the initial frames at the end of data collection and analysing the duplicate reflections.

H atoms were placed geometrically and refined with a riding model including free rotation about C—C bonds, and with $U_{\rm iso}$ constrained to be 1.2 (1.5 for methyl groups) times $U_{\rm eq}$ of the carrier atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: local programs. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

We thank EPSRC for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1222). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Sulfoximidooxirane

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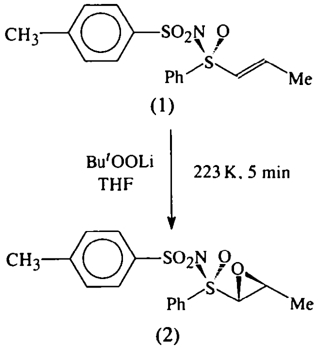
Abstract

The crystal structure of the title compound, *S*-(*trans*-3-methyl-2-oxiranyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximide, $C_{16}H_{17}NO_4S_2$, has two independent molecules in the asymmetric unit, which differ significantly only in the conformation of the (*p*-tolylsulfonyl)sulfoximide group. The powerful electron-withdrawing properties of the sulfoximide substituent produce a marked difference in the C—O bond lengths of the oxirane ring, the nearer bond being substantially shortened relative to the distal bond. The observed structure further demonstrates the high degree of diastereoselectivity in the nucleophilic epoxidation of vinylsulfoximides with lithium *tert*-butylperoxide.

Comment

The title compound is one of a series prepared in a study of nucleophilic epoxidation of vinylsulfoximides by lithium *tert*-butylperoxide (Bailey, Clegg, Jackson & Meth-Cohn, 1993). As part of that study we reported the crystallographic characterization of the corresponding isopropyl (in place of methyl) derivative, which served to demonstrate a high degree of diastereoselectivity in the epoxidation. The present structure provides additional support for the conclusion that the observed sense of diastereoselectivity in these reactions is a general phenomenon. Preferential addition to the β-face of the double bond of vinylsulfoximides has been rationalized on the basis of steric hindrance of the α-face by the sulfoximide group, as revealed by crystallographic analysis (Dong, Pyne, Skelton & White, 1993).

The two crystallographically independent molecules of the title compound, (2), have essentially the same geometry for the oxirane ring and its immediate substituents. They differ only slightly in the orientations of the phenyl group attached to sulfur, and the main difference is in the conformation of the sulfonyl group at the N atom, with approximately 10° difference in the S—N—S—C torsion angle. In both molecules, the sulfoximide S═O bond approximately eclipses the oxirane ring C—C bond whereas in the isopropyl analogue (Bailey *et al.*, 1993), it eclipses the nearer C—O bond.



For both molecules in the asymmetric unit, as for the isopropyl analogue, the two ring C—O bonds are very different in length. In general, there is no clear correlation between the C—O bond lengths and the electronic properties of the substituents for oxirane structures (Clegg & Kelly, 1994; Clegg, Ranelli & Jackson, 1995), except for a relatively small number of structures containing very strongly electron-withdrawing substituents such as cyano, nitro or sulfonyl. A survey of the April 1996 release of the Cambridge Structural Database (Allen & Kennard, 1993) shows 24 such structures with sulfone, sulfoximide and related substituents. There is considerable variation in the C—O bond lengths (even in the title compound the two independent molecules have significantly different lengths for the C—O bond nearer to the sulfoximide substituent, for which there is no obvious explanation), but the near C—O bond is almost invariably shorter than the distal C—O bond with a mean difference of 0.027 (14) Å. The sulfoximides (three structures in addition to the title compound) show particularly marked differences, with a mean of 0.054 (16) Å, reflecting the powerful electron-withdrawing properties of such groups.

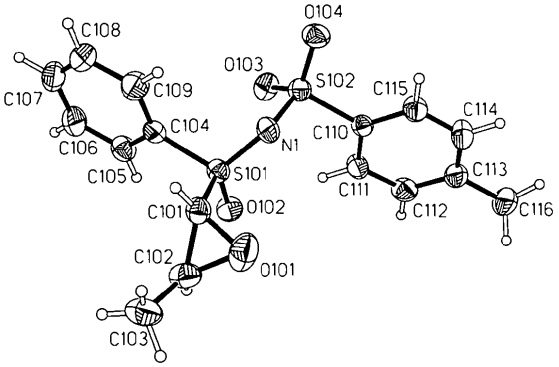


Fig. 1. The structure of one molecule with atom labels and 50% probability ellipsoids for non-H atoms; the numbering scheme for the second molecule follows the same pattern.

