Acta Cryst. (1998). **C54**, 94–95

Ethyl (*E*)-2-Furyl-2-(hydroxyimino)acetate

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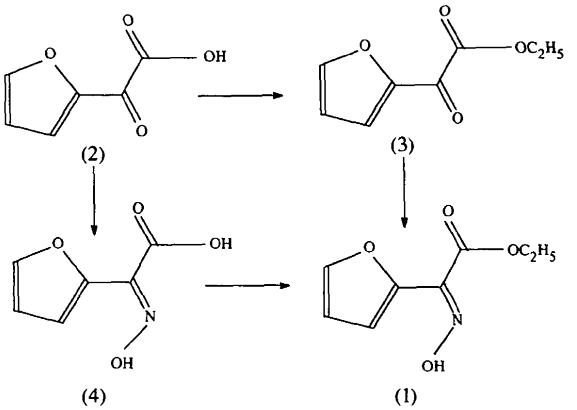
(*Received 9 April 1997; accepted 4 July 1997*)

Abstract

In the title compound, $C_8H_9NO_4$, the hydrogen bonds between the oxime O atoms and the N and O atoms of the neighbouring asymmetric unit result in the dimerization of the molecules, with $D\cdots A$ distances of 2.774 (3) and 3.144 (3) Å for O—H···N and O—H···O, respectively. The hydrogen-bridged centrosymmetric dimers are cross-linked *via* additional weaker intermolecular hydrogen bonds between the CH_3 group and the other O atom of the dimer, forming a polymeric network. The $D\cdots A$ distance of this second-order interaction (C—H···O) is 3.450 (2) Å. Structure analysis indicates that the oxime is in an *E* configuration. The whole molecule is planar, with a maximum deviation from the least-squares plane of 0.104 (2) Å.

Comment

Optically active α-amino acids constitute important materials in biology, medicine, biochemistry and chemistry. Many attempts have been made to develop an asymmetric synthesis of α-amino acids (Barrett, 1985; Williams, 1989). A new enantioselective synthesis of α-amino acids in which the key step is the enantioselective reduction of *E*- and *Z*-furyl ketone oxime ethers with chiral boron complexes has been reported (Demir, 1997). The chirality of the amino acid was fully controlled through the choice of the geometric isomer of the oxime. Using the same method, we tried to synthesize optically active furyl glycine starting from 2-(2-furyl)-2-(hydroxyimino)acetic acid ethyl ester, (1), *via* an enantioselective reduction of the C═N bond. As shown in the scheme below, compound (1) was synthesized starting from 2-(2-furyl)glyoxalic acid, (2), in two different ways. Conversion of (2) to 2-(2-furyl)glyoxalic acid ethyl ester, (3), and to (4) was performed using the literature method of Salolabals, Hillers & Latvijas (1964). The reaction of (3) with hydroxylamine hydrochloride in pyridine gave (1) in good yield. The esterification of (4) was carried out in ethanol in the presence of base.



The geometry of oxime (1) is very important, because the enantioselectivity of the reduction reaction depends on the geometry of the C═N bond. The reaction of an oxime with a known geometry makes it possible to suggest a mechanism for enantioselective reduction. With compound (1), it was not possible to determine the *E*/*Z* geometry of the oxime using spectroscopic methods, so an X-ray analysis was performed and determined that the oxime (1) is in an *E* configuration.

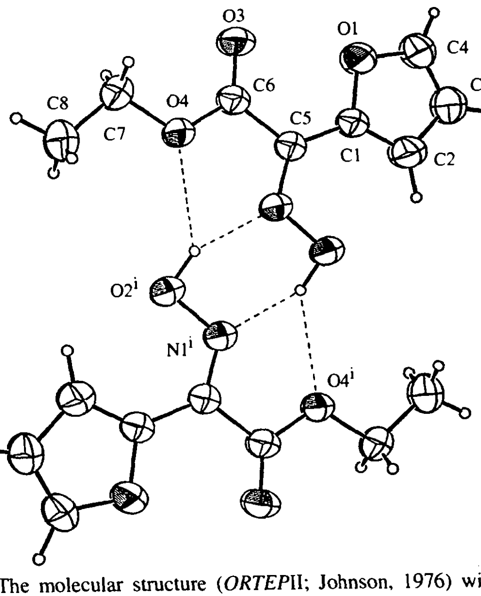


Fig. 1. The molecular structure (*ORTEP*II; Johnson, 1976) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii [symmetry code: (i) $1-x$, $-y$, $1-z$].

