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) Å
b = 6.488 (3) Å
c = 7.180 (4) Å
β = 96.68 (2)°
V = 928.8 (9) Å^3
Z = 4
D_x = 1.453 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 15.8–19.5°
μ = 0.100 mm^{-1}
T = 296 K
Plate
0.5 × 0.5 × 0.1 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_{int} = 0.059
θ_{max} = 27.5°
$h = -25 \rightarrow 25$
$k = -8 \rightarrow 0$
$l = 0 \rightarrow 9$
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
$w = 4F_o^2/\sigma^2(F_o^2)$

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

Table 1. *Selected geometric parameters (Å, °)*

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 (Å, °)*

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: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC 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: *ORTEP*II (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.

References

Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lapin, I. P. & Politi, V. (1993). *Pharmacol. Res.* **28**, 129–134.

Martin, D. W., Mayes, P. A. & Rodwell, V. W. (1983). *Harper's Review of Biochemistry*, 19th ed., pp. 301–302. Tokyo: Marzen Asia.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Moroni, F., Russi, P., Carla, V., De Luca, G. & Politi, V. (1991). *Adv. Exp. Med. Biol.* **294**, 299–308.

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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···$\pi_{C=C}$ Interactions

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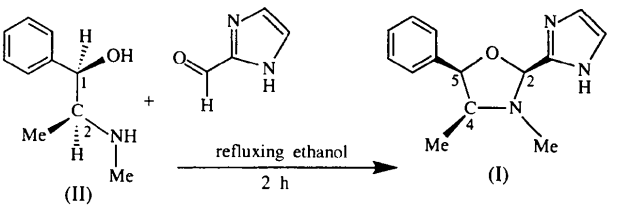
Abstract

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

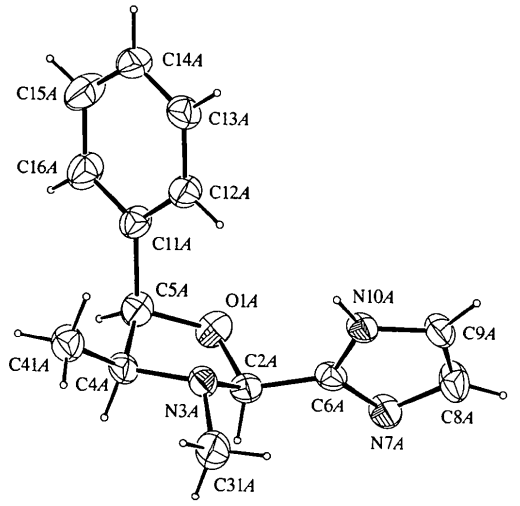
bonding between the imidazolyl rings, forming one-dimensional chains with alternating N···N distances of 2.866 (3)/2.883(3) and 2.945 (3)/2.956(3) Å. Inter-chain C_{arene}—H···π_{arene}, C_{arene}—H···O and C_{sp^3}—H···$\pi_{C=C}$ interactions generate a three-dimensional network.



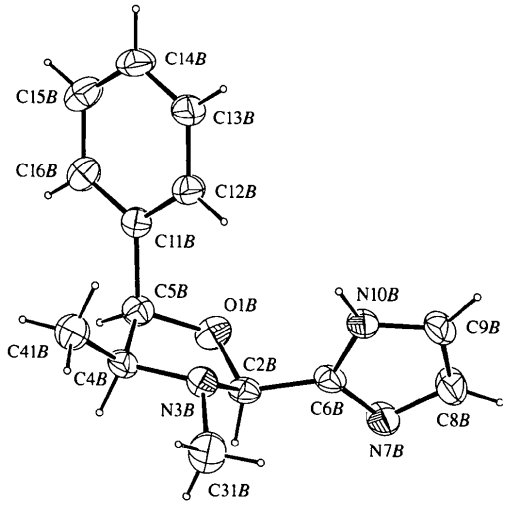
Comment

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.

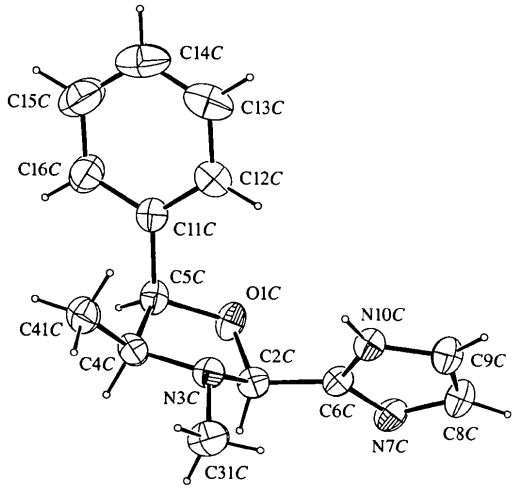
Compound (I) crystallizes in space group $P2_1$ with four independent molecules (*A*, *B*, *C* and *D*) in the asymmetric unit which differ slightly in conformation but retain the same 2*S*,4*S*,5*R* configuration in the 1,3-oxazolidine ring. The absolute structure can be de-



