678 reflections
83 parameters
H-atom parameters not refined

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(1)	0.73840 (7)	−0.3847 (4)	−0.6651 (5)	6.02 (6)
C(1)	0.70348 (9)	−0.4255 (5)	−0.4967 (6)	4.45 (7)
C(2)	0.68723 (9)	−0.1722 (6)	−0.4012 (6)	4.10 (7)
C(3)	0.64888 (9)	−0.1980 (6)	−0.2249 (5)	3.97 (7)
C(4)	0.63170 (8)	0.0571 (5)	−0.1276 (6)	3.90 (7)
C(5)	0.59305 (9)	0.0307 (5)	0.0450 (6)	3.86 (7)
C(6)	0.57582 (9)	0.2849 (6)	0.1444 (5)	3.92 (7)
C(7)	0.53668 (9)	0.2586 (5)	0.3151 (5)	3.71 (7)
C(8)	0.51936 (8)	0.5142 (5)	0.4132 (6)	3.88 (6)

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

O(1)—C(1)	1.416 (3)	C(5)—C(6)	1.519 (4)
C(1)—C(2)	1.497 (4)	C(6)—C(7)	1.521 (4)
C(2)—C(3)	1.517 (4)	C(7)—C(8)	1.524 (4)
C(3)—C(4)	1.519 (4)	C(8)—C(8^{i})	1.520 (5)
C(4)—C(5)	1.514 (4)		
O(1)—C(1)—C(2)	109.4 (2)	C(4)—C(5)—C(6)	113.9 (2)
C(1)—C(2)—C(3)	112.9 (2)	C(5)—C(6)—C(7)	113.9 (2)
C(2)—C(3)—C(4)	113.8 (3)	C(6)—C(7)—C(8)	113.8 (2)
C(3)—C(4)—C(5)	113.6 (2)	C(7)—C(8)—C(8^{i})	113.4 (3)

Symmetry code: (i) $-x, -y, -z$.

The structure was determined by direct methods using *SHELXS*-86 (Sheldrick, 1985) and successive Fourier syntheses (Beurskens *et al.*, 1992). Non-H atoms were refined anisotropically and H atoms were fixed in idealized positions. All calculations were performed using the *TEXSAN* software package (Molecular Structure Corporation, 1992).

The authors wish to express their gratitude to Professor Y. Yoshimura of Ritsumeikan University for useful discussions and suggestions.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71786 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1052]

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Acta Cryst. (1994). C**50**, 948–950

5-Nitro-2-furaldehyde Semicarbazone

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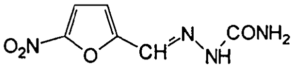
(*Received* 8 *December* 1993; *accepted* 4 *January* 1994)

Abstract

The molecules of the title compound, $C_6H_6N_4O_4$, are linked through bifurcated hydrogen bonds. A three-dimensional network of molecules is observed.

Comment

A perspective view showing the atomic numbering scheme and hydrogen bonding is given in Fig. 1. The crystal contains well ordered molecules of 5-nitro-2-furaldehyde semicarbazone, (I), in the form also observed in crystals of 5-nitrofuran-2-aldoxime (Matsuoka, Furukawa, Takao, Kitao, Hamada & Nakatsu, 1991). The bond lengths are similar to within 0.03 Å. The title compound has a *trans* conformation, while 5-nitrofuran-2-aldoxime (Matsuoka *et al.*, 1991) is *cis* with respect to the double bond of the side chain (C21=N22).



(I)

The C3=C2—C21=N22 planar group of atoms does not display any conjugation effect between double bonds. A comparison of the bond lengths with those given by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) and Burke-Laing & Laing (1976) shows bond orders 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 177.2 (3)°. The side chain is also planar and its least-squares plane makes a dihedral angle of 7.8 (1)° with the furan ring. The whole molecule is nearly planar [except for the H atoms, and O25 and N25 which deviate by 0.115 (2) and 0.142 Å, respectively]. An examination of the torsion angles (except for those with H atoms) shows a deviation from either 0 or 180° not larger than 4.6°.

