Refinement

Refinement on F^2
$R(F) = 0.030$
$wR(F^2) = 0.080$
$S = 1.13$
567 reflections
115 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + 0.0425F_o^2]$
$(\Delta/\sigma)_{\max} = 0.03$
$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXL*93 (Sheldrick, 1993)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.8168 (2)	0.4839	0.2696 (2)	0.038 (1)
O2	0.8653 (4)	−0.0586 (8)	0.0535 (2)	0.064 (1)
O3	1.0886 (3)	0.1174 (8)	0.1948 (2)	0.063 (1)
O4	0.7920 (3)	1.1446 (8)	0.5261 (2)	0.045 (1)
N1	0.9158 (4)	0.1098 (9)	0.1390 (2)	0.045 (1)
N2	0.8180 (3)	0.9223 (8)	0.4431 (2)	0.037 (1)
C1	0.6377 (4)	0.6235 (10)	0.2922 (2)	0.038 (1)
C2	0.4776 (4)	0.5279 (9)	0.2132 (3)	0.046 (1)
C3	0.5575 (4)	0.3163 (10)	0.1381 (3)	0.046 (1)
C4	0.7612 (4)	0.2999 (9)	0.1757 (2)	0.039 (1)
C5	0.6468 (4)	0.8476 (9)	0.3854 (3)	0.039 (1)

Table 2. *Selected geometric parameters* (Å, °)

O1—C4	1.347 (4)	N2—C5	1.272 (3)
O1—C1	1.366 (4)	C1—C2	1.358 (4)
O2—N1	1.230 (4)	C1—C5	1.441 (5)
O3—N1	1.224 (3)	C2—C3	1.397 (5)
O4—N2	1.382 (3)	C3—C4	1.348 (4)
N1—C4	1.413 (4)		
C4—O1—C1	104.8 (2)	O1—C1—C5	118.6 (2)
O3—N1—O2	124.0 (3)	C1—C2—C3	106.9 (3)
O3—N1—C4	118.9 (3)	C4—C3—C2	105.4 (3)
O2—N1—C4	117.0 (2)	O1—C4—C3	112.5 (3)
C5—N2—O4	111.8 (2)	O1—C4—N1	116.9 (2)
C2—C1—O1	110.4 (3)	C3—C4—N1	130.4 (3)
C2—C1—C5	130.9 (3)	N2—C5—C1	121.3 (3)

Computations were performed using the *SHELXL*93 package (Sheldrick, 1993).

One of us (VKB) is thankful to the Am. Crystallogr. Assoc./USNCCr Fund for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 1304–1306

5-Nitrofuran-2-aldoxime

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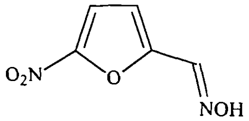
(*Received* 26 *May* 1994; *accepted* 15 *July* 1994)

Abstract

The molecules of the title compound, $C_5H_4N_2O_4$, are linked through hydrogen bonds. Chains along the [100] direction are observed.

Comment

The present compound is one of a large series of heterocyclic nitro compounds that are being analysed in an attempt to elucidate the underlying structural parameters required for bioactivity. Although the molecular structure and crystal packing of the compound have been discussed (Matsuoka *et al.*, 1991), no atomic coordinates were reported. As the coordinates are necessary for performing molecular fitting between analogues, the crystal structure has been re-analysed.



A perspective view showing the atomic numbering scheme and hydrogen bonds is given in Fig. 1. The crystal contains well ordered molecules of 5-nitro-2-aldoxime in the form observed in crystals of 5-nitro-2-furaldehyde semicarbazone (Olszak, Peeters, Blaton & De Ranter, 1994). The bond lengths are similar to within 0.025 Å. The title compound has a *cis* conformation while the one cited is *trans* with respect to the double bond of the side chain (C21=N22). A comparison with the bond lengths given by Matsuoka *et al.* (1991) for the title compound shows they are the same to within 0.019 Å for bonds involving non-H atoms.