Experimental

The synthesis of compound (2) from (1) (see scheme) has been described previously (Bailey *et al.*, 1993). Crystals were obtained by vapour diffusion of petroleum ether into a solution in ethyl acetate.

Crystal data

$C_{16}H_{17}NO_4S_2$
$M_r = 351.43$
Monoclinic
$P2_1/n$
$a = 16.149\,(8)$ Å
$b = 12.969\,(8)$ Å
$c = 17.075\,(9)$ Å
$\beta = 110.59\,(4)°$
$V = 3347.7\,(32)$ Å^3
$Z = 8$
$D_x = 1.395$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28 reflections
$\theta = 10.71–12.35°$
$\mu = 0.337$ mm^{-1}
$T = 160\,(2)$ K
Block
0.45 × 0.20 × 0.20 mm
Colourless

Data collection

Stoe–Siemens diffractometer with Cryostream cooler (Cosier & Glazer, 1986)
ω/θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: none
5738 measured reflections
5265 independent reflections

3528 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0607$
$\theta_{\rm max} = 24.02°$
$h = -18 \rightarrow 18$
$k = -9 \rightarrow 14$
$l = -17 \rightarrow 19$
5 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0395$
$wR(F^2) = 0.1242$
$S = 1.074$
5255 reflections
419 parameters
H atoms riding (see text)
$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 3.8537P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.037$
$\Delta\rho_{\rm max} = 0.295$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.294$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S101	0.90401 (5)	0.20906 (6)	0.70495 (5)	0.0297 (2)
S102	1.07784 (5)	0.14941 (6)	0.77364 (5)	0.0300 (2)
N1	0.9991 (2)	0.2311 (2)	0.7678 (2)	0.0315 (6)
O101	0.8367 (2)	0.3060 (2)	0.8049 (2)	0.0604 (8)
O102	0.86132 (15)	0.1122 (2)	0.70824 (15)	0.0365 (6)
O103	1.0529 (2)	0.0832 (2)	0.70164 (15)	0.0398 (6)
O104	1.15732 (15)	0.2086 (2)	0.7923 (2)	0.0408 (6)
C101	0.8455 (2)	0.3149 (3)	0.7274 (2)	0.0333 (8)
C102	0.7575 (2)	0.2958 (3)	0.7296 (2)	0.0430 (9)
C103	0.6913 (3)	0.3799 (3)	0.7147 (3)	0.0522 (11)
C104	0.8953 (2)	0.2361 (3)	0.6011 (2)	0.0315 (8)
C105	0.8413 (2)	0.1736 (3)	0.5373 (2)	0.0390 (9)
C106	0.8309 (3)	0.1983 (3)	0.4558 (2)	0.0453 (9)
C107	0.8733 (2)	0.2825 (3)	0.4376 (2)	0.0456 (10)
C108	0.9266 (3)	0.3432 (3)	0.5015 (2)	0.0474 (10)
C109	0.9381 (2)	0.3212 (3)	0.5838 (2)	0.0431 (9)
C110	1.0897 (2)	0.0713 (3)	0.8617 (2)	0.0277 (7)
C111	1.0333 (2)	−0.0123 (3)	0.8522 (2)	0.0366 (8)
C112	1.0469 (2)	−0.0787 (3)	0.9192 (2)	0.0408 (9)
C113	1.1137 (2)	−0.0627 (3)	0.9952 (2)	0.0383 (8)
C114	1.1688 (2)	0.0221 (3)	1.0027 (2)	0.0428 (9)
C115	1.1571 (2)	0.0890 (3)	0.9366 (2)	0.0367 (8)
C116	1.1265 (3)	−0.1351 (3)	1.0670 (2)	0.0491 (10)
S201	0.59601 (5)	0.94923 (6)	0.28797 (5)	0.0292 (2)
S202	0.42287 (5)	0.88659 (7)	0.23764 (6)	0.0336 (2)
N2	0.4970 (2)	0.9711 (2)	0.2356 (2)	0.0324 (6)
O201	0.6387 (2)	1.0363 (2)	0.16655 (15)	0.0423 (6)
O202	0.6354 (2)	0.8511 (2)	0.28124 (15)	0.0369 (6)
O203	0.4501 (2)	0.8293 (2)	0.31461 (15)	0.0422 (6)
O204	0.3412 (2)	0.9425 (2)	0.2145 (2)	0.0458 (7)
C201	0.6467 (2)	1.0511 (3)	0.2512 (2)	0.0304 (7)
C202	0.7264 (2)	1.0294 (3)	0.2313 (2)	0.0357 (8)
C203	0.7901 (2)	1.1124 (3)	0.2312 (3)	0.0447 (9)
C204	0.6171 (2)	0.9784 (3)	0.3940 (2)	0.0325 (8)
C205	0.6716 (2)	0.9126 (3)	0.4544 (2)	0.0420 (9)
C206	0.6866 (3)	0.9336 (4)	0.5378 (3)	0.0534 (11)
C207	0.6484 (3)	1.0181 (4)	0.5599 (3)	0.0521 (11)
C208	0.5951 (3)	1.0829 (4)	0.4997 (3)	0.0544 (11)
C209	0.5783 (2)	1.0644 (3)	0.4155 (2)	0.0446 (9)
C210	0.4151 (2)	0.8007 (3)	0.1551 (2)	0.0305 (7)
C211	0.4568 (2)	0.7064 (3)	0.1719 (2)	0.0350 (8)