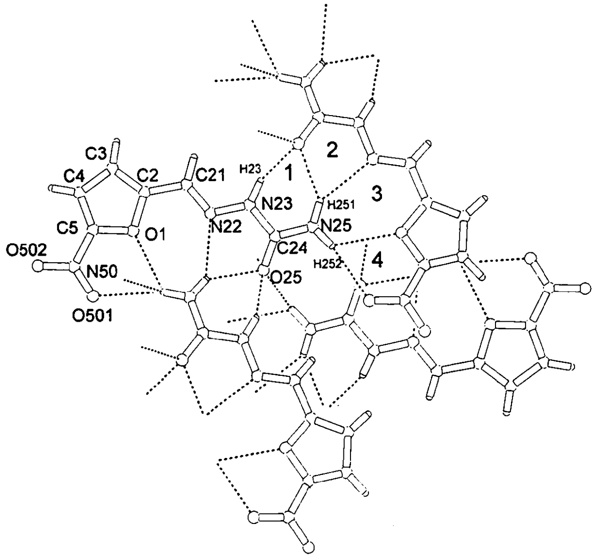


Fig. 1. The atomic numbering scheme and hydrogen bonds

The molecules are linked by bifurcated hydrogen bonds, which are formed by molecules related by the twofold screw axis and inversion, resulting in a three-dimensional network of bonds (see Fig. 1). The linked molecules form four rings. Rings 2 and 4 are five membered and in envelope conformations, the six-membered ring, 1, is planar and ring 3 is seven-membered with a deformed sofa conformation [N22, C21, C2, O1 in one plane and N25, H251, H252 in another; the two planes cross at an angle of 151 (3)°].

Experimental

Crystal data

$C_6H_6N_4O_4$
M_r = 198.14
Monoclinic
$P2_1/a$
a = 9.943 (1) Å
b = 8.402 (1) Å
c = 10.220 (1) Å
β = 101.18 (1)°
V = 837.6 (2) Å^3
Z = 4

D_x = 1.571 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 30 reflections
θ = 10.55–17.83°
μ = 0.126 mm^{-1}
T = 293 K
Block
0.10 × 0.10 × 0.20 mm
Yellow

Data collection

Stoe Stadi-4 four-circle diffractometer
ω scans
4066 measured reflections

$\theta_{\max}$ = 27.50°
$h = -13 \rightarrow 13$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 13$

1927 independent reflections
948 observed reflections [$I > 2.0\sigma(I)$]
$R_{\rm int}$ = 0.0151

3 standard reflections
frequency: 60 min
intensity variation: < 3.0%

Refinement

Refinement on F
R = 0.0428
wR = 0.0765
S = 0.939
948 reflections
152 parameters
All H-atom parameters refined
$w = 1.4108/[\sigma^2(F) + 0.0090F^2]$

$(\Delta/\sigma)_{\max}$ = 0.017
$\Delta\rho_{\max}$ = 0.20 e Å^{-3}
$\Delta\rho_{\min}$ = −0.19 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreetti, 1989)

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

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

	x	y	z	$U_{\rm eq}$
O1	0.5045 (2)	−0.1910 (3)	0.7317 (2)	0.0558 (8)
C2	0.5349 (3)	−0.0332 (5)	0.7280 (3)	0.057 (1)
C21	0.4607 (3)	0.0748 (4)	0.7990 (3)	0.057 (1)
N22	0.3694 (3)	0.0192 (3)	0.8586 (3)	0.049 (8)
N23	0.3031 (3)	0.1228 (3)	0.9251 (3)	0.054 (9)
C24	0.1998 (3)	0.0645 (4)	0.9849 (3)	0.047 (9)
O25	0.1642 (2)	−0.0760 (2)	0.9700 (2)	0.060 (8)
N25	0.1433 (3)	0.1685 (3)	1.0541 (3)	0.057 (1)
C3	0.6327 (4)	−0.0108 (7)	0.6546 (4)	0.076 (2)
C4	0.6667 (4)	−0.1598 (7)	0.6115 (4)	0.080 (2)
C5	0.5880 (3)	−0.2641 (5)	0.6595 (3)	0.063 (1)
N50	0.5761 (4)	−0.4322 (5)	0.6502 (3)	0.074 (1)
O501	0.4918 (4)	−0.5009 (3)	0.7038 (3)	0.087 (1)
O502	0.6553 (3)	−0.4999 (5)	0.5895 (3)	0.107 (2)

