

Experimental

The very thin brown plate crystal used for analysis was obtained by the slow evaporation of an ethanol solution of the title compound at room temperature.

Crystal data

$C_{11}H_9NO_3$
 $M_r = 203.20$
 Monoclinic
 $P2_1/c$
 $a = 20.074(2) \text{ \AA}$
 $b = 6.488(3) \text{ \AA}$
 $c = 7.180(4) \text{ \AA}$
 $\beta = 96.68(2)^\circ$
 $V = 928.8(9) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.453 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 15.8\text{--}19.5^\circ$
 $\mu = 0.100 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Plate
 $0.5 \times 0.5 \times 0.1 \text{ mm}$
 Brown

Data collection

Rigaku AFC-5R diffractometer
 ω - 2θ scans
 Absorption correction: none
 2513 measured reflections
 2334 independent reflections
 1376 reflections with $I > \sigma(I)$

$R_{\text{int}} = 0.059$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -25 \rightarrow 25$
 $k = -8 \rightarrow 0$
 $l = 0 \rightarrow 9$
 3 standard reflections every 150 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.059$
 $wR(F^2) = 0.120$
 $S = 1.66$
 1376 reflections
 148 parameters
 H atoms: see below
 $w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\text{max}} = 0.013$
 $\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C11	1.368 (3)	C3—C10	1.453 (4)
O2—C12	1.213 (3)	C10—C11	1.325 (4)
O3—C12	1.317 (3)	C11—C12	1.477 (4)
C2—C3—C10	126.5 (3)	O1—C11—C10	121.5 (3)
C9—C3—C10	126.6 (3)	C10—C11—C12	125.3 (3)
C3—C10—C11	126.3 (3)	O2—C12—O3	123.6 (3)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3...O2 ⁱ	0.96 (4)	1.80 (4)	2.760 (3)	175 (3)
O1—H11...O2 ⁱⁱ	0.88 (3)	1.97 (4)	2.727 (3)	143 (3)

Symmetry codes: (i) $1 - x, -1 - y, -z$; (ii) $1 - x, -y, -z$.

All H atoms were located from difference Fourier maps. Only the H atoms of the O—H and N—H groups were refined isotropically because of the low data/parameter ratio; others were fixed at calculated positions.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984)

and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1267). Services for accessing these data are described at the back of the journal.

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N—H...N Hydrogen Bonding in the Four Independent Molecules of (2*S*,4*S*,5*R*)-(–)-2-(1*H*-Imidazol-2-yl)-3,4-dimethyl-5-phenyl-1,3-oxazolidine, with C—H... π _{arene}, C—H...O and C—H... π _{C=C} Interactions

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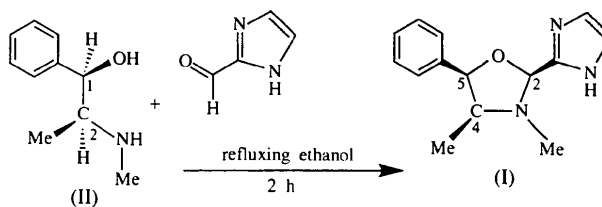
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Abstract

The title compound, $C_{14}H_{17}N_3O$, prepared from (1*R*,2*S*)-(–)-ephedrine, crystallizes in space group $P2_1$ with four molecules in the asymmetric unit. The molecules, in pairs, take part in intermolecular N—H...N hydrogen

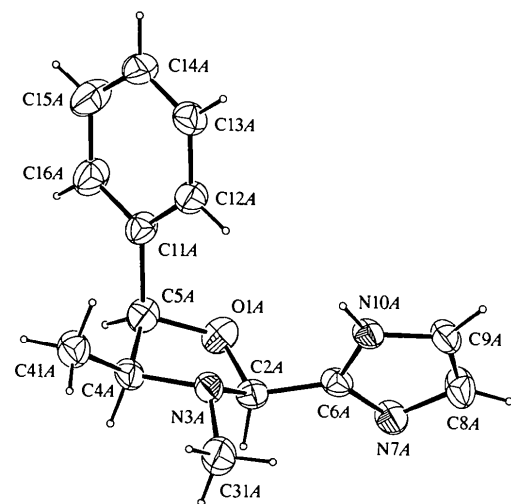
bonding between the imidazolyl rings, forming one-dimensional chains with alternating N...N distances of 2.866(3)/2.883(3) and 2.945(3)/2.956(3) Å. Inter-chain C_{arene}—H...π_{arene}, C_{arene}—H...O and C_{sp³}—H...π_{C=C} interactions generate a three-dimensional network.



