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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^{t}BuCO-ψ[CO-N(OH)]-Gly-NH^{i}Pr

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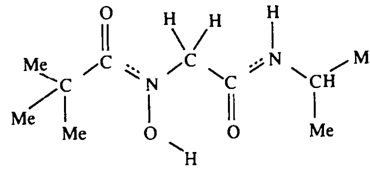
Abstract

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

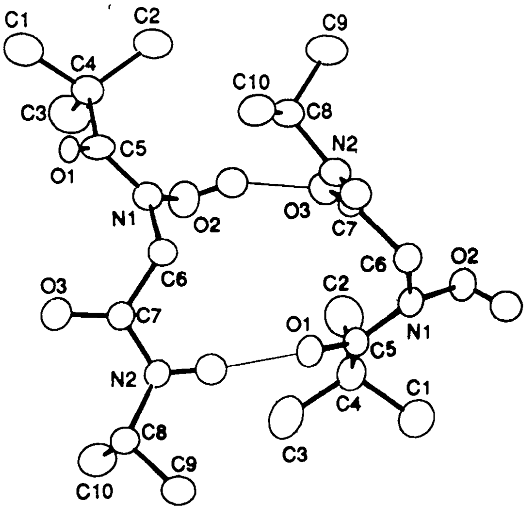


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of molecules *A* (left) and *B* (right) associated by the N(2)—H(N2)···O(1) and O(2)—H(O2)···O(3′) hydrogen bonds.

cognate peptide in the solid state, characterized by $\varphi = 112(1)$ and $-142(1)°$ (Aubry, Marraud, Protas & Néel, 1973), shows that *N*-hydroxylation of a peptide chain can induce a conformational change related to the strong proton-donating ability of the OH site.

Experimental

Crystal data

$C_{10}H_{20}N_2O_3$
$M_r = 216.28$
Triclinic
$P\bar{1}$
$a = 9.598\ (1)$ Å
$b = 11.636\ (2)$ Å
$c = 12.759\ (2)$ Å
$\alpha = 110.64\ (2)°$
$\beta = 107.07\ (2)°$
$\gamma = 96.58\ (2)°$
$V = 1236$ Å^3
$Z = 4$
$D_x = 1.16$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 295 reflections
$\theta = 20–30°$
$\mu = 0.624$ mm^{-1}
$T = 25$ K
Parallelepiped
0.2 × 0.15 × 0.1 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4323 measured reflections
4228 independent reflections
3648 observed reflections $[I > \sigma(I)]$

$\theta_{max} = 70°$
$h = -11 \rightarrow 10$
$k = -13 \rightarrow 12$
$l = 0 \rightarrow 14$
3 standard reflections frequency: 120 min intensity decay: 6%

Refinement

Refinement on F
$R = 0.074$
$wR = 0.087$
$S = 10.3$
3648 reflections
392 parameters
Only coordinates of H atoms refined
$w = 55/[\sigma^2(F) + 0.0001F^2]$

$(\Delta/\sigma)_{max} = 0.44$
$\Delta\rho_{max} = 0.82$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}
Extinction correction: none
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)

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Molecule *A*				
C(1)	0.9617 (6)	0.0516 (5)	0.6618 (5)	6.7 (2)
C(2)	0.6869 (6)	0.0134 (4)	0.6249 (5)	6.5 (2)
C(3)	0.8057 (7)	0.1288 (6)	0.5238 (5)	7.0 (2)
C(4)	0.8244 (4)	0.1064 (3)	0.6381 (3)	4.6 (1)
C(5)	0.8636 (5)	0.2311 (3)	0.7565 (4)	6.0 (1)
O(1)	0.9632 (3)	0.2576 (3)	0.8443 (3)	2.24 (7)
N(1)	0.7618 (3)	0.3069 (3)	0.7473 (3)	4.26 (9)
O(2)	0.6393 (3)	0.2853 (3)	0.6437 (3)	5.52 (9)
C(6)	0.7841 (4)	0.4235 (3)	0.8494 (4)	4.5 (1)
C(7)	0.8675 (4)	0.5402 (3)	0.8467 (3)	4.2 (1)
O(3)	0.9890 (3)	0.5447 (2)	0.8322 (3)	6.8 (1)
N(2)	0.8083 (3)	0.6386 (3)	0.8701 (3)	4.21 (9)
C(8)	0.8878 (4)	0.7663 (3)	0.8963 (4)	4.4 (1)
C(9)	0.8177 (5)	0.8598 (4)	0.9680 (5)	5.6 (1)
C(10)	0.8881 (6)	0.7813 (5)	0.7834 (5)	6.9 (2)
H(O2)	0.556 (4)	0.254 (4)	0.670 (4)	
H(N2)	0.707 (4)	0.625 (4)	0.882 (4)	
Molecule *B*				
C(1′)	0.1849 (5)	0.6286 (5)	0.6453 (5)	6.7 (2)
C(2′)	0.2731 (6)	0.4405 (5)	0.5370 (4)	6.8 (2)
C(3′)	0.4508 (6)	0.6505 (6)	0.6597 (5)	7.7 (2)
C(4′)	0.3153 (4)	0.5613 (4)	0.6505 (3)	4.7 (1)
C(5′)	0.3580 (4)	0.5288 (3)	0.7595 (3)	3.6 (1)
O(1′)	0.4878 (2)	0.5680 (2)	0.8363 (2)	4.21 (7)
N(1′)	0.2567 (3)	0.4544 (3)	0.7763 (3)	3.98 (8)
O(2′)	0.1118 (3)	0.3984 (2)	0.6918 (2)	4.73 (8)
C(6′)	0.3020 (4)	0.3958 (4)	0.8603 (4)	4.2 (1)
C(7′)	0.3936 (4)	0.3013 (3)	0.8227 (3)	3.8 (1)
O(3′)	0.3960 (3)	0.2585 (2)	0.7204 (2)	4.71 (8)
N(2′)	0.4669 (3)	0.2677 (3)	0.9090 (3)	4.35 (9)
C(8′)	0.5496 (4)	0.1672 (3)	0.8890 (4)	5.0 (1)
C(9′)	0.4432 (6)	0.0398 (4)	0.8349 (5)	6.8 (2)
C(10′)	0.6689 (6)	0.1915 (5)	1.0067 (5)	7.0 (2)
H(O2′)	0.052 (4)	0.440 (3)	0.744 (3)	
H(N2′)	0.468 (4)	0.320 (4)	0.993 (4)	

