ORGANIC COMPOUNDS

Acta Cryst. (1995). C**51**, 1575–1577

Two Cyanacrylamides

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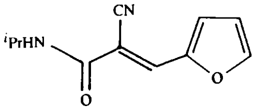
(*Received* 19 *November* 1992; *accepted* 8 *June* 1995)

Abstract

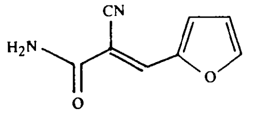
N-Isopropyl-2-cyano-3-furylacrylamide, $C_{11}H_{12}N_2O_2$, (I), displays intermolecular hydrogen bonding between N and O atoms. The crystal is probably stabilized by a network of hydrogen bonds and by van der Waals forces. 2-Cyano-3-furylacrylamide, $C_8H_6N_2O_2$, (II), shows no unusual intramolecular or intermolecular distances or angles. The molecules in the crystal are packed at normal van der Waals distances.

Comment

A number of cyano furylacrylamides $X—C_4H_3O—CH{=}C(CN)—CONHR$ (X = H, NO_2, Cl, Br, I; R = H, C_nH_{2n+1}, $CH_2C_4H_3O$, $CH_2C_6H_5$) have been investigated (Bartroli, 1985). We have now determined the structures of two cyano furylacrylamides, (I) and (II).



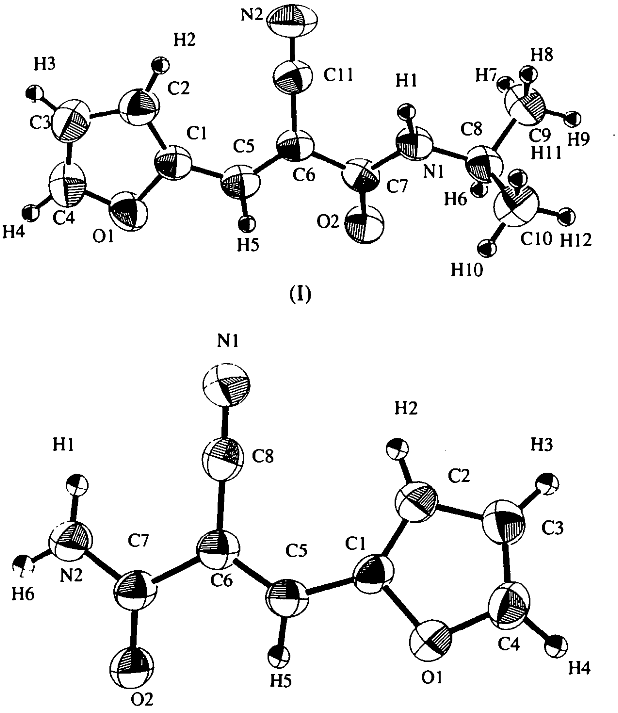
(I)



(II)

Compounds (I) and (II) were prepared from the reaction of furanic aldehydes and cyanacetamides with a catalytic inorganic phase as described by Bartroli, Lami, Quincoses & Peseke (1984). Bartroli (1985) has studied the crystallization of these compounds. The single crystals used in X-ray analysis for both compounds were obtained by slow crystallization from ethanol.

The molecular structures of compounds (I) and (II) are illustrated in Fig. 1 (*ORTEP*II; Johnson, 1976). In compound (I), there is an intermolecular approach of less than 3.4 Å involving non-H atoms (Pauling, 1960). The length of the hydrogen bond N(1)···O(2) between the amine N atom and carbonyl O atom is 3.018 (3) Å. The molecules in the crystal are connected by hydrogen bonds along [100]. In (II), the molecules in the crystal are packed at normal van der Waals distances.



(I)

(II)

Fig. 1. Views of (I) and (II) showing the numbering schemes used. Displacement ellipsoids are drawn at the 50% level.

Experimental

Compounds (I) and (II) were prepared from the reaction of furanic aldehydes and cyanacetamides with a catalytic inorganic phase, as described by Bartroli, Lami, Quincoses & Peseke (1984). Crystals used in the X-ray analyses were obtained by slow crystallization from ethanol (Bartroli, 1984).