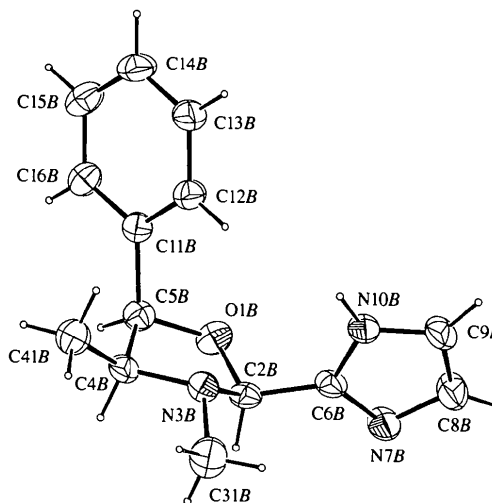
Comment

Amino acid derivatives continue to be an important class of chiral compounds with applications in asymmetric synthesis and catalysis. The title compound, (I), a derivative of (1*R*,2*S*)-(-)-ephedrine, (II), is of current interest as a chiral auxiliary.

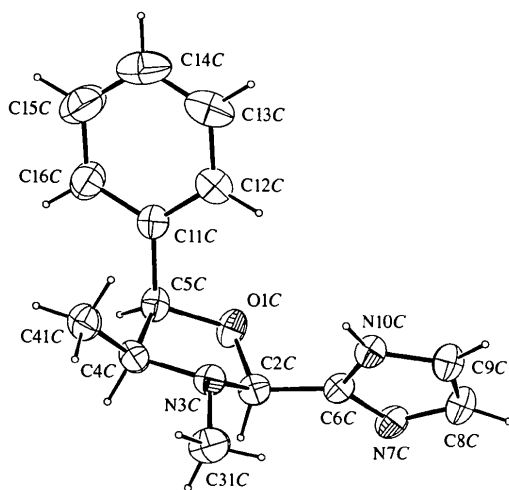
Compound (I) crystallizes in space group *P*2₁ with four independent molecules (*A*, *B*, *C* and *D*) in the asymmetric unit which differ slightly in conformation but retain the same 2*S*,4*S*,5*R* configuration in the 1,3-oxazolidine ring. The absolute structure can be de-



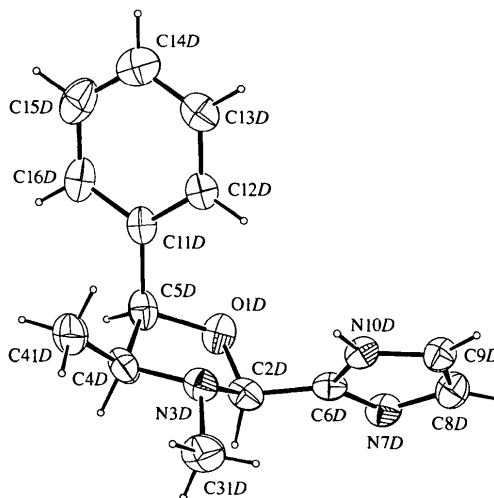
Molecule A



Molecule B



Molecule C



Molecule D

Fig. 1. Views of molecules A, B, C and D with the atomic numbering schemes. Displacement ellipsoids are drawn at the 30% probability level.

duced from the known absolute configuration of the (1*R*,2*S*)-(-)-ephedrine used in the synthesis. Views of the four molecules with the atomic numbering schemes are shown in Fig. 1. Bond lengths and angles are unexceptional and in accord with anticipated values (Orpen *et al.*, 1994). The oxazolidine rings adopt an envelope conformation, with N3 0.566 (3)–0.615 (3) Å from the O1/C2/C4/C5 plane. Torsion-angle differences in molecules *A*, *B*, *C* and *D* are evident from C4—C5—C11—C12, which has values of 57.9 (4), 61.0 (3), 83.3 (3) and 78.1 (3)°, respectively (Table 1). Examination of the structure with *PLATON* (Spek, 1997*a*) showed that there were no solvent-accessible voids in the crystal lattice.

