized $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$. Isotropic extinction parameter x refined to $18{\cdot}3\,(4) \times 10^{-7}$, F values multiplied by $(1 - xF^2/\sin\sigma)$. Final $R = 0{\cdot}060$, $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2} = 0{\cdot}044$ and $S = 2{\cdot}96$ for 3228 reflections [reflections 111 and $1\bar{1}1$ having $\Delta(F) > 45\sigma(F)$ excluded from refinement]. Highest peak on final difference map was a residue of the Br atom (0·78 e Å^{-3}), max. $\Delta/\sigma = 0{\cdot}3$. Atomic scattering factors those of *SHELX*76 (Sheldrick, 1976).

To determine absolute configuration the structure was refined using atomic scattering factors with $f'' = 0$, and then structure factors were calculated with $+f''$ and $-f''$. The discrepancy indices were: $R(+) = 0{\cdot}0653$, $R_w(+) = 0{\cdot}0477$ and $R(-) = 0{\cdot}0900$, $R_w(-) = 0{\cdot}0720$ for 180 parameters (without extinction correction) and 3219 reflections with $\Delta(F)/\sigma(F) > 45$. The absolute configuration was established by Hamilton's (1965) $\mathscr{R}$ test [$\mathscr{R} = R_w(-)/R_w(+) = 1{\cdot}509$, $\mathscr{R}_{(1,3039,\,0{\cdot}005)} \simeq 1{\cdot}00129$].

Structure solved and refined using *SHELX*76 (Sheldrick, 1976); programs included in *CRYPOZ* program library (Jaskólski, 1982) used for data reduction and calculation of molecular geometry; *PLUTO* (Motherwell & Clegg, 1978) used for drawings. Calculations performed on RIAD 32 and RIAD 20 computers.

Atomic parameters for the correct enantiomer are given in Table 1.*

Discussion. The crystal structure consists of molecules held together by van der Waals forces. Only two intermolecular contacts involving the methoxycarbonyl group are shorter than the sum of van der Waals radii: C(14)—O[x, $\bar{y}$, z] 3·094 (7) and C(15)—Br[$1+x$, $y-1$, $1+z$] 3·502 (9) Å.

The structure of the molecule and the labelling of atoms are shown in Fig. 1. The molecular geometry is presented in Table 2.

Both benzene rings are planar within experimental error; the dihedral angle between the least-squares planes of these rings is 36·3 (9)°.

The $-\mathrm{COOCH_3}$ group, having a typical geometry for this functional group (Borthwick, 1980; Brückner, Malpezzi & Grassi, 1983; Oddon, Reboul, Rocheville-Divorne, Larice & Roggero, 1983), is twisted by 6·3 (9)° from the benzene ring to which it is bonded.

The C(sp^2)—Br distance and lengths of bonds involving the S atom suggest an interaction between substituents in the *para*-substituted benzene ring. The C(4)—Br bond length is normal for this type of bond in *p*-bromophenyl derivatives [1·870 (6) to 1·914 (4) Å; see *e.g.* Oliver, Mullica, Milligan, Karban, McAtee &

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{\rm eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	$U_{\rm eq}$
Br	0·00698 (7)	0·2500	−0·18515 (6)	0·0711 (3)
C(1)	0·3368 (5)	0·211 (1)	0·2328 (5)	0·041 (2)
C(2)	0·3200 (6)	0·034 (1)	0·1537 (5)	0·045 (2)
C(3)	0·2209 (6)	0·041 (1)	0·0273 (6)	0·049 (2)
C(4)	0·1399 (5)	0·233 (2)	−0·0168 (5)	0·052 (2)
C(5)	0·1541 (6)	0·410 (1)	0·0624 (7)	0·058 (3)
C(6)	0·2534 (6)	0·396 (1)	0·1862 (6)	0·055 (2)
C(7)	0·4433 (5)	0·198 (1)	0·3621 (4)	0·042 (2)
S	0·5809 (1)	0·3965 (3)	0·3995 (1)	0·0423 (5)
O	0·5203 (4)	0·6244 (7)	0·3399 (4)	0·056 (2)
C(8)	0·6242 (4)	0·265 (1)	0·2989 (4)	0·035 (2)
C(9)	0·7040 (5)	0·0620 (9)	0·3312 (5)	0·034 (2)
C(10)	0·7324 (6)	−0·021 (1)	0·2467 (6)	0·055 (2)
C(11)	0·6833 (7)	0·083 (1)	0·1341 (6)	0·064 (3)
C(12)	0·6065 (6)	0·284 (1)	0·1068 (5)	0·062 (2)
C(13)	0·5770 (6)	0·374 (1)	0·1883 (5)	0·052 (2)
C(14)	0·7597 (6)	−0·045 (1)	0·4519 (6)	0·045 (2)
O(1)	0·7356 (4)	0·0140 (8)	0·5257 (4)	0·058 (2)
O(2)	0·8428 (4)	−0·217 (1)	0·4688 (4)	0·072 (2)
C(15)	0·9046 (7)	−0·330 (1)	0·5846 (6)	0·080 (3)