As shown in Fig. 1, compound (1) consists of hydrogen-bonded centrosymmetric dimers. The bifurcated hydrogen bond (O2—H2′···N1^{i} and O2—H2′···O4^{i}) within the dimer has $D\cdots A$ distances of 2.774 (3) and 3.144 (3) Å, respectively [symmetry code: (i) $1-x$, $-y$, $1-z$]. An additional weaker intermolecular hydrogen bond, C8—H81···O3^{ii}, crosslinks the dimers, so that a network of hydrogen bonds holds the structure together [symmetry code: (ii) $\frac{5}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$]. The $D\cdots A$ distance of this weaker interdimeric second-order interaction is longer [3.450 (2) Å] than the corresponding intradimeric distances. The furyl ring is planar with double-bond distances between C1═C2 [1.335 (5) Å] and C3═C4 [1.311 (6) Å]. The C5—N1 bond length is 1.289 (4) Å. A calculation of the least-squares plane through all non-H atoms shows that the molecule is basically planar with a maximum deviation of 0.104 (2) Å for O3. The torsion angles about the C═N bond are 2.0 (4) (O2—N1—C5—C1) and −178.4 (2)° (O2—N1—C5—C6). The bond angles around C5 range from 112.1 (3) to 126.0 (3)° and the sum of three bond angles is 360°.

Experimental

To the mixture of compound (3) (4.2 g, 25 mmol) and pyridine (3.95 g, 50 mmol) in ethanol (20 mmol), hydroxylamine hydrochloride (2.1 g, 30 mmol) was added. The mixture was stirred for 72 h at room temperature, and then H_2O (50 ml) was added. The mixture was extracted with ether (50 ml) and washed with 2 *M* HCl solution and brine, and dried over $MgSO_4$. Evaporation of the solvent gave a crude oil. Purification of the crude product by flash column chromatography (1:2 EtOAc/hexane) afforded 3.43 g (75%) of a colourless solid, which was crystallized from ethyl acetate (m.p. 345–346 K). IR(KBr): 3300–3220, 2980, 1750 cm^{-1}. ^1H NMR($CDCl_3$): δ 1.45 (*t*, 3H, *J* = 7 Hz, CH_3), 4.45 (*q*, 2H, *J* = 7 Hz, CH_2), 6.58 (*m*, 1H, C-4 H furan ring), 7.46 (*m*, 1H, C-3 H furan ring), 7.59 (*m*, 1H, C-5 H furan ring). Analysis: calculated for $C_8H_9NO_4$ (183.15), C 52.45, H 4.95, N 7.64%; found: C 52.66, H 5.12, N 7.58%.

Crystal data

$C_8H_9NO_4$
$M_r = 183.165$
Monoclinic
$P2_1/n$
$a = 4.4880$ (11) Å
$b = 11.4945$ (13) Å
$c = 16.6699$ (15) Å
$\beta = 92.868$ (3)°
$V = 858.9$ (3) Å^3
$Z = 4$
$D_x = 1.4164$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11.70$–21.13°
$\mu = 0.094$ mm^{-1}
$T = 295$ K
Prism
0.35 × 0.15 × 0.15 mm
Brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2439 measured reflections
2174 independent reflections
1168 reflections with $I > \sigma(I)$

$R_{\rm int} = 0.013$
$\theta_{\rm max} = 28.06°$
$h = -5 \rightarrow 0$
$k = -15 \rightarrow 0$
$l = -22 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: 1.24%

Refinement

Refinement on *F*
$R = 0.061$
$wR = 0.063$

$(\Delta/\sigma)_{\rm max} = 0.00011$
$\Delta\rho_{\rm max} = 0.201$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.334$ e Å^{-3}

$S = 0.91$
1168 reflections
118 parameters
H atoms riding, see below
$w = 1/[\sigma F^2 + (0.02F)^2 + 1.0]$, except $w = 0$ if $F^2 < \sigma(F^2)$

Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1—C1	1.366 (4)	C1—C2	1.335 (5)
O1—C4	1.361 (4)	C1—C5	1.449 (4)
O2—N1	1.384 (3)	C2—C3	1.410 (5)
O3—C6	1.187 (4)	C3—C4	1.311 (6)
O4—C6	1.326 (4)	C5—C6	1.509 (4)
O4—C7	1.459 (4)	C7—C8	1.492 (5)
N1—C5	1.289 (4)		
C1—O1—C4	106.6 (3)	N1—C5—C6	112.1 (3)
C6—O4—C7	116.7 (2)	C1—C5—C6	121.9 (3)
O2—N1—C5	114.8 (2)	O3—C6—C5	124.8 (3)
O1—C1—C5	118.3 (3)	O4—C6—C5	111.1 (3)
C2—C1—C5	133.3 (3)	O4—C7—C8	106.9 (3)
N1—C5—C1	126.0 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2′···O4$^{\rm i}$	0.949	2.374	3.144 (3)	137.9
O2—H2′···N1$^{\rm i}$	0.949	1.938	2.774 (3)	145.7
C8—H81···O3$^{\rm ii}$	0.960	2.543	3.450 (2)	157.2

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $\frac{5}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

H atoms were placed geometrically 0.95 Å from the parent atoms, except that of the hydroxyl group, which was located in a difference map. All H atoms were refined for a few cycles, except those on the furyl ring, and then a riding model was used for all H atoms, with $U_{\rm iso}({\rm H}) = 1.3U_{\rm eq}({\rm C,O})$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *MolEN* version of *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

The authors acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1113). Services for accessing these data are described at the back of the journal.

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