A variety of intermolecular interactions are present in the structure of (I). Two distinct one-dimensional chains are formed in the *a*-axis direction comprising two alternating N—H···N hydrogen bonds each (Fig. 2). Inter-chain C_{sp³}—H···π_{C=C} (imidazole), C_{arene}—H···π_{arene} and C_{arene}—H···O interactions generate a three-dimensional network (Table 2) (C89*C* and C89*D* are the C8*C*/C9*C* and C8*D*/C9*D* double-bond centres; C44*C* and C44*D* are the phenyl-ring centroids of molecules *C* and *D*). We have previously noted the association of C—H···π_{arene} interactions in a calix[6]arene, where a polymeric self-inclusion process is observed (Böhmer *et al.*, 1994), and in a calix[5]arene, where a one-dimensional molecular zipper is formed (Gallagher

et al., 1994); the interesting crystal-packing effects are influenced largely by the C—H···π_{arene} interactions.

Crystal structures with more than one molecule in the asymmetric unit are not uncommon. In space group *P*2₁, there are 74 structures with *Z* = 8 from a total of 8101 (*R* factor < 0.10) in the April 1997 release (167 797 entries) of the Cambridge Structural Database (Allen *et al.*, 1991). The four independent molecules in 1-methyl-*N,N'*-bis(salicylidene)-2,4-phenylenediamine pack in pairs, forming herring-bone aromatic–aromatic contacts (Alcock *et al.*, 1996).

The rationalization of packing interactions in crystals with several independent molecules is difficult (Karthe *et al.*, 1993) due to the existence of dimers or oligomers in solution crystallizing to yield multiple formula units in the asymmetric unit (Desiraju, 1989). The concept of 'quasi-equivalence', where two or more 'quasi-equivalent' modes of interaction of a molecule with its neighbours are present and all participate in the crystal packing, can be used to explain the presence of crystallographically independent molecules where intermolecular interactions are prominent. In (I), the intricate interplay of the different hydrogen-bonding interactions presumably accounts for the observed presence of four molecules in the asymmetric unit. Further studies are in progress on related chiral molecules with a view to examining the hydrogen-bonding interactions.

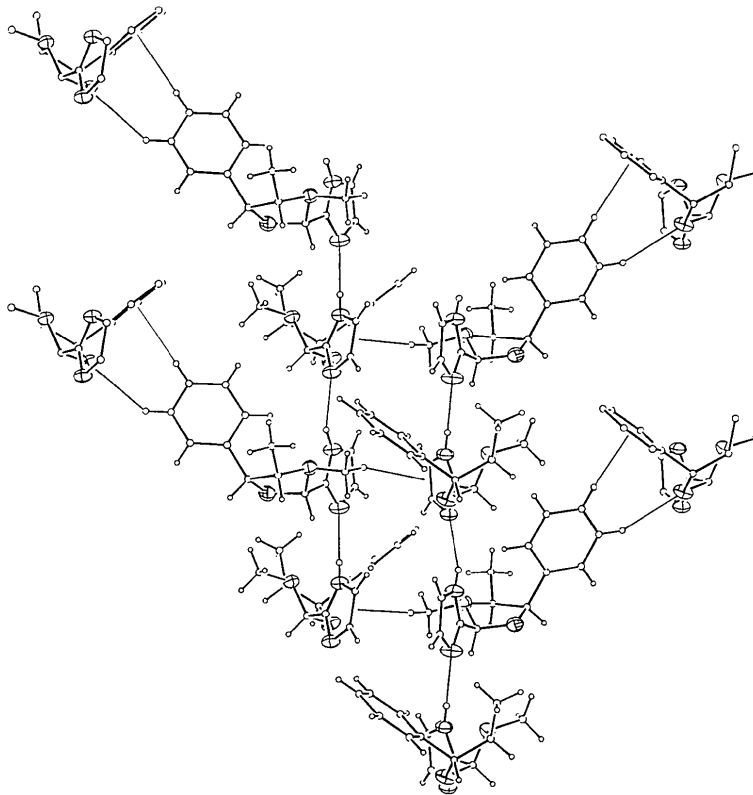


Fig. 2. A view of the intermolecular interactions in the crystal structure of (I).

Experimental

The title compound was prepared by refluxing imidazole-2-carboxaldehyde (0.96g, 0.01 mol) and (1*R*,2*S*)-(-)-ephedrine (1.65 g, 0.01 mol) in ethanol (20 ml) for 2 h. On cooling, the product was filtered and recrystallized from ethanol [2.1 g, 86%; m.p. 456–457 K, $[\alpha]_D^{20} = -85^\circ$ ($c = 1.0$, ethanol)].