The planar C3=C2—C21=N22 group of atoms does not show conjugation between the double bonds. A comparison of the bond lengths with those given by Allen *et al.* (1987) and Burke-Laing & Laing (1976)

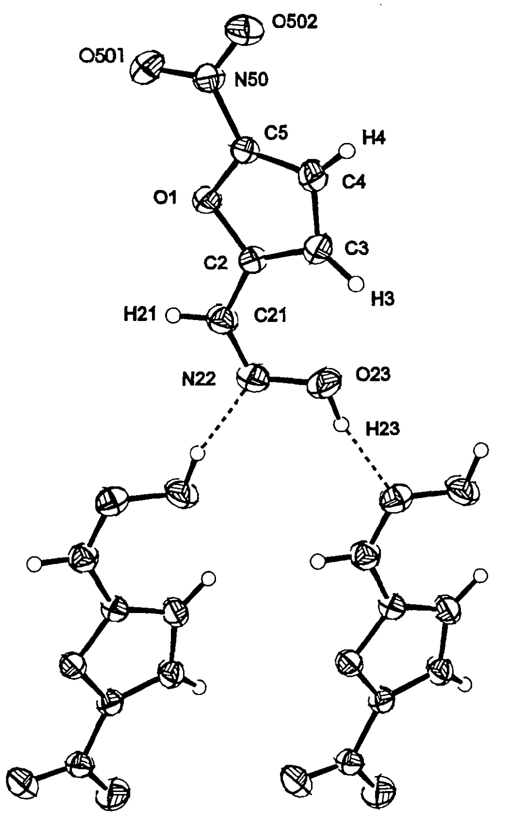


Fig. 1. The atomic numbering scheme and hydrogen bonds. Displacement ellipsoids are plotted at the 40% probability level.

shows a bond order of two for C3═C2 and C21═N22, and one for C2—C21.

The furan ring is planar to within experimental error. The plane of the nitro substituent crosses the five-membered ring plane at an angle of 0.85 (5)°. The side chain is also planar and its least-squares plane makes a dihedral angle of 6.52 (5)° with the furan ring. The molecule, except for the C21 and O23 atoms, is almost planar (to within 0.06 Å). The slight deviation from planarity of the side chain [C21 and O23 are 0.082 (1) and 0.114 (1) Å, respectively, out of the plane] is caused by the *cis* conformation [O23···H3 distance is 2.40 (2) Å] and by hydrogen bonding.

The molecules are linked by intermolecular hydrogen bonds O23—H23···N22, where N22 belongs to the molecule related by $x+\frac{1}{2}$, $-y-\frac{1}{2}$, $-z$. The O23···N22 and H23···N22 distances are 2.820 (2) and 1.97 (2) Å, respectively, and the angle O23—H23···N22 is 170 (2)°. Thus the crystal structure is built from chains of molecules linked by hydrogen bonds around the 2_1 screw axis; these chains run in the [100] direction.

Experimental

Crystal data

$C_5H_4N_2O_4$
$M_r = 156.10$
Orthorhombic
$P2_12_12_1$
$a = 5.3330\ (4)$ Å
$b = 5.6330\ (6)$ Å
$c = 21.203\ (3)$ Å
$V = 637.0\ (1)$ Å^3
$Z = 4$
$D_x = 1.6278$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 50 reflections
$\theta = 21.50$–$28.44°$
$\mu = 0.1347$ mm^{-1}
$T = 293$ K
Block
$0.20 \times 0.10 \times 0.10$ mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
ω scans
Absorption correction: none
3176 measured reflections
1458 independent reflections
1244 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0123$
$\theta_{\rm max} = 27.50°$
$h = -6 \rightarrow 6$
$k = 0 \rightarrow 7$
$l = -27 \rightarrow 27$
3 standard reflections frequency: 60 min intensity decay: <3.0%

Refinement

Refinement on F^2
$R(F) = 0.0255$
$wR(F^2) = 0.0685$
$S = 1.101$
1451 reflections
116 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.189$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.146$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.0306 (2)	0.4555 (1)	0.11689 (4)	0.0379 (2)
C2	0.1844 (2)	0.2700 (2)	0.10019 (5)	0.0356 (3)
C21	0.0793 (2)	0.1147 (2)	0.05255 (6)	0.0428 (3)
N22	0.1849 (2)	−0.0599 (2)	0.02526 (5)	0.0462 (3)
O23	0.4288 (2)	−0.0945 (2)	0.04624 (5)	0.0555 (3)
C3	0.3979 (2)	0.2736 (3)	0.13548 (6)	0.0434 (3)
C4	0.3785 (2)	0.4712 (2)	0.17634 (6)	0.0434 (4)
C5	0.1566 (2)	0.5710 (2)	0.16251 (5)	0.0351 (3)
N50	0.0398 (2)	0.7762 (2)	0.18854 (5)	0.0409 (3)
O501	−0.1643 (2)	0.8378 (2)	0.16800 (5)	0.0585 (4)
O502	0.1553 (2)	0.8787 (2)	0.23016 (5)	0.0586 (3)

