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1-(1-Cyanocyclohexyl)-1-hydroxy-3-phenylurea

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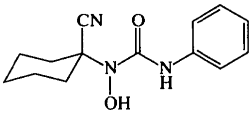
Abstract

In the crystals of the title compound, $C_{14}H_{17}N_3O_2$, there are two molecules (*A* and *B*) in the asymmetric unit. The conformation of the hydroxamic acid moiety, O=C—N—O, is antiperiplanar for both molecules. The phenyl substituent is in a synperiplanar conformation, with O=C—N—C torsion angles of 1.8 (2) and 2.1 (2)° for *A* and *B*, respectively. The corresponding torsion angles of the cyclohexyl substituents are −32.0 (2) and −30.8 (2)°, respectively. The cyclohexyl ring adopts a chair conformation in both molecules, with the hydroxamic acid moiety in an equatorial position and the cyano group in an axial position. The plane of the phenyl group is twisted with respect to the central urea plane [38.71 (7) and 43.08 (7)° for molecules *A* and *B*, respectively]. No other significant differences in bond lengths, angles or torsion angles between molecules *A* and *B* are observed. The crystal packing shows that the *A* and *B* molecules are interconnected by hydrogen bonds, OH···O and NH···N, in the direction of the *a* axis.

Comment

The title compound, (I), was first synthesized by Zinner & Krüger (1975) in a reaction between the corresponding hydroxylaminocarbonitrile and phenylisocyanate. It was observed that this type of substituted hydroxamic acid gives a positive Fe^{III} colour test only by using a non-aqueous Fe^{III} chloride solution (Krüger & Zinner, 1978). The conformation of a hydroxamic acid with very bulky substituents is expected to influence the ability of the compound to form a coloured complex with Fe^{III}. Limited flexibility might prevent the molecule from adopting the *sp* (synperiplanar) conformation of O=C—N—O, which is most favourable to complex formation (Larsen, 1988). X-ray structure determination of the title compound was carried out in order to establish the conformation of the hydroxamic acid moiety in the crystalline state of the compound.



(I)

There are two molecules of the title compound (*A* and *B*) in the asymmetric unit (Fig. 1). The conformations of the *A* and *B* molecules are very similar (see Table 1). The only conspicuous conformational deviation observed is in the twist of the phenyl ring with respect to the central urea moiety, the dihedral angles between the corresponding least-squares planes being 38.71 (7) and 43.08 (7)° for molecules *A* and *B*, respectively. The urea moiety is nearly planar with a maximum deviation from the least-squares plane through O2, C8, N1 and N3 of 0.017 (1) Å in both molecules. The hydroxyl O atom O1 is not included in this plane, the deviations being 0.429 (2) and 0.441 (2) Å in molecules *A* and *B*, respectively. This means that the N1 atom has a high degree of pyramidalization, which is also reflected in the distances of the N1 atoms from the planes defined by C1, C8 and O1 [0.371 (1) and 0.365 (1) Å for molecules *A* and *B*, respectively]. The other N atom (N3) has a completely planar configuration in both molecules.

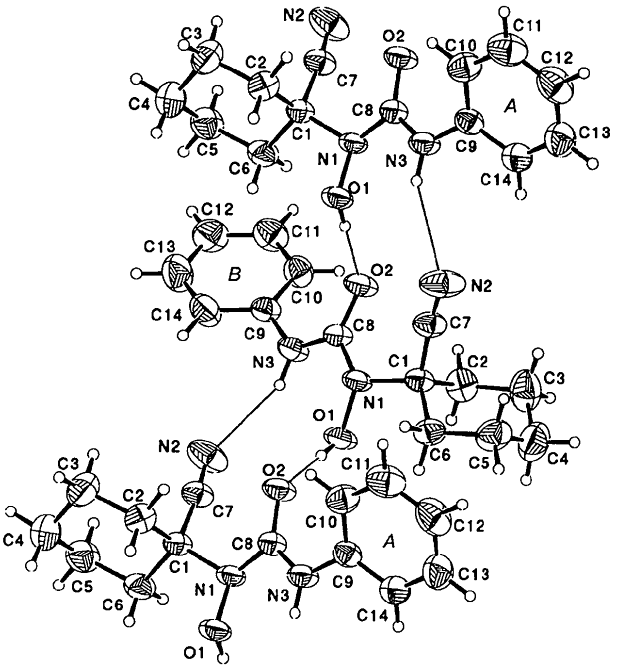


Fig. 1. The structures of molecules *A* and *B* of the title compound, which are linked together by hydrogen bonds (thin lines). The atom-labelling scheme is shown; displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