Crystal data

C ₁₄ H ₁₇ N ₃ O	Mo <i>K</i> α radiation
<i>M_r</i> = 243.31	λ = 0.71073 Å
Monoclinic	Cell parameters from 25 reflections
<i>P</i> 2 ₁	<i>a</i> = 9.9403 (6) Å
	<i>b</i> = 25.4021 (14) Å
	<i>c</i> = 10.5870 (5) Å
	β = 91.808 (5)°
	<i>V</i> = 2671.9 (3) Å ³
<i>Z</i> = 8	Block
<i>D_x</i> = 1.210 Mg m ⁻³	0.45 × 0.25 × 0.25 mm
<i>D_m</i> not measured	Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> _{int} = 0.008
ω–2θ scans	θ _{max} = 27.0°
Absorption correction: none	<i>h</i> = –12 → 12
6273 measured reflections	<i>k</i> = 0 → 32
5953 independent reflections	<i>l</i> = 0 → 13
4034 reflections with <i>I</i> > 2σ(<i>I</i>)	3 standard reflections
	frequency: 120 min
	intensity decay: 2.0%

Refinement

Refinement on <i>F</i> ²	Δρ _{max} = 0.14 e Å ⁻³
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.038	Δρ _{min} = –0.13 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.088	Extinction correction: <i>SHELXL97</i>
<i>S</i> = 1.009	Extinction coefficient: 0.0132 (9)
5953 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
650 parameters	
H atoms constrained	
<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0484 <i>P</i>) ²]	
where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3	
(Δ/σ) _{max} = 0.001	

Table 1. Selected torsion angles (°)

O1A—C2A—C6A—N10A	85.0 (3)
O1B—C2B—C6B—N10B	77.6 (3)
O1C—C2C—C6C—N10C	90.0 (3)
O1D—C2D—C6D—N10D	98.1 (3)
O1A—C5A—C11A—C16A	119.6 (3)
O1B—C5B—C11B—C16B	122.6 (3)
O1C—C5C—C11C—C16C	145.7 (3)
O1D—C5D—C11D—C16D	138.4 (2)

Table 2. Hydrogen-bonding geometry (Å, °)

C89C and C89D are the C8C/C9C and C8D/C9D double-bond centres; C44C and C44D are the phenyl-ring centroids of molecules *C* and *D*.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N10A—H10A...N7C ⁱ	0.86	2.18	2.956 (3)	151
N10B—H10B...N7D ⁱ	0.86	2.09	2.883 (3)	153
N10C—H10C...N7A	0.86	2.10	2.945 (3)	166
N10D—H10D...N7B	0.86	2.03	2.866 (3)	165
C31B—H31E...C89C	0.96	2.75	3.695 (4)	170

C31A—H31B...C89D ⁱ	0.96	2.94	3.845 (4)	158
C14A—H14A...C44C ⁱⁱ	0.93	2.72	3.629 (4)	167
C15A—H15A...O1C ⁱⁱ	0.93	3.02	3.766 (4)	138
C14B—H14B...C44D ⁱⁱⁱ	0.93	2.58	3.509 (4)	174
C15B—H15B...O1D ⁱⁱⁱ	0.93	2.72	3.590 (4)	156

Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) 1 + *x*, *y*, 1 + *z*; (iii) 1 + *x*, *y*, *z* – 1.

Compound (I), which is chiral, crystallized in the monoclinic system in space group *P*2₁ or *P*2₁/*m* from the systematic absences, with *P*2₁ confirmed by the analysis. H atoms were allowed for as riding atoms, with C—H distances in the range 0.93–0.98 Å, and N—H distances of 0.86 Å. A full 'Friedel' data set for this structure was not collected because the anomalous dispersion terms for O, N and C are so small. The absolute structure was not determined [Flack (1983) parameter = –0.1 (11)] by our X-ray analysis, but can be inferred from the known absolute configuration of the (1*R*,2*S*)-(-)-ephedrine starting material used in the synthesis.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD2* in *NRCVAX96* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*). Program(s) used to refine structure: *NRCVAX96* and *SHELXL97* (Sheldrick, 1997*b*). Molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976), *PLATON* (Spek, 1997*a*) and *PLUTON* (Spek, 1997*b*). Software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *WordPerfect* macro *PRPCIF97* (Ferguson, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1179). Services for accessing these data are described at the back of the journal. Two views showing details of the hydrogen-bonding interactions have also been deposited.