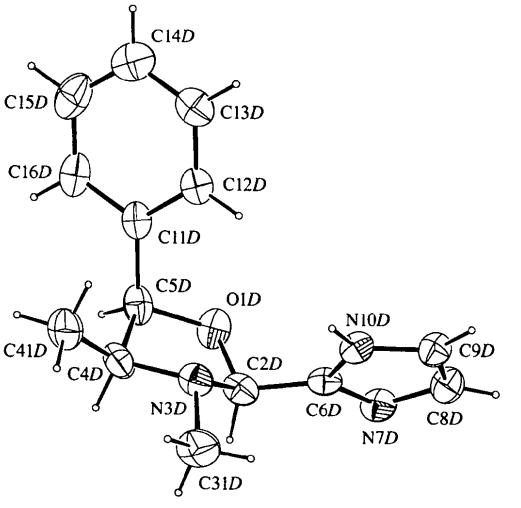
Molecule *A*



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_{sp^3}—H···$\pi_{C=C}$(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 $P2_1$, 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.

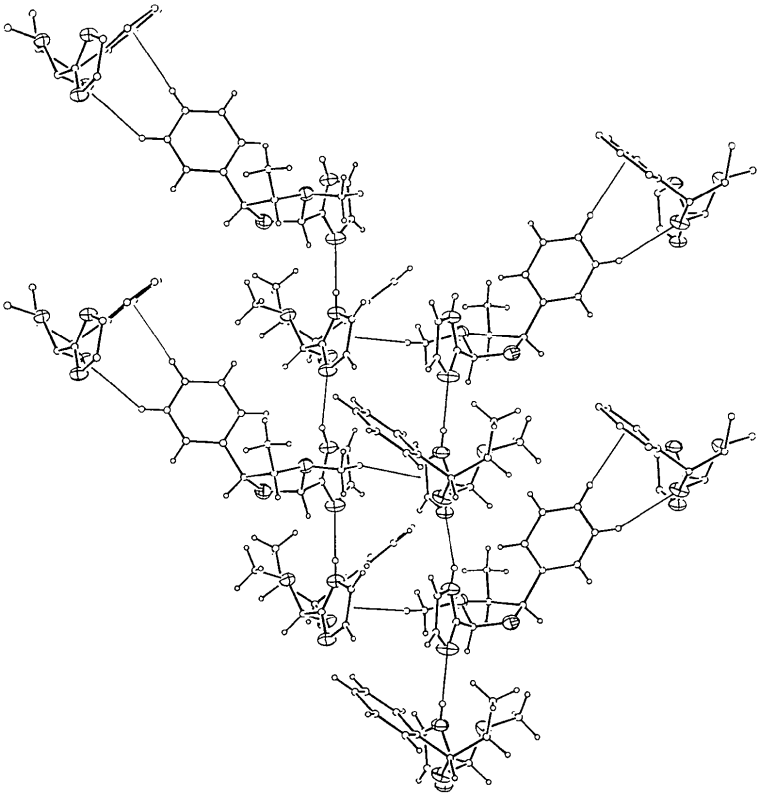


Fig. 2. A view of the intermolecular interactions in the crystal structure of (I).

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, $[\alpha]_D^{20} = -85°$ (c = 1.0, ethanol)].

Crystal data

$C_{14}H_{17}N_3O$
M_r = 243.31
Monoclinic
$P2_1$
a = 9.9403 (6) Å
b = 25.4021 (14) Å
c = 10.5870 (5) Å
β = 91.808 (5)°
V = 2671.9 (3) Å^3
Z = 8
D_x = 1.210 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9.68–19.27°
μ = 0.079 mm^{-1}
T = 294 (1) K
Block
0.45 × 0.25 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
6273 measured reflections
5953 independent reflections
4034 reflections with $I > 2\sigma(I)$
R_{int} = 0.008
θ_{max} = 27.0°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 32$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.088
S = 1.009
5953 reflections
650 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0132 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected torsion angles (°)*

O1*A*—C2*A*—C6*A*—N10*A*	85.0 (3)
O1*B*—C2*B*—C6*B*—N10*B*	77.6 (3)
O1*C*—C2*C*—C6*C*—N10*C*	90.0 (3)
O1*D*—C2*D*—C6*D*—N10*D*	98.1 (3)
O1*A*—C5*A*—C11*A*—C16*A*	119.6 (3)
O1*B*—C5*B*—C11*B*—C16*B*	122.6 (3)
O1*C*—C5*C*—C11*C*—C16*C*	145.7 (3)
O1*D*—C5*D*—C11*D*—C16*D*	138.4 (2)