Compound (I)

Crystal data

$C_{11}H_{12}N_2O_2$
M_r = 204
Monoclinic
$P2_1/n$
a = 5.083 (2) Å
b = 15.551 (6) Å
c = 13.647 (5) Å
β = 98.94 (3)°
V = 1065.6 (7) Å^3
Z = 4
D_x = 1.27 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 20 reflections
θ = 3–40°
μ = 0.695 mm^{-1}
T = 293 K
Prismatic
0.9 × 0.16 × 0.1 mm
Transparent, colourless

Acta Crystallographica Section C
ISSN 0108-2701 ©1995

Data collection

Nicolet *R*3 four-circle diffractometer
$2\theta/\theta$ scans
Absorption correction: none
1685 measured reflections
1685 independent reflections
1095 observed reflections [$I > 3\sigma(I)$]

$\theta_{\max} = 45°$
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 16$
$l = -14 \rightarrow 14$
2 standard reflections monitored every 50 reflections
intensity decay: <5%

Refinement

Refinement on *F*
$R = 0.045$
$wR = 0.057$
$S = 3.16$
1095 reflections
234 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\max} = 0.1$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ c Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (II)

Crystal data

$C_8H_6N_2O_2$
$M_r = 162$
Triclinic
$P\bar{1}$
$a = 9.876$ (3) Å
$b = 10.325$ (4) Å
$c = 3.870$ (8) Å
$\alpha = 93.86$ (2)°
$\beta = 97.61$ (2)°
$\gamma = 103.52$ (3)°
$V = 378.3$ (4) Å^3
$Z = 2$
$D_x = 1.42$ Mg m^{-3}

Cu *Kα* radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 0$–$20°$
$\mu = 0.843$ mm^{-1}
$T = 293$ K
Prismatic
0.68 × 0.1 × 0.06 mm
Transparent, colourless

Data collection

Nicolet *R*3 four-circle diffractometer
$2\theta/\theta$ scans
Absorption correction: none
949 measured reflections
804 independent reflections
1020 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.03$
$\theta_{\max} = 45°$
$h = -1 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -4 \rightarrow 4$
2 standard reflections frequency: 50 min
intensity decay: 5%

Refinement

Refinement on *F*
$R = 0.064$
$wR = 0.067$
$S = 1.19$
804 reflections
144 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\max} = 0.1$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{\rm eq}$
(I)				
O(1)	0.6139 (1)	0.5655 (1)	0.9080 (1)	5.3 (1)
O(2)	0.6859 (3)	0.2530 (1)	0.9586 (1)	5.3 (1)
N(1)	1.0962 (4)	0.2158 (1)	0.9307 (2)	4.2 (1)
N(2)	1.2737 (5)	0.3688 (2)	0.7659 (2)	6.4 (1)
C(1)	0.7966 (4)	0.5111 (2)	0.8756 (2)	4.1 (1)
C(2)	0.9406 (6)	0.5576 (2)	0.8199 (2)	5.4 (1)
C(3)	0.8466 (7)	0.6423 (2)	0.8169 (2)	5.9 (2)
C(4)	0.6496 (6)	0.6443 (2)	0.8707 (2)	5.6 (1)
C(5)	0.7893 (5)	0.4251 (2)	0.9084 (2)	4.2 (1)
C(6)	0.9361 (4)	0.3578 (1)	0.8869 (2)	3.8 (1)
C(7)	0.8953 (4)	0.2709 (2)	0.9286 (2)	4.0 (1)
C(8)	1.0952 (5)	0.1278 (2)	0.9681 (2)	4.5 (1)
C(9)	1.2268 (7)	0.0700 (2)	0.9012 (3)	5.8 (2)
C(10)	1.2299 (7)	0.1230 (3)	1.0743 (2)	6.1 (2)
C(11)	1.1251 (5)	0.3654 (2)	0.8207 (2)	4.4 (1)
(II)				
O(1)	0.1344 (2)	−0.0618 (2)	0.8938 (5)	4.66 (5)
O(2)	0.0177 (2)	0.3532 (2)	0.6722 (7)	5.03 (5)
N(1)	0.4865 (3)	0.3479 (3)	0.5816 (8)	6.56 (9)
N(2)	0.2009 (3)	0.5009 (2)	0.5247 (6)	4.89 (8)
C(1)	0.2227 (2)	0.0467 (2)	0.7854 (6)	3.56 (5)
C(2)	0.3412 (3)	0.0121 (3)	0.7218 (7)	4.42 (1)
C(3)	0.3283 (3)	−0.1211 (3)	0.7964 (7)	4.70 (9)
C(4)	0.2034 (3)	−0.1607 (3)	0.8969 (7)	4.50 (1)
C(5)	0.1657 (3)	0.1606 (3)	0.7498 (6)	3.69 (7)
C(6)	0.2272 (2)	0.2831 (3)	0.6709 (6)	3.62 (7)
C(7)	0.1407 (3)	0.3833 (3)	0.6227 (6)	3.80 (9)
C(8)	0.3702 (3)	0.3182 (3)	0.6196 (7)	4.39 (1)