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

Molecule *A*		Molecule *B*	
C(1)—C(4)	1.527 (8)	C(1′)—C(4′)	1.548 (7)
C(2)—C(4)	1.535 (7)	C(2′)—C(4′)	1.526 (6)
C(3)—C(4)	1.534 (8)	C(3′)—C(4′)	1.516 (8)
C(4)—C(5)	1.589 (5)	C(4′)—C(5′)	1.522 (6)
C(5)—O(1)	1.151 (5)	C(5′)—O(1′)	1.249 (3)
C(5)—N(1)	1.396 (6)	C(5′)—N(1′)	1.342 (5)
N(1)—O(2)	1.407 (4)	N(1′)—O(2′)	1.392 (3)
N(1)—C(6)	1.452 (4)	N(1′)—C(6′)	1.454 (6)
C(6)—C(7)	1.512 (6)	C(6′)—C(7′)	1.519 (6)
C(7)—O(3)	1.231 (5)	C(7′)—O(3′)	1.232 (5)
C(7)—N(2)	1.316 (5)	C(7′)—N(2′)	1.331 (5)
N(2)—C(8)	1.463 (5)	N(2′)—C(8′)	1.478 (5)
C(8)—C(9)	1.518 (7)	C(8′)—C(9′)	1.495 (6)
C(8)—C(10)	1.512 (8)	C(8′)—C(10′)	1.504 (7)
C(1)—C(4)—C(2)	109.2 (4)	C(1′)—C(4′)—C(2′)	110.7 (3)
C(1)—C(4)—C(3)	106.7 (5)	C(1′)—C(4′)—C(3′)	108.1 (4)
C(1)—C(4)—C(5)	104.2 (3)	C(1′)—C(4′)—C(5′)	111.5 (4)
C(2)—C(4)—C(3)	112.4 (4)	C(2′)—C(4′)—C(3′)	108.8 (4)
C(2)—C(4)—C(5)	108.9 (4)	C(2′)—C(4′)—C(5′)	109.3 (3)
C(3)—C(4)—C(5)	114.9 (3)	C(3′)—C(4′)—C(5′)	108.4 (3)
C(4)—C(5)—O(1)	124.8 (4)	C(4′)—C(5′)—O(1′)	122.3 (3)
C(4)—C(5)—N(1)	113.8 (3)	C(4′)—C(5′)—N(1′)	120.9 (3)
O(1)—C(5)—N(1)	121.3 (4)	O(1′)—C(5′)—N(1′)	116.8 (4)
C(5)—N(1)—O(2)	125.9 (3)	C(5′)—N(1′)—O(2′)	121.4 (4)
C(5)—N(1)—C(6)	119.5 (3)	C(5′)—N(1′)—C(6′)	121.5 (3)
O(2)—N(1)—C(6)	114.5 (3)	O(2′)—N(1′)—C(6′)	114.2 (3)
N(1)—C(6)—C(7)	114.2 (4)	N(1′)—C(6′)—C(7′)	112.0 (4)
C(6)—C(7)—O(3)	121.3 (4)	C(6′)—C(7′)—O(3′)	122.2 (4)
C(6)—C(7)—N(2)	115.9 (4)	C(6′)—C(7′)—N(2′)	114.1 (4)
O(3)—C(7)—N(2)	122.5 (4)	O(3′)—C(7′)—N(2′)	123.7 (3)
C(7)—N(2)—C(8)	123.5 (3)	C(7′)—N(2′)—C(8′)	123.3 (3)
N(2)—C(8)—C(9)	107.9 (4)	N(2′)—C(8′)—C(9′)	110.2 (4)
N(2)—C(8)—C(10)	111.7 (3)	N(2′)—C(8′)—C(10′)	108.4 (3)
C(9)—C(8)—C(10)	113.2 (4)	C(9′)—C(8′)—C(10′)	112.6 (5)