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

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*.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10*A*—H10*A*···N7*C*^{i}	0.86	2.18	2.956 (3)	151
N10*B*—H10*B*···N7*D*^{i}	0.86	2.09	2.883 (3)	153
N10*C*—H10*C*···N7*A*	0.86	2.10	2.945 (3)	166
N10*D*—H10*D*···N7*B*	0.86	2.03	2.866 (3)	165
C31*B*—H31E···C89*C*	0.96	2.75	3.695 (4)	170
C31*A*—H31*B*···C89*D*^{i}	0.96	2.94	3.845 (4)	158
C14*A*—H14*A*···C44*C*^{ii}	0.93	2.72	3.629 (4)	167
C15*A*—H15*A*···O1*C*^{ii}	0.93	3.02	3.766 (4)	138
C14*B*—H14*B*···C44*D*^{iii}	0.93	2.58	3.509 (4)	174
C15*B*—H15*B*···O1*D*^{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 $P2_1$ or $P2_1/m$ from the systematic absences, with $P2_1$ 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: *SET*4 and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1997*a*) and *PLUTON* (Spek, 1997*b*). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PRPCIF*97 (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.

References

Alcock, N. W., Clase, H. J., Willey, G. R. & Daly, L. T. (1996). *Acta Cryst.* C**52**, 2340–2343.
Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.
Böhmer, V., Kraft, D., Vogt, W., Ferguson, G. & Gallagher, J. F. (1994). *J. Chem. Soc. Perkin Trans.* 1, pp. 1221–1230.
Desiraju, G. R. (1989). In *Materials Science Monographs*, Vol. 54, *Crystal Engineering, The Design of Organic Solids*. Amsterdam: Elsevier.
Enraf–Nonius (1992). *CAD-4-PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Ferguson, G. (1997). *PRPCIF*97. *A WordPerfect*-5.1 *Macro to Merge and Polish CIF Format Files from NRCVAX*96 *and SHELXL*97 *Programs*. University of Guelph, Canada.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Gallagher, J. F., Ferguson, G., Böhmer, V. & Kraft, D. (1994). *Acta Cryst.* C**50**, 73–77.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Karthe, P., Sadasivan, C. & Gautham, N. (1993). *Acta Cryst.* B**49**, 1069–1071.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1994). *Structure Correlation*, Vol. 2, edited by H.-B. Bürgi & J. D. Dunitz, Appendix A. Weinheim, Germany: VCH Publishers.
Sheldrick, G. M. (1997*a*). *SHELXS97. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1997*a*). *PLATON. Molecular Geometry Program.* Version of May 1997. University of Utrecht, The Netherlands.
Spek, A. L. (1997*b*). *PLUTON. Molecular Graphics Program.* Version of May 1997. University of Utrecht, The Netherlands.

Acta Cryst. (1998). C**54**, 1335–1341

Conformational Variations in Vinylsulfoximines

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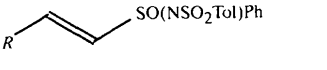
Abstract

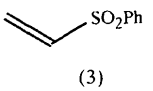
In a series of vinylsulfoximines {*S*-ethenyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximide [(1*c*); $C_{15}H_{15}NO_3S_2$], (*E*)-*S*-phenyl-*S*-(prop-1-enyl)-*N*-(*p*-tolylsulfonyl)sulfoximide [(1*d*); $C_{16}H_{17}NO_3S_2$], (*E*)-*S*-(2-cyclohexylethenyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximide [(1*e*); $C_{21}H_{25}NO_3S_2$], (*E*)-*S*-phenyl-*S*-(4-phenylbut-1-enyl)-*N*-(*p*-tolylsulfonyl)sulfoximide [(1*f*); $C_{23}H_{23}NO_3S_2$], (*E*)-*S*-(3-methyl-1-trimethylsilylbut-1-enyl)-*N*-(*p*-tolylsulfonyl)-*S*-(2-trimethylsilylphenyl)sulfoximide [(2*a*); $C_{24}H_{37}NO_3S_2Si_2$], (*E*)-*S*-(2-phenyl-1-trimethylsilylethenyl)-*N*-(*p*-tolylsulfonyl)-*S*-(2-trimethylsilylphenyl)sulfoximide [(2*b*); $C_{27}H_{35}NO_3S_2Si_2$], (*E*)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)-*S*-(1-trimethylsilylprop-1-enyl)sulfoximide [(2*d*); $C_{19}H_{25}NO_3S_2Si$]} and in phenyl vinyl sulfone [(3); $C_8H_8O_2S$], 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

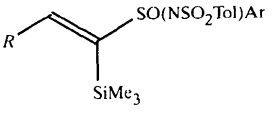
The sulfoximine group has been used as a chiral equivalent of the sulfone group in order to control the stereochemical outcome of reactions (Pyne, 1992, and references therein). Specifically, the role of the sulfoximine group in controlling the diastereoselectivity of addition reactions to vinylsulfoximines 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.



(1)



(3)



(2)

(1*a*), (2*a*) $R = {}^{i}Pr$, Ar = *o*-$Me_3SiC_6H_4$
(1*b*), (2*b*) R = Ph, Ar = *o*-$Me_3SiC_6H_4$
(1*c*) R = H
(1*d*), (2*d*) R = Me, Ar = Ph
(1*e*) $R = c$-C_6H_{11}
(1*f*) $R = PhCH_2CH_2$

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,