Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.106$
$S = 1.019$
7782 reflections
441 parameters
H-atom treatment mixed (see below)
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 1.0P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.248$ e Å^{-3}
$\Delta\rho_{\min} = -0.230$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Preliminary examination and data collection were performed using a Siemens CCD automated single-crystal X-ray diffractometer, using graphite-monochromated Mo $K\alpha$ radiation. Intensity data were collected using ω scans and a double-pass method was used to avoid spurious peaks. The first 50 frames of data were recollected at the end of the data collection to monitor crystal decay. No absorption corrections were applied to the data. Non-H atoms were refined anisotropically to convergence. Only the H atoms connected to C5 and C6 in the case of (6*b*) were refined freely. Other H atoms were treated as riding [$U_{iso}(H) = 1.2U_{eq}(C)$ and C—H = 0.95 Å].

For all compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1995); program(s) used to refine structures: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1078). Services for accessing these data are described at the back of the journal.

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2-[(Z)-2-(*p*-Anisidino)-3,3,3-trifluoropropenyl]-4,4-dimethyl-2-oxazoline

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Abstract

The title compound, $C_{15}H_{17}F_3N_2O_2$, is a C-protected N-substituted β-enamino acid derivative. Bond lengths suggest π conjugation between the oxazoline (4,5-dihydro-1,3-oxazole) ring and the enamine double-bond moiety. Intramolecular hydrogen bonding is found between the N atom attached to the aromatic ring and the heterocyclic N atom. Because of steric hindrance between the aromatic ring and the trifluoromethyl group, the plane of the former adopts an almost perpendicular position with respect to the oxazoline ring plane.

Comment

Acyclic β-enamino acid derivatives (Bartoli *et al.*, 1995) have been used frequently as intermediates in the synthesis of natural products and other synthetic compounds possessing biological activity. They are regarded as important building blocks in the synthesis of alkaloids (Cook *et al.*, 1994), β-amino acids and β-lactams (Bartoli *et al.*, 1994), among others, and they have also been applied with success in asymmetric syntheses (Potin *et al.*, 1990; Ando *et al.*, 1994). Furthermore, if such compounds contain F atoms, they are even more attractive for use in the fields of medicinal

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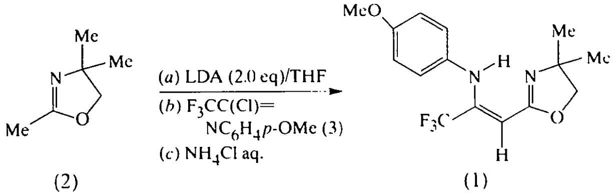
and agricultural chemistry due to the unique properties that organofluorinated compounds present (Tamura *et al.*, 1993; Huang & Yuang, 1995).

As a consequence of our interest in the preparation of masked β-enamino acid derivatives, we have recently developed an easy route to this type of compound by reaction of azaenolates of 2-alkyl-2-oxazolines with nitriles (Díaz *et al.*, 1992) and imidoyl chlorides (Fustero *et al.*, 1996). Related to these studies, we present here the first report of a structure of a masked β-enamino acid derivative containing a trifluoromethyl group, namely the title compound, (1).



(2) (1)

The structure consists of an oxazoline ring and an aromatic ring connected by an N—C=C chain containing a trifluoromethyl group. Bonds distances and angles are in agreement with those of other oxazoline and aromatic structures (Bell *et al.*, 1985; Eng-Wilmot & van der Helm, 1980). With respect to the plane through the oxazoline ring, the atomic displacements are of the order of 10^{-2} Å, indicating near planarity. Near planarity is also observed for the N1—C3—C5—C6—N2···H1 cyclic system, where the atomic displacements are of the order of 10^{-3} Å. The dihedral angle between these planes is 2.0 (1)°, as a result of an intramolecular hydrogen bond (Bürgi & Dunitz, 1994) between N1 and N2 (Table 2). The C6—C5 [1.441 (4) Å] and C5—C3 [1.340 (4) Å] distances suggest the formation of a π-delocalized system that extends to include the N2 atom. This bonding pattern is consistent with that proposed theoretically by Tang *et al.* (1990). The dihedral angle between the oxazole ring and the aromatic ring is 88.1 (1)°, indicating an *s-cis* disposition. The orientation of the trifluoromethyl substituent is determined by the weak intramolecular C5—H5···F3 interaction.

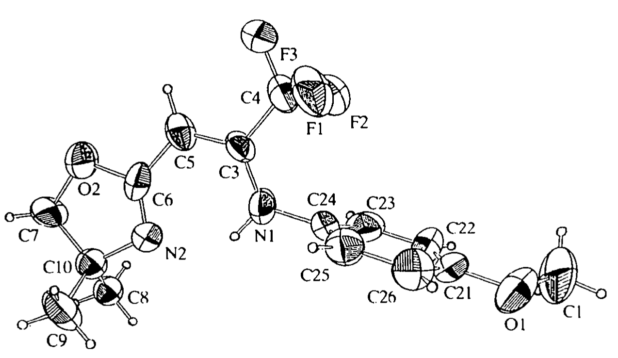


Fig. 1. View of (1) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small circles of arbitrary radii.