		A	*B*
C(4)—C(5)—N(1)—C(6)	ω_0	179.7 (4)	163.6 (3)
C(5)—N(1)—O(2)—H	ν	105 (2)	−119 (3)
C(5)—N(1)—C(6)—C(7)	φ	95.1 (5)	−64.4 (4)
N(1)—C(6)—C(7)—N(2)	ψ	133.1 (4)	165.0 (3)
C(6)—C(7)—N(2)—C(8)	ω_1	166.7 (3)	173.3 (3)

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

	H···O	N/O···O	N/O—H···O
N(2)—H···O(1$^{\text{i}}$)	1.98 (4)	2.953 (4)	157 (3)
N(2′)—H···O(1$^{\text{i}}$′)	1.98 (4)	3.001 (4)	169 (3)
O(2)—H···O(3′)	1.83 (5)	2.810 (4)	157 (4)
O(2′)—H···O(3$^{\text{ii}}$)	1.65 (4)	2.655 (4)	163 (4)

Symmetry codes: (i) $1 - x, 1 - y, 2 - z$; (ii) $x - 1, y, z$.

The high value of the *R* factor results from the poor quality of the crystals. The H atoms attached to N and O atoms were placed at 1.03 Å from the respective parent atom in the direction obtained from the refinement (Taylor & Kennard, 1983).

Program used to solve the structure: *SHELXS*86 (Sheldrick, 1985). Program used for full-matrix least-squares refinement: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

The authors thank D. Bayeul for technical assistance.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3-Diamino-5-hydrophenazinium Chloride Trihydrate

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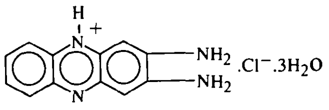
Abstract

The three rings of the phenazinium molecule of the title compound, $C_{12}H_{11}N_4^+.Cl^-.3H_2O$, are all coplanar, and protonation occurs preferentially on an aromatic N atom rather than the amino N atoms. The C—C and C—N bond lengths of the unsubstituted side of the molecule agree closely with those of phenazine, but those on the substituted side differ from those of phenazine and 1,2-benzenediamine.

Comment

In the synthesis of mono-*N*-acetyl-1,2-benzenediamine from acetyl chloride and 1,2-benzenediamine, some red crystalline needles were obtained as a by-product. These were shown *via* single-crystal structure determination to be 2,3-diamino-5-hydrophenazinium chloride trihydrate, (I). It is of interest to note that protonation occurs on a ring N atom rather than an amino N atom. This is consistent with the greater basicity of pyridine (p*K* = 5.25) compared with aniline (p*K* = 4.63). The mechanism for the formation of this product is not obvious. However, it has been reported that exposure of 2,3-napthalenediamine to light gives some of the corresponding phenazine (Cukor & Lott, 1965). The same cation, but with perchlorate as anion, was obtained in the cupric chloride oxidation of *o*-phenylenediamine (*i.e.* 1,2-benzenediamine) (Peng & Liaw, 1986). They postulate that it is formed *via* *o*-benzoquinonediimine as an intermediate. They also find protonation on an aromatic N atom, without giving any details.



(I)

The numbering scheme and the geometry of the molecule are shown in Fig. 1. Of the 18 directly bonded C—C or C—N distances, there are five where the disagreement is greater than 3σ. In each case, the difference arises from the greater asymmetry of bond lengths between the protonated and unprotonated sides of the cation, as found by Peng & Liaw (1986). This could possibly arise from the position of the anions.

The organic portion is essentially planar (Table 3). The C—C and C—N bond lengths of the unsubstituted side of the molecule agree closely with those found for phenazine (Herbstein & Schmidt, 1955; Wozniak, Kariuki & Jones, 1991). The corresponding bond lengths on the amino-substituted side of the molecule differ from those observed for *o*-phenylenediamine (Stahlhandske, 1981).

The crystal is stabilized by a complex hydrogen-bonding network that extends from the Cl atom to the two water molecules (*W*1 and *W*2), whose H atoms were found directly, then on to adjacent layers (*W*1 to the non-protonated ring atom N1, and *W*2 to another *W*1), and from the Cl atom to the N3—H and N4—H groups, then on to adjoining layers (N3 to another Cl and N4 to another *W*2). The third water molecule, *W*3, for which only one H atom was found directly, appears to be hydrogen bonded to the protonated ring atom N3.