Table 2. *Selected geometric parameters* (Å, °)

O1—C2	1.374 (1)	O23—H23	0.86 (2)
O1—C5	1.346 (1)	C3—C4	1.415 (1)
C2—C21	1.449 (1)	C4—C5	1.342 (1)
C2—C3	1.363 (1)	C5—N50	1.424 (1)
C21—N22	1.272 (1)	N50—O501	1.222 (1)
N22—O23	1.388 (1)	N50—O502	1.221 (1)
C2—O1—C5	104.8 (1)	C3—C4—C5	105.1 (1)
O1—C2—C3	110.2 (1)	O1—C5—C4	113.2 (1)
O1—C2—C21	114.1 (1)	C4—C5—N50	129.8 (1)
C21—C2—C3	135.6 (1)	O1—C5—N50	116.9 (1)
C2—C21—N22	127.8 (1)	C5—N50—O502	116.3 (1)
C21—N22—O23	112.2 (1)	C5—N50—O501	118.8 (1)
N22—O23—H23	106 (1)	O501—N50—O502	124.9 (1)
C2—C3—C4	106.6 (1)		

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX*2.1 (McArdle, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

The authors thank Norwich Eaton Pharmaceuticals, Inc. (Norwich, New York) for providing the crystals. One of them (TAO) is indebted to the Research Council of the Katholieke Universiteit Leuven (Belgium) for a Senior Fellowship (No. F/92/32).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 1306–1310

Two Methyl-Substituted Carbapenem Antibiotic Precursors

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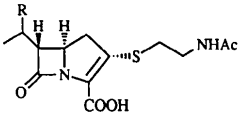
(*Received* 5 *October* 1994; *accepted* 12 *December* 1994)

Abstract

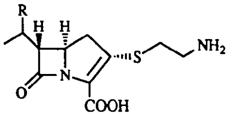
Carbapenem antibiotics are characterized by the presence of the 7-oxo-1-azabicyclo[3.2.0]hept-2-ene-2-carboxylic acid system. These new bicyclic β-lactam antibiotics are rapidly degraded by dehydropeptidase-I. The introduction of a methyl group at the C1 position of the carbapenem skeleton improves the dehydropeptidase stability. The crystal structure determinations of two synthetic methyl-substituted carbapenem precursors, 4-benzyl-6-methoxy-3-propylsulfonyl-2-{2,2,2′,2′-tetramethyl-[4,4′-bi([1,3]dioxolanyl)-5-yl]}-1-azabicyclo[3.2.0]heptane-7-one, $C_{27}H_{39}NO_8S$, and 3-ethylthio-4-(2-furylmethyl)-6-methoxy-2-{2,2,2′,2′-tetramethyl-[4,4′-bi([1,3]dioxolanyl)-5-yl]}-1-azabicyclo[3.2.0]heptane-7-one, $C_{24}H_{35}NO_7S$, established their stereochemistry unambiguously. The absolute configuration was deduced from that of the chiral D-glucosamine auxiliary.

Comment

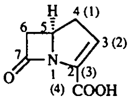
Carbapenem antibiotics such as PS-5, (1) (Yamamoto *et al.*, 1980), PS-6, (2) (Ishikura, 1979), and thienamycin, (3) (Kahan *et al.*, 1979), comprise an interesting family of streptomycete metabolites characterized by the presence of the 7-oxo-1-azabicyclo[3.2.0]hept-2-ene-2-carboxylic acid system (4).



(1) R = H
(2) R = Me



(3)



(4)

The potent antibacterial properties and the challenging chemical problems have made these new bicyclic β-lactams major synthetic objectives. A disadvantage of these compounds is that they are rapidly degraded in the kidney by dehydropeptidase-I (DHP-I) (Kahan *et al.*, 1979). The introduction of a methyl group into the 1-position of the carbapenem skeleton considerably improves the DHP stability (Neu, Novelli & Chin, 1989).

The synthesis of 1,2,3,6-tetrasubstituted carbapenem (6) from the readily available 1,3,4-trisubstituted azetidin-2-ones (5) (Barton *et al.*, 1990), in which the five-membered ring is formed by radical cyclization, has been reported recently (Anaya *et al.*, 1993). In continuing to explore the use of radical cyclization in the preparation of methyl-substituted carbapenem antibiotic precursors, we have synthesized compound (8) in 62% yield from the monocyclic β-lactam (7), which was obtained by Staudinger reaction using D-glucosamine as the chiral auxiliary (to be published). The X-ray struc-