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

(I)			
O(1)—C(1)	1.378 (3)	C(2)—C(3)	1.400 (4)
O(1)—C(4)	1.352 (3)	C(3)—C(4)	1.327 (5)
O(2)—C(7)	1.231 (3)	C(5)—C(6)	1.344 (3)
N(1)—C(7)	1.331 (3)	C(6)—C(7)	1.493 (3)
N(1)—C(8)	1.460 (3)	C(6)—C(11)	1.422 (4)
N(2)—C(11)	1.143 (3)	C(8)—C(9)	1.510 (4)
C(1)—C(2)	1.345 (3)	C(8)—C(10)	1.506 (4)
C(1)—C(5)	1.414 (4)		
C(1)—O(1)—C(4)	107.3 (2)	C(5)—C(6)—C(11)	121.8 (2)
C(7)—N(1)—C(8)	124.6 (2)	C(7)—C(6)—C(11)	117.7 (2)
O(1)—C(1)—C(2)	107.7 (2)	O(2)—C(7)—N(1)	123.2 (2)
O(1)—C(1)—C(5)	115.3 (2)	O(2)—C(7)—C(6)	120.7 (2)
C(2)—C(1)—C(5)	137.0 (3)	N(1)—C(7)—C(6)	116.1 (2)
C(1)—C(2)—C(3)	108.0 (3)	N(1)—C(8)—C(9)	108.7 (2)
C(2)—C(3)—C(4)	106.8 (3)	N(1)—C(8)—C(10)	110.9 (2)
O(1)—C(4)—C(3)	110.1 (3)	C(9)—C(8)—C(10)	112.0 (3)
C(1)—C(5)—C(6)	128.7 (3)	N(2)—C(11)—C(6)	177.6 (3)
C(5)—C(6)—C(7)	120.4 (2)		
(II)			
O(1)—C(1)	1.377 (3)	C(1)—C(5)	1.425 (4)
O(1)—C(4)	1.353 (3)	C(2)—C(3)	1.405 (4)
O(2)—C(7)	1.226 (3)	C(3)—C(4)	1.324 (4)
N(1)—C(8)	1.150 (3)	C(5)—C(6)	1.343 (4)
N(2)—C(7)	1.325 (3)	C(6)—C(7)	1.494 (4)
C(1)—C(2)	1.348 (3)	C(6)—C(8)	1.418 (4)
C(1)—O(1)—C(4)	106.1 (2)	O(1)—C(1)—C(5)	114.7 (2)
O(1)—C(1)—C(2)	108.5 (2)	C(2)—C(1)—C(5)	136.5 (2)
C(1)—C(2)—C(3)	107.6 (2)	C(2)—C(3)—C(4)	106.2 (2)
O(1)—C(4)—C(3)	111.4 (3)	C(1)—C(5)—C(6)	129.2 (2)
C(7)—C(6)—C(8)	119.2 (2)	C(5)—C(6)—C(8)	121.9 (3)
O(2)—C(7)—C(6)	118.9 (2)	N(2)—C(7)—C(6)	118.0 (2)
N(1)—C(8)—C(6)	179.1 (3)	O(2)—C(7)—N(2)	122.9 (2)
O(1)—C(1)—C(2)—C(3)	−0.8 (3)	O(2)—C(7)—C(6)—C(8)	−179.0 (2)
O(1)—C(1)—C(5)—C(6)	175.5 (2)	N(1)—C(8)—C(6)—C(7)	61 (17)
O(1)—C(4)—C(3)—C(2)	−0.2 (3)	N(2)—C(7)—C(6)—C(8)	1.6 (3)