Experimental

The synthesis (see scheme above) was carried out according to the method of Tamura *et al.* (1993). To a stirred solution of lithium diisopropylamide (LDA) (10.0 mmol) in 15 ml of tetrahydrofuran (THF) at 351 K and under a nitrogen atmosphere, a solution of 2-methyl-2-oxazoline (5.0 mmol) in THF (15 ml) was slowly added. The resulting yellow solution was stirred at low temperature for 2 h and then *N*-(*p*-anisidino)-2,2,2-trifluoroacetimidoyl chloride, (3) (5.0 mmol), in THF (15 ml) was added dropwise. The mixture was stirred at low temperature for an additional hour (TLC) and then quenched with 30 ml of aqueous saturated NH_4Cl. The aqueous layer was extracted with CH_2Cl_2 (3 × 25 ml) and the combined organics were washed with brine. The organic layer was separated, dried with anhydrous $MgSO_4$ and filtered. Finally, the solvents were removed and the crude product purified by flash chromatography in silica gel, using a mixture of hexane–ethyl acetate (9:1) as eluent, to yield 1.2 g (77%) of a yellow solid identified as compound (1), which was recrystallized from hexane–chloroform (1:1).

Crystal data

$C_{15}H_{17}F_3N_2O_2$
$M_r = 314.31$
Monoclinic
$P2_1/n$
$a = 9.109\ (1)$ Å
$b = 10.740\ (2)$ Å
$c = 16.040\ (1)$ Å
$\beta = 99.0\ (1)°$
$V = 1549.9\ (3)$ Å^3
$Z = 4$
$D_x = 1.347$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4.56–11.41°$
$\mu = 0.114$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.23 × 0.19 × 0.17 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
5523 measured reflections
2665 independent reflections
1069 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.078$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 18$
3 standard reflections every 200 reflections intensity decay: 1.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.130$
$S = 0.878$
2665 reflections
206 parameters
H atoms: located (ΔF map)/calculated

$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.137$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.134$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

F1—C4	1.319 (4)	N1—C3	1.357 (4)
F2—C4	1.335 (4)	N1—C24	1.428 (4)
F3—C4	1.332 (4)	N2—C6	1.266 (4)
O1—C1	1.364 (5)	N2—C10	1.483 (4)
O1—C21	1.365 (4)	C3—C5	1.340 (4)
O2—C6	1.357 (3)	C5—C6	1.441 (4)
O2—C7	1.443 (4)		
C6—O2—C7	105.2 (3)	N2—C6—O2	118.3 (3)
C3—N1—C24	128.3 (2)	N2—C6—C5	127.1 (3)
C5—C3—N1	123.5 (3)	C22—C21—O1	124.9 (4)
C3—C5—C6	122.3 (3)	C23—C24—C25	119.1 (3)
C24—N1—C3—C5	−176.2 (3)	C3—C5—C6—O2	−179.4 (3)
N1—C3—C5—C6	0.5 (5)	C1—O1—C21—C22	15.0 (6)
C7—O2—C6—C5	176.4 (3)	C3—N1—C24—C25	91.3 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N2	0.86	2.05	2.728 (4)	135
C5—H5···F3	0.93	2.30	2.668 (4)	103

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *MolEN* (Fair, 1989). Data reduction: *PROCESS* in *MolEN*. Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976) in *MolEN*. Software used to prepare material for publication: *SHELXL*93. Computer facilities: University of Valencia.

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(±)-6,7-Dihydro-1,6,11-trimethyl-5*H*-dibenz[*c*,*e*]azepine

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Abstract

In the title compound, $C_{17}H_{19}N$, the central seven-membered azepine ring adopts a twisted-boat conformation. The molecule exhibits a huge deviation from planarity by rotation of the two fused *ortho*-methyl-substituted phenyl rings around the central C12—C14 single bond. The dihedral angle between the planes of these two rings amounts to 56.05 (4)°, with a *cisoid* arrangement around the C12—C14 bond. Because of this non-planarity, the molecule is axially chiral.

Comment

Dihydrodibenzazepine derivatives have been shown to be potent hypolipidemic agents in rodents; treatment with 6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine resulted in a reduction of the cholesterol, neutral lipid and triglyceride content in mouse and rat liver (Hall *et al.*, 1986). In addition, some of these compounds have been shown to be specific anti-epinephrine antagonists (Wenner, 1951). In the search for compounds related to such classes of