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Conformational Variations in Vinylsulfoximines

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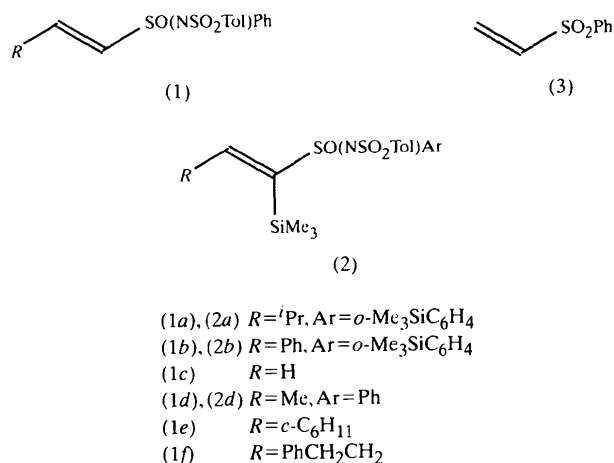
Abstract

In a series of vinylsulfoximines {*S*-ethenyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximide [(1*c*); C₁₅H₁₅NO₃S₂], (*E*)-*S*-phenyl-*S*-(prop-1-enyl)-*N*-(*p*-tolylsulfonyl)sulfoximide [(1*d*); C₁₆H₁₇NO₃S₂], (*E*)-*S*-(2-cyclohexylethenyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximide [(1*e*); C₂₁H₂₅NO₃S₂], (*E*)-*S*-phenyl-*S*-(4-phenylbut-1-enyl)-*N*-(*p*-tolylsulfonyl)sulfoximide [(1*f*); C₂₃H₂₃NO₃S₂], (*E*)-*S*-(3-methyl-1-trimethylsilylbut-1-enyl)-*N*-(*p*-tolylsulfonyl)-*S*-(2-trimethylsilylphenyl)sulfoximide [(2*a*); C₂₄H₃₇NO₃S₂-Si₂], (*E*)-*S*-(2-phenyl-1-trimethylsilylethenyl)-*N*-(*p*-tolylsulfonyl)-*S*-(2-trimethylsilylphenyl)sulfoximide [(2*b*); C₂₇H₃₅NO₃S₂Si₂], (*E*)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)-*S*-(1-trimethylsilylprop-1-enyl)sulfoximide [(2*d*); C₁₉H₂₅NO₃-S₂Si]} and in phenyl vinyl sulfone [(3); C₈H₈O₂S], the vinyl double bond is found to be approximately *syn*-coplanar with either the S=O or the S=N bond, the preference between these two being correlated in most cases with the size of the terminal vinyl substituent. Addition of trimethylsilyl groups at the α position of the vinyl group, and in the *ortho* position of the phenyl substituent on S, introduces further steric constraints, so that the substituted phenyl group becomes *syn*-coplanar with the vinyl double bond. The observed

conformations may also be preferred in solution, as they are consistent with the observed diastereoselectivity of addition reactions of vinylsulfoximines.

Comment

The sulfoximine group has been used as a chiral equivalent of the sulfone group in order to control the stereochemical outcome of reactions (Pyne, 1992, and references therein). Specifically, the role of the sulfoximine group in controlling the diastereoselectivity of addition reactions to vinylsulfoximines has been explored, since these compounds are chiral equivalents of the synthetically useful vinyl sulfones. The outcome of conjugate addition reactions (*e.g.* Pyne, 1986*a,b*; Bailey *et al.*, 1993; Jackson *et al.*, 1996) and cycloaddition reactions (Glass *et al.*, 1984; David *et al.*, 1995) of vinyl sulfones has been studied. While the stereochemical outcome of these reactions clearly depends on, amongst other factors, the conformational preferences of the vinylsulfoximine group in solution, studies of the solid-state conformations can yield useful data. Thus, we have already reported on the structure of the vinylsulfoximine (1*a*) (Bailey *et al.*, 1993), in which the C=C and S=N bonds are approximately *syn*-coplanar. This is in contrast to the analogous vinylsulfoximine (1*b*) (Dang *et al.*, 1993), in which the C=C and S=O bonds are essentially coplanar. We report here the single-crystal X-ray structure analysis of a series of four additional vinylsulfoximines, (1*c*)–(1*f*), and three α -silylvinylsulfoximines, (2*a*), (2*b*) and (2*d*), with a view to establishing the conformational trends that exist. For the purpose of comparison, we also present the structure of phenyl vinyl sulfone, (3), as the archetypal vinyl sulfone.



The key structural feature of the vinyl sulfone, (3) (Fig. 1), is that the C=C and one of the S=O bonds are almost *syn*-coplanar [the C=C–S=O torsion angles are 4.85 (18) and –125.14 (16)°]. This may reflect the fact that the O atom is the smaller group at the S,