C212	0.4484 (2)	0.6389 (3)	0.1065 (2)	0.0397 (9)
C213	0.4009 (2)	0.6662 (3)	0.0248 (2)	0.0430 (9)
C214	0.3615 (3)	0.7631 (3)	0.0093 (2)	0.0462 (10)
C215	0.3678 (2)	0.8305 (3)	0.0740 (2)	0.0427 (9)
C216	0.3935 (3)	0.5948 (4)	−0.0466 (3)	0.0681 (14)

Table 2. *Selected geometric parameters (Å, °)*

S101—O102	1.443 (3)	S201—O202	1.445 (2)
S101—N1	1.560 (3)	S201—N2	1.559 (3)
S101—C101	1.783 (3)	S201—C201	1.781 (3)
S102—O104	1.432 (3)	S202—O204	1.434 (3)
S102—O103	1.436 (3)	S202—O203	1.438 (3)
S102—N1	1.630 (3)	S202—N2	1.632 (3)
O101—C101	1.383 (4)	O201—C201	1.418 (4)
O101—C102	1.466 (5)	O201—C202	1.461 (4)
C101—C102	1.455 (5)	C201—C202	1.469 (4)
C102—C103	1.485 (5)	C202—C203	1.488 (5)
S101—N1—S102	118.8 (2)	S201—N2—S202	118.5 (2)
C101—O101—C102	61.3 (2)	C201—O201—C202	61.4 (2)
O101—C101—C102	62.1 (2)	O201—C201—C202	60.7 (2)
C101—C102—O101	56.5 (2)	O201—C202—C201	57.9 (2)

C101—S101—N1—S102	177.2 (2)
C110—S102—N1—S101	−99.2 (2)
O102—S101—C101—C102	−11.7 (3)
S101—C101—C102—C103	−155.9 (3)
C101—S101—C104—C105	−109.5 (3)
C201—S201—N2—S202	171.5 (2)
C210—S202—N2—S201	−89.6 (2)
O202—S201—C201—C202	−8.7 (3)
S201—C201—C202—C203	−157.0 (3)
C201—S201—C204—C205	−114.1 (3)

The measured data consisted of a complete unique set together with a partial set of Friedel opposites. In view of the marked decline in intensity at higher Bragg angles (mean $I/\sigma < 0.6$ at $\theta = 22°$) and the significant decay in standard reflections, data collection was restricted to $\theta_{\max} = 24°$.

H atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with $U_{\rm iso}$ constrained to be 1.2 (1.5 for methyl groups) times $U_{\rm eq}$ of the carrier atom.

Checks on cell symmetry show that the two independent molecules are related by an approximate non-crystallographic inversion centre.

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1221). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-4-*tert*-Butylcyclohexyl 2,4-Dinitrobenzenesulfenate

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Abstract

The low-temperature structure of *trans*-4-*tert*-butylcyclohexyl 2,4-dinitrobenzenesulfenate, $C_{16}H_{22}N_2O_5S$, is reported. The C—O bond distance is 1.473 (2) Å. A close contact exists between a 2-nitro O atom and the sulfenate S atom which is evidence for a significant interaction between these two; the pattern of bond distances in the aromatic ring and the nitro groups is consistent with this.

Comment

As part of our structural studies on the factors influencing C—O bond distances (White, 1995; White & Robertson, 1992), we required accurate C—O bond distances for an equatorial cyclohexyl 2,4-dinitrobenzenesulfenate ester for comparison purposes. The C—O bond distance is a useful probe for detecting the presence of electronic interactions in organic compounds (Amos, Handy, Jones & Kirby, 1992; White, 1995; White & Robertson, 1992). We chose *trans*-4-*tert*-butylcyclohexyl 2,4-dinitrobenzenesulfenate, (1), for this study.

Compound (1) was prepared by esterification of *trans*-4-*tert*-butylcyclohexanol, (2), with 2,4-nitrobenzenesulfenyl chloride in diethyl ether in the presence of one equivalent of pyridine.