The cyclohexyl ring is observed to be in a chair conformation in both molecules *A* and *B*, with the cyano group in an axial position and the hydroxamic acid moiety in an equatorial position. The conformation of the hydroxamic acid moiety is found to be *ap* (antiperiplanar), with O=C—N—O torsion angles of −162.1 (1) and −161.5 (1)°, respectively, for molecules *A* and *B*. The *ap* conformation has been observed in crystal structures of almost all secondary hydroxamic acids in the Cambridge Structural Database (version of October 1996; Allen & Kennard, 1993). Solution studies (IR and NMR) have revealed that in polar (but non-aqueous) solvents, secondary hydroxamic acids might exist predominantly in the *sp* conformation (Brown *et al.*, 1996) and the formation of metal complexes should be possible. Theoretical studies (*ab initio* molecular orbital calculations; Brown *et al.*, 1996) on isolated formohydroxamic acid predict similar stability of the *ap* and *sp* conformations, whereas calculations on the monohydrate of formohydroxamic acid indicate that the addition of a water molecule makes the *sp* conformation more stable. Thus, the observation that the present secondary hydroxamic acid gives a positive Fe^{III} colour test only in non-aqueous ethanolic solution is difficult to explain. The *ap* conformation, which is the preferred conformation in the crystalline state, might be stabilized by hydrogen-bonded water molecules in aqueous solutions, thereby preventing the spontaneous formation of a stable Fe^{III} complex.

The *A* and *B* molecules are linked together in the crystals in the direction of the *a* axis by two types of hydrogen bonds: O1*A*—H···O2*B* and N3*A*—H···N2*B* (see Table 2 and Fig. 1). No hydrogen bonds connect the molecules along the *b* and *c* axes.

Experimental

The title compound was kindly provided by Professor G. Zinner, Department of Pharmaceutical Chemistry, The Technical University of Braunschweig, Germany. Single crystals were obtained by slow cooling of a hot solution in ethanol and acetone (m.p. 411–413 K).

Crystal data

$C_{14}H_{17}N_3O_2$
$M_r = 259.31$
Triclinic
$P\overline{1}$
$a = 10.0301\ (6)$ Å
$b = 11.7403\ (7)$ Å
$c = 11.7660\ (7)$ Å
$\alpha = 95.559\ (5)^\circ$
$\beta = 90.617\ (5)^\circ$
$\gamma = 97.323\ (5)^\circ$
$V = 1367.4\ (1)$ Å^3
$Z = 4$
$D_x = 1.260$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 22 reflections
$\theta = 31.76–41.85^\circ$
$\mu = 0.701$ mm^{-1}
$T = 295\ (2)$ K
Needle
0.76 × 0.10 × 0.06 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
12186 measured reflections
5644 independent reflections
3818 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$

$\theta_{\rm max} = 74.90^\circ$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$
3 standard reflections
every 300 reflections
frequency: 166 min
intensity decay: 3.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.117$
$S = 0.973$
5644 reflections
345 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0727P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.148$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.327$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

	Molecule *A*	Molecule *B*
C1—C7	1.476 (2)	1.479 (2)
C1—N1	1.484 (2)	1.480 (2)
C7—N2	1.140 (2)	1.135 (2)
N1—C8	1.397 (2)	1.400 (2)
N1—O1	1.415 (1)	1.413 (1)
C8—O2	1.237 (2)	1.236 (2)
C8—N3	1.335 (2)	1.333 (2)
N3—C9	1.414 (2)	1.422 (2)
C9—C14	1.383 (2)	1.376 (2)
C7—C1—N1	107.8 (1)	107.6 (1)
C7—C1—C2	109.8 (1)	110.4 (1)
N1—C1—C2	112.5 (1)	112.5 (1)
C7—C1—C6	106.7 (1)	106.7 (1)
N1—C1—C6	109.3 (1)	109.2 (1)
N2—C7—C1	173.1 (2)	173.4 (2)
C8—N1—O1	112.0 (1)	112.0 (1)
C8—N1—C1	118.0 (1)	118.2 (1)
O1—N1—C1	110.6 (1)	110.9 (1)
O2—C8—N3	124.7 (1)	124.7 (1)
O2—C8—N1	119.7 (1)	119.4 (1)
N3—C8—N1	115.6 (1)	115.8 (1)
C8—N3—C9	125.7 (1)	124.9 (1)
C14—C9—N3	118.3 (1)	118.8 (1)
C10—C9—N3	122.0 (1)	121.5 (1)
C1—C2—C3—C4	54.4 (2)	53.3 (2)
C2—C3—C4—C5	−55.1 (2)	−55.0 (2)
C3—C4—C5—C6	56.0 (2)	56.9 (2)
C4—C5—C6—C1	−56.0 (2)	−57.1 (2)
C5—C6—C1—C2	54.4 (2)	54.2 (2)
C6—C1—C2—C3	−53.7 (2)	−52.4 (2)
C1—N1—C8—O2	−32.0 (2)	−30.8 (2)
O1—N1—C8—O2	−162.1 (1)	−161.5 (1)
O2—C8—N3—C9	1.8 (2)	2.1 (2)
C8—N3—C9—C10	40.2 (2)	43.8 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O2*B*	0.82	1.91	2.723 (2)	173
O1*B*—H1*B*···O2*A*$^{\rm i}$	0.82	1.93	2.742 (2)	174
N3*A*—H3*A*···N2*B*	0.86	2.37	3.146 (2)	151
N3*B*—H3*B*···N2*A*$^{\rm i}$	0.86	2.35	3.139 (2)	154