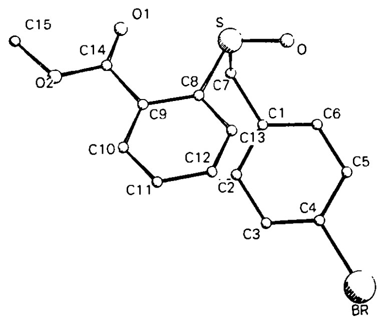

Fig. 1. A perspective view of the molecule.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39752 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *and torsion angles* (°) *in the central part of the molecule*

C(1)–C(2)	1·380 (10)	C(8)–C(9)	1·423 (8)
C(2)–C(3)	1·418 (10)	C(9)–C(10)	1·395 (11)
C(3)–C(4)	1·377 (10)	C(10)–C(11)	1·383 (12)
C(4)–Br	1·893 (6)	C(11)–C(12)	1·402 (11)
C(4)–C(5)	1·391 (11)	C(12)–C(13)	1·383 (11)
C(5)–C(6)	1·397 (11)	C(13)–C(8)	1·378 (9)
C(6)–C(1)	1·362 (9)	C(9)–C(14)	1·463 (10)
C(1)–C(7)	1·467 (8)	C(14)–O(1)	1·188 (10)
C(7)–S	1·854 (6)	C(14)–O(2)	1·341 (8)
S–O	1·495 (5)	O(2)–C(15)	1·426 (10)
S–C(8)	1·809 (6)		
C(1)–C(2)–C(3)	122·3 (5)	S–C(8)–C(9)	122·8 (4)
C(2)–C(3)–C(4)	118·1 (5)	S–C(8)–C(13)	116·1 (4)
C(3)–C(4)–Br	119·6 (5)	C(9)–C(8)–C(13)	121·1 (5)
C(3)–C(4)–C(5)	120·1 (6)	C(8)–C(9)–C(14)	120·4 (4)
C(5)–C(4)–Br	120·2 (5)	C(8)–C(9)–C(10)	117·5 (5)
C(4)–C(5)–C(6)	119·6 (6)	C(10)–C(9)–C(14)	122·0 (6)
C(5)–C(6)–C(1)	121·9 (6)	C(9)–C(10)–C(11)	122·2 (6)
C(6)–C(1)–C(2)	117·9 (5)	C(10)–C(11)–C(12)	118·3 (6)
C(6)–C(1)–C(7)	122·3 (5)	C(11)–C(12)–C(13)	121·5 (6)
C(2)–C(1)–C(7)	119·9 (5)	C(12)–C(13)–C(8)	119·4 (6)
C(1)–C(7)–S	112·3 (4)	C(9)–C(14)–O(1)	124·8 (6)
C(7)–S–O	106·4 (3)	C(9)–C(14)–O(2)	110·9 (5)
O–S–C(8)	104·2 (3)	O(1)–C(14)–O(2)	124·3 (5)
C(7)–S–C(8)	96·9 (3)	C(14)–O(2)–C(15)	115·6 (5)
C(2)–C(1)–C(7)–S	105·4 (6)		
C(6)–C(1)–C(7)–S	–73·6 (6)		
C(1)–C(7)–S–O	45·0 (4)		
C(1)–C(7)–S–C(8)	–62·1 (4)		
C(7)–S–C(8)–C(9)	–81·7 (5)		
C(7)–S–C(8)–C(13)	99·3 (5)		
O(1)–C(14)–O(2)–C(15)	–0·6 (7)		
O–S–C(8)–C(9)	169·5 (4)		
O–S–C(8)–C(13)	–9·6 (4)		
S–C(8)–C(9)–C(14)	–2·6 (5)		
C(8)–C(9)–C(14)–O(1)	6·4 (7)		
C(10)–C(9)–C(14)–O(2)	3·0 (7)		
C(9)–C(14)–O(2)–C(15)	179·0 (6)		

Belew, 1979; Iitaka, Watanabe, Harrison & Harrison, 1969; Pyżalska, Pyżalski & Borowiak, 1980; Kaftory, 1979; Destro, 1979; Liu & Davis, 1980; Bryan, Hartley, Peckler, Fujita, Nagao & Seno, 1980]. The C(1)–C(7) distance is shorter than expected for a $C(sp^2)$–$C(sp^3)$ bond, but the C(7)–S distance is significantly longer than the C(methylene)–S single bond found in sulfoxides, for example: 1·802 (2) (Svinning, Mo & Bruun, 1976), 1·813 (2) (Hoyos-Guerrero, Martínez-Carrera & García-Blanco, 1983), 1·815 (8) (Kozioł, Księżopolski & Janczewski, 1983), 1·817 (4) Å (Tranqui, Richard, Vicat & Fillion, 1974).

