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

C₁₂H₁₀N₂O
Mᵣ = 203.20
Monoclinic
P₂₁/c
a = 20.074 (2) Å
b = 6.488 (3) Å
\( \gamma = 96.68^\circ \)
\( \beta = 928.8 (9) \) Å
Z = 4
\( D_x = 1.453 \) Mg m⁻³

Data collection

Rigaku AFC-5R diffractometer
w-2θ scans
2513 measured reflections
2334 independent reflections
1376 reflections with I > 2σ(I)
R(int) = 0.059
θ(max) = 27.5°
θ = -25 to 25
k = -8 to 0
l = 0 to 9

Refinement

Refinement on F²
R(F) = 0.059
wR(F²) = 0.120
S = 1.66
1376 reflections
148 parameters
H atoms: see below
w = 4F²/σ²(F²)

Selected geometric parameters (Å, °)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1--C11</td>
<td>1.368 (3)</td>
<td>C3--C10</td>
</tr>
<tr>
<td>O2--C12</td>
<td>1.213 (3)</td>
<td>C10--C11</td>
</tr>
<tr>
<td>C3--C13</td>
<td>1.317 (3)</td>
<td>C11--C12</td>
</tr>
<tr>
<td>C2--C3--C10</td>
<td>126.5 (3)</td>
<td>O1--C11--C10</td>
</tr>
<tr>
<td>C9--C3--C10</td>
<td>126.6 (3)</td>
<td>C10--C11--C12</td>
</tr>
<tr>
<td>C3--C10--C11</td>
<td>126.3 (3)</td>
<td>O2--C12--O3</td>
</tr>
</tbody>
</table>

Hydrogen-bonding geometry (Å, °)

<table>
<thead>
<tr>
<th>Bond</th>
<th>D···A</th>
<th>D···H</th>
<th>H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2--H3···O2'</td>
<td>0.96 (4)</td>
<td>1.80 (4)</td>
<td>2.760 (3)</td>
</tr>
<tr>
<td>O1--H1···O2''</td>
<td>0.88 (3)</td>
<td>1.97 (4)</td>
<td>2.727 (3)</td>
</tr>
</tbody>
</table>

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 anisotropically because of the low data/parameter ratio; others were fixed at calculated positions.


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


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


N···H···N Hydrogen Bonding in the Four Independent Molecules of (2S,4S,5R)-(-)-2-(1H-Imidazol-2-yl)-3,4-dimethyl-5-phenyl-1,3-oxazolidine, with UtaH···N H...O and C···HN and C···πC=C=C Interactions

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(Received 16 January 1998; accepted 16 March 1998)

Abstract

The title compound, C₁₄H₁₇N₅O, prepared from (1R,2S)-(-)-ephedrine, crystallizes in space group P2₁ with four molecules in the asymmetric unit. The molecules, in pairs, take part in intermolecular N···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_aren−H···π_aren, C_aren−H···O and C_sp3−H···π_C=O 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 (1R,2S)-(−)-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 2S,4S,5R configuration in the 1,3-oxazolidine ring. The absolute structure can be de-
duced from the known absolute configuration of the (1R,2S)-(−)-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, 1997a) 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 Csp3—H⋯π(arene) and Csp3—H⋯π(arene) interactions generate a three-dimensional network (Table 2) (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). 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 (0.96 g, 0.01 mol) and (1R,2S)-(-)-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, \([\alpha]D^2 = -85^\circ\) (c = 1.0, ethanol)].

Crystal data

\(\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}\)

Mo K\(\alpha\) radiation

\(\lambda = 0.71073\) Å

Cell parameters from 25 reflections

\(a = 9.9403\) (6) Å,
\(b = 10.5870\) (5) Å,
\(\beta = 91.808\) (5)°

\(V = 2671.9\) (3) Å\(^3\)

\(Z = 8\)

Colorless

\(D_m = 1.210\) Mg m\(^{-3}\)

Crystallography

Data collection

Enraf-Nonius CAD-4 diffractometer

\(\omega\)-2\(\phi\) scans

Absorption correction: none

6273 measured reflections

5953 independent reflections

Extinction correction:

\(R_{	ext{int}} = 0.008\)

\(\theta_{\text{max}} = 27.0^\circ\)

\(h = -12 \rightarrow 12\)

\(k = 0 \rightarrow 32\)

\(l = 0 \rightarrow 13\)