O(2)—C(7)—C(6)—C(5)	3.3 (4)	C(1)—C(2)—C(3)—C(4)	0.6 (3)
N(1)—C(8)—C(6)—C(5)	−121.9 (3)	C(1)—C(5)—C(6)—C(7)	175.5 (2)
N(2)—C(7)—C(6)—C(5)	−176.1 (2)	C(2)—C(1)—C(5)—C(6)	−9.1 (5)
C(1)—C(5)—C(6)—C(8)	−2.2 (4)	C(4)—O(1)—C(1)—C(5)	177.3 (2)
C(3)—C(2)—C(1)—C(5)	−176.4 (3)		

The structures were solved by direct methods using *MITHRIL* (Gilmore, 1984). All computations were performed on a VAX computer and plots drawn on a Tektronix plotter with *TEXSAN* (Molecular Structure Corporation, 1985).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1059). 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). C**51**, 1577–1579

^{t}BuCO-ψ[CO-N(OH)]-Gly-NH^{i}Pr

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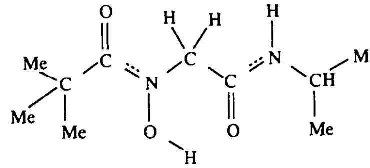
(*Received* 15 *November* 1993; *accepted* 26 *May* 1994)

Abstract

The title compound, *N*-hydroxy-*N*-pivaloyl-glycine isopropylamide, $C_{10}H_{20}N_2O_3$, crystallizes with two independent molecules adopting two different extended conformations. The planar *trans* hydroxamide group has similar dimensions to the standard peptide bond. The hydroxamide N—OH group, which is roughly perpendicular to the hydroxamide plane, is engaged in a short contact with the glycine carbonyl group.

Comment

There are only a small number of crystal structures of *N*-hydroxy peptides reported in the literature (Buseti, Ottenheijm, Zeegers, Ajo & Casarin, 1987; Dupont, Lecoq, Mangeot, Aubry, Boussard & Marraud, 1993) and the possible intra- or intermolecular interaction modes of the *N*-hydroxyl group need to be specified. By slow evaporation of a methanol solution, we have obtained single crystals of the title compound, (I), deriving from *N*-hydroxyglycine.



(I)

The structure shows that in both independent molecules, *A* and *B*, the hydroxamide group adopts a *trans* planar conformation with dimensions similar to those of the standard peptide group (Benedetti, 1977). In both cases, the N—O—H plane is practically perpendicular to the hydroxamide plane. Molecules *A* and *B* (Fig. 1) differ essentially in their φ and ν angles which are rotated by up to nearly 160° (Table 2). They are connected by a complex network of hydrogen bonds in which each molecule of *A* is connected to two molecules of *B* and each molecule of *B* to one molecule of *A* and one of *B* (Table 3).

This crystal structure confirms the preferential perpendicular orientation and the strong proton-donating properties of the hydroxamide O—H bond, as illustrated by shorter O···O distances compared to N···O distances (Table 3). Comparison of the conformations adopted by molecules *A* and *B* with that of the ^{t}BuCO-Gly-NH^{i}Pr

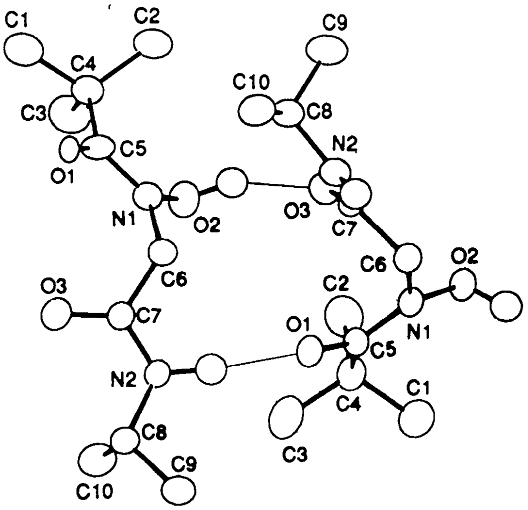


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of molecules *A* (left) and *B* (right) associated by the N(2)—H(N2)···O(1) and O(2)—H(O2)···O(3′) hydrogen bonds.

Acta Crystallographica Section C
ISSN 0108-2701 ©1995