The S–C(8) bond length is very close to the S–$C(sp^2)$ distance observed in methyl *p*-tolyl sulfoxide (de la Camp & Hope, 1970) and in 3-bis(phenylsulfinyl)methyl-1,2-dimethylcyclopropene (Beckhaus, Kimura, Watson, Venier & Kojić-Prodić, 1979). The C–S–C angle is typical of sulfoxides. When comparing the S–O distance with that in other sulfoxide groups (*e.g.* de la Camp & Hope, 1970; Svinning *et al.*, 1976; Hoyos-Guerrero *et al.*, 1983; Kozioł *et al.*, 1983; Tranqui *et al.*, 1974; Kimura, Ward, Watson & Venier, 1979; normal value being about 1·50–1·51 Å), some shortening is evident.

The chiral S atom was found to have the *S* configuration.

The conformation about the S–C(7) bond is *sc–sc*. The S–O bond is *transoid* in relation to the $-COOCH_3$ group, the intramolecular S–O(1) (carbonyl) distance being 2·776 (5) Å. Therefore, generally, this orientation is like that of (*S*)-2-(methylsulfinyl)benzoic acid (Dahlén, 1974), but the presence of the unsubstituted $-COOH$ group in the second compound causes different inter- and intramolecular interactions.

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References

Beckhaus, H., Kimura, M., Watson, W. H., Venier, C. G. & Kojić-Prodić, B. (1979). *Acta Cryst.* B**35**, 3119–3122.

Borthwick, P. W. (1980). *Acta Cryst.* B**36**, 628–632.

Brückner, S., Malpezzi, L. & Grassi, M. (1983). *Acta Cryst.* C**39**, 592–594.

Bryan, R. F., Hartley, P., Peckler, S., Fujita, E., Nagao, Y. & Seno, K. (1980). *Acta Cryst.* B**36**, 1709–1710.

Camp, U. de la & Hope, H. (1970). *Acta Cryst.* B**26**, 846–853.

Dahlén, B. (1974). *Acta Cryst.* B**30**, 642–646.

Destro, R. (1979). *Acta Cryst.* B**35**, 1714–1717.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Hoyos-Guerrero, M. A., Martínez-Carrera, S. & García-Blanco, S. (1983). *Acta Cryst.* C**39**, 118–119.

Iitaka, Y., Watanabe, I., Harrison, I. T. & Harrison, S. (1969). *Acta Cryst.* B**25**, 1299–1310.

Janczewski, M. & Janowski, W. (1978). *Ann. Univ. Mariae Curie-Skłodowska, Sect. AA*, **33**, 119–155.

Janczewski, M., Jurczak, J. & Majewski, W. (1984). *Pol. J. Chem.* In the press.

Janczewski, M. & Księżopolski, J. (1984). *Pol. J. Chem.* In the press.

Janczewski, M., Księżopolski, J. & Rak-Najda, T. (1981). *Pol. J. Chem.* **55**, 535–546.

Janczewski, M., Majewski, W., Radkiewicz, S. & Grzegórski, S. (1983). *Ann. Univ. Mariae Curie-Skłodowska, Sect. AA.* In the press.

Jaskólski, M. (1982). Collected Abstracts of the Fourth Symposium on Organic Crystal Chemistry, Poznań 1982, pp. 70–71.

Kaftory, M. (1979). *Acta Cryst.* B**35**, 1717–1719.

Kimura, M., Ward, M. A., Watson, W. H. & Venier, C. G. (1979). *Acta Cryst.* B**35**, 3122–3124.

Kozioł, A. E., Księżopolski, J. & Janczewski, M. (1983). *Pol. J. Chem.* **57**, 41–47.

Liu, L.-K. & Davis, R. E. (1980). *Acta Cryst.* B**36**, 173–176.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Oddon, Y., Reboul, J. P., Rocheville-Divorne, C., Larice, J. L. & Roggero, J. P. (1983). *Acta Cryst.* C**39**, 603–605.

Oliver, J. D., Mullica, D. F., Milligan, W. O., Karban, J., McAtee, J. L. & Belew, J. S. (1979). *Acta Cryst.* B**35**, 2273–2276.

Pyżalska, D., Pyżalski, R. & Borowiak, T. (1980). *Acta Cryst.* B**36**, 1672–1675.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Svinning, T., Mo, F. & Bruun, T. (1976). *Acta Cryst.* B**32**, 759–764.

Tranqui, D., Richard, P., Vicat, J. & Fillion, H. (1974). *Acta Cryst.* B**30**, 673–679.