3 standard reflections

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 independent reflections

650 parameters

H atoms constrained

\(w = 1/[\sigma^2(F^2) + (0.0484P)^2]\)

where \(P = (F^2 + 2F^2)/3\)

\((\Delta/\sigma)_{\text{max}} = 0.001\)

Table 1. Selected torsion angles (°)

<p>| | | | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>01A-C2A-C6A-N10A</td>
<td>85.0 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>01B-C2B-C6B-N10B</td>
<td>77.6 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>01C-C2C-C6C-N10C</td>
<td>90.0 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>01D-C2D-C6D-N10D</td>
<td>98.1 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>01A-C5A-C11A-C16A</td>
<td>119.6 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>01B-C5B-C11B-C16B</td>
<td>122.5 (3)</td>
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<td></td>
</tr>
<tr>
<td>01C-C5C-C11C-C16C</td>
<td>145.7 (3)</td>
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<tr>
<td>01D-C5D-C11D-C16D</td>
<td>138.4 (2)</td>
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</tr>
</tbody>
</table>

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

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C89C and C89D are the phenyl-ring centroids of molecules C and D.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C31B-H31E-C89C</td>
<td>0.96</td>
<td>2.75</td>
<td>3.695 (4)</td>
<td>170</td>
</tr>
<tr>
<td>C14A-H14A-C44A</td>
<td>0.93</td>
<td>2.72</td>
<td>3.629 (4)</td>
<td>167</td>
</tr>
<tr>
<td>C15A-H15A-O11A</td>
<td>0.93</td>
<td>3.02</td>
<td>3.766 (4)</td>
<td>138</td>
</tr>
<tr>
<td>C14B-H14B-C44B</td>
<td>0.93</td>
<td>2.58</td>
<td>3.509 (4)</td>
<td>174</td>
</tr>
<tr>
<td>C15B-H15B-O11B</td>
<td>0.93</td>
<td>2.72</td>
<td>3.590 (4)</td>
<td>156</td>
</tr>
</tbody>
</table>

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 (1R,2S)-(-)-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: DATRD4 in NRCVAX96 (Gabe et al., 1989).

Program(s) used to solve structure: SHELX97 (Sheldrick, 1997a). Program(s) used to refine structure: NRCVAX96 and SHELXL97 (Sheldrick, 1997b). Molecular graphics: NRCVAX96, ORTEPII (Johnson, 1976), PLATON (Spek, 1997a) and PLUTON (Spek, 1997b). Software used to prepare material for publication: NRCVAX96, SHELXL97 and WordPerfect macro PRPCIF97 (Ferguson, 1997).

JFG thanks the Research and Postgraduate Committee of Dublin City University, the Royal Irish Academy and Forbairt for generous funding of a research visit to the University of Guelph (June–August, 1997) and especially Professor George Ferguson for use of his diffractometer and computer system.

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


Conformational Variations in Vinylsulfoximines

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(Received 12 December 1997; accepted 24 March 1998)

Abstract

In a series of vinylsulfoximines {S-ethenyl-S-phenyl-N-(p-tolylsulfonyl)sulfoximide [(1c)]; C15H15NO3S2}, (E)-S-phenyl-S-(prop-1-enyl)-N-(p-tolylsulfonyl)sulfoximide [(1d)]; C16H17NO3S2], (E)-S-(2-cyclohexylethenyl)-S-phenyl-N-(p-tolylsulfonyl)sulfoximide [(1e)]; C21H25NO3S2}, (E)-S-(4-phenylbut-1-enyl)-N-(p-tolylsulfonyl)sulfoximide [(1f)]; C23H23NO3S2], (E)-S-(3-methyl-1-trimethylsilylbut-1-enyl)-N-(p-tolylsulfonyl)-S-(2-trimethylsilylphenyl)sulfoximide [(2a)]; C24H33NO3S2], (E)-S-(2-phenyl-1-trimethylsilylethenyl)-N-(p-tolylsulfonyl)-S-(2-trimethylsilylphenyl)sulfoximide [(2b)]; C27H35NO3S2], (E)-S-phenyl-N-(p-tolylsulfonyl)-S-(1-trimethylsilylprop-1-enyl)sulfoximide [(2d)]; C19H25NO3S2], 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, 1986a,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 (1a) (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 (1b) (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, (1c)–(1f), and three α-silylvinylnsulfoximines, (2a), (2b) and (2d), 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 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,