Symmetry code: (i) $x - 1, y, z$.

H-atom positions were calculated and confirmed in difference Fourier maps. The H atoms were refined as riding atoms with fixed isotropic displacement parameters. The program *PLATON*94 (Spek, 1994) with the module *MISSYM* (Le Page, 1987, 1988) was used to check for missed symmetry and found no extra crystallographic symmetry. *PARST*95 (Nardelli, 1996) located a pseudosymmetry between molecules *A* and *B* (pseudo-twofold axis, pseudo inversion centre). The reflection data were analyzed and it was observed that the reflections $0kl$ are systematically absent for $l = 2n + 1$. This indicates the monoclinic space group $P2/c$ (interchanging *a* and *b*). However, the unit-cell angles are clearly different from 90° for two of the angles and the program *TRACER* (Lawton & Jacobson, 1965), which checks for other possible unit cell options, did not find any new solution. The conclusion is that the correct space group is $P\bar{1}$, but pseudosymmetry elements show that it is close to the monoclinic space group $P2/c$.

Data reduction: *DREADD* (Blessing, 1987, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1102). Services for accessing these data are described at the back of the journal.

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Four Methyl Azolyl-3-propenoates

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Abstract

The structures of four azolyl-3-propenoic esters, methyl (*E*)-3-(imidazol-4-yl)propenoate, (2), as its hemihydrate, $C_7H_8N_2O_2.0.5H_2O$, methyl (*E*)-3-(pyrrol-2-yl)-propenoate, $C_8H_9NO_2$, (3), methyl (*E*)-3-(imidazol-2-yl)propenoate, $C_7H_8N_2O_2$, (4), and methyl (*Z*)-3-(imidazol-2-yl)propenoate, $C_7H_8N_2O_2$, (5), are reported. In the pyrrole and imidazole derivatives, (3) and (4), the N—H function has an *s-Z* configuration with respect to the propenoate chain, whereas in the urocanate, (2), protonation has occurred at the N atom further from the side chain. In (5), an intramolecular N—H···O hydrogen bond causes a relative widening of the angles in the side chain. In all four compounds, both the azole rings and the side chains are almost planar. In the hemihydrate of (2), there is extensive hydrogen bonding, primarily of the type N—H···O but supplemented by much longer C—H···O interactions. In (3) and (4), the hydrogen bonding is much simpler, with molecules linked into ribbons *via* N—H···O contacts.

Comment

(*E*)-Urocanic acid, (1), is a naturally occurring metabolite of histidine, which comprises *ca* 0.5% of the dry weight of the epidermis. It is thought that (1) acts as a natural photoprotecting agent (Morrison, 1985) and for this reason there are many recent patents covering the uses of esters of (1) as components of sunscreens. Although the structure of (1) itself has been known for 20 years (Hawkinson, 1977; Svinning & Sørum, 1979), it occurs in the solid state as a zwitterion, (1*a*), and so is not directly relevant to the corresponding ester structure. In this paper, we report structural data for a series of four azolyl-3-propenoic esters comprising methyl (*E*)-urocanate, (2) (as the hemihydrate), the corresponding pyrrol-2-yl and imidazol-2-yl derivatives, (3) and (4), and the imidazol-2-yl (*Z*)-propenoate, (5) (McNab & Thornley, 1997; Campbell *et al.*, 1997).

In the structure of (3), there are two molecules per asymmetric unit and in (5) there are three molecules;

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