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

O1—C2	1.362 (4)	C24—O25	1.233 (3)
O1—C5	1.360 (4)	C24--N25	1.317 (4)
C2—C21	1.450 (5)	C3—C4	1.390 (8)
C2—C3	1.352 (5)	C4—C5	1.330 (6)
C21—N22	1.276 (4)	C5—N50	1.419 (5)
N22—N23	1.352 (4)	N50—O501	1.230 (5)
N23—C24	1.383 (4)	N50—O502	1.232 (5)
C2—O1—C5	105.2 (3)	O25—C24—N25	124.0 (3)
O1—C2—C3	109.8 (4)	C2—C3—C4	107.2 (4)
O1—C2—C21	117.3 (3)	C3—C4—C5	106.3 (4)
C21—C2—C3	132.9 (4)	O1—C5—C4	111.6 (4)
C2—C21—N22	119.2 (3)	C4—C5—N50	132.7 (3)
C21—N22—N23	117.8 (3)	O1—C5—N50	115.7 (3)
N22—N23—C24	118.1 (3)	C5—N50—O502	116.1 (4)
N23—C24—N25	115.7 (3)	C5—N50—O501	119.5 (4)
N23—C24—O25	120.3 (3)	O501—N50—O502	124.4 (4)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	A	D—H	H···A	D···A	D—H···A
N23	H23	O25$^{\rm i}$	0.92 (3)	1.87 (3)	2.743 (3)	160 (3)
N25	H251	N22$^{\rm i}$	0.91 (3)	2.32 (3)	3.088 (4)	143 (3)
N25	H251	O25$^{\rm i}$	0.91 (3)	2.14 (4)	2.918 (3)	144 (3)
N25	H252	O1$^{\rm i}$	0.91 (4)	2.49 (4)	3.097 (4)	124 (3)
N25	H252	O501$^{\rm i}$	0.91 (4)	2.51 (4)	3.353 (5)	154 (3)
N25	H252	O25$^{\rm ii}$	0.91 (4)	2.46 (4)	3.118 (4)	129 (3)

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

H atoms were refined with constraints; H atoms connected to C atoms were refined at a distance of 0.938 (95) ±0.05 Å and H atoms attached to N25 were refined at a distance of 0.954 ±0.025 Å. Data collection and cell refinement: *DIF*4

(Stoe & Cie, 1992*a*). Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX-76* (Sheldrick, 1976). Molecular graphics: *PLUTON*93 (Spek, 1993). 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.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1082). 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. (1994). C**50**, 950–952

An Unusual C-4a Hydroxylated Decahydroquinolone

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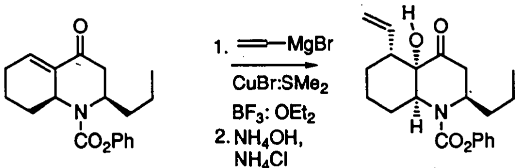
(*Received* 26 *July* 1993; *accepted* 21 *December* 1993)

Abstract

The crystal structure and the relative stereochemistry of the four asymmetric centers of an unusual C-4a hydroxylated decahydroquinolone, phenyl 1,2α,3,4,4aα,5β,6,7,8,8aα-decahydro-4a-hydroxy-4-oxo-2-propyl-5-vinylquinoline-1-carboxylate, $C_{21}H_{27}NO_4$, are reported. The H and OH groups at the ring juncture are *cis* to each other as are the two H atoms α to the N atom. The vinyl and OH groups are also *cis* to each other. The N atom is sp^2 hybridized.

Comment

The title compound (I) was obtained during our model studies aimed at the synthesis of (±)-gephyrotoxin (Comins & Joseph, 1991; Fujimoto, Kishi & Blount, 1980; Hart & Kanai, 1983; Overman, Lesuisse & Hashimoto, 1983). It was synthesized by the copper-catalyzed addition of vinylmagnesium bromide to the enone (II) at 195 K, and quenching the reaction mixture cold, as shown below. The reaction was completely stereoselective (Comins & Dehghani, 1991). The relative stereochemistry is shown in Fig. 1, which shows that the introduction of the OH group α to the carbonyl occurs from the same face as the vinyl substituent, the ring juncture is *cis*, and both H atoms α to the N atom are *cis*. The N atom is sp^2 hybridized; the sum of the three bond angles around the N atom is 359.8°.



(II) (I)

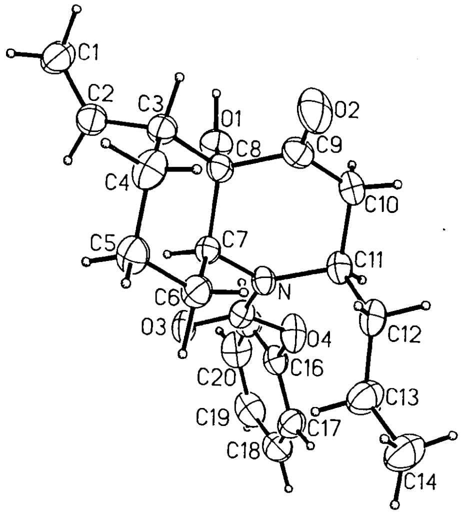


Fig. 1. Displacement ellipsoid plot (30% probability ellipsoids) showing the numbering scheme and the relative configurations of the four asymmetric centers (C3, C7, C8, C11). For clarity, atom C15 (which is attached to N) and the phenyl carbon C21 are not labeled.

Acta Crystallographica Section C
ISSN 0108-2701 ©1994