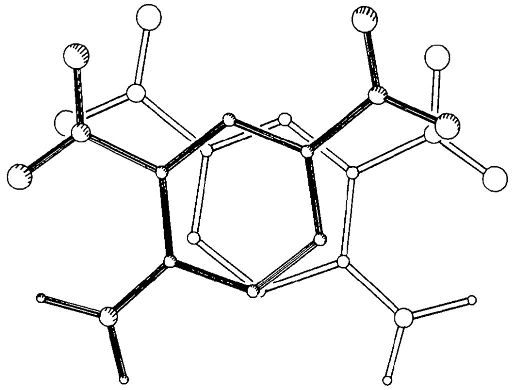

Fig. 3. Partial overlap (*ca* 75%) of aromatic nuclei 3·61 (7) Å apart, related by the twofold rotation axis at $x = 0, z = -\frac{1}{4}$.

Comparing the latter structure to the current one, many analogies can be detected such as the overall arrangement of the molecules (including the inversion centre), interactions with all O atoms, bifurcation of hydrogen bridges and stacking in the lattice (Fig. 3). The assumed correlation between acidity and crystal stability (Hilgenfeld & Saenger, 1981) is supported by the present structure which involves the more acidic 2,4-dinitroaniline, and by the fact that only poor crystals (and data) of the 1:2 adduct of 18-crown-6 and the less acidic *p*-nitroaniline (Weber, unpublished) could be obtained.

Due to the steric requirements of 2,4-dinitrophenylhydrazine, the system of hydrogen bridges in its complex with 18-crown-6 is quite intricate; the macrocycle, however, stays relatively free of conformational strain and keeps its approximate D_{3d} symmetry. In contrast, the rather 'simple' system of hydrogen bridges in the 2,4-dinitroaniline complex forces the ligand into an unusual strained conformation. This is further evidence for the structural versatility of a cyclic oligoether.

Diffractometer programs were written by Dr W. Clegg, Göttingen, and programs for structure solution and refinement by GMS. The authors are grateful to Dr W. M. Müller and Professor F. Vögtle, Bonn (FRG), for providing the sample, and the Verband der Chemischen Industrie for financial support.

References

Bombieri, G., de Paoli, G. & Immirzi, A. (1978). *J. Inorg. Nucl. Chem.* **40**, 799–802.

Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.

Dhaneshwar, N. N., Tavale, S. S. & Pant, L. M. (1978). *Acta Cryst.* B**34**, 2507–2509.

Dunitz, J. D., Dobler, M., Seiler, P. & Phizackerley, R. P. (1974). *Acta Cryst.*. B**30**, 2733–2738.

Goldberg, I. (1975). *Acta Cryst.* B**31**, 754–762.

Goldberg, I. (1978). *Acta Cryst.* B**34**, 3387–3390.

Hilgenfeld, R. & Saenger, W. (1981). *Z. Naturforsch. Teil B*, **36**, 242–247.

Holden, J. R., Dickinson, C. & Bock, C. M. (1972). *J. Phys. Chem.* **76**, 3597–3602.

Kaufmann, R., Knöchel, A., Kopf, J., Oehler, J. & Rudolph, G. (1977). *Chem. Ber.* **110**, 2249–2253.

Kawai, R., Kashino, S. & Haisa, M. (1976). *Acta Cryst.* B**32**, 1972–1975.

Knöchel, A., Kopf, J., Oehler, J. & Rudolph, G. (1978*a*). *Chem. Commun.* pp. 595–596.

Knöchel, A., Kopf, J., Oehler, J. & Rudolph, G. (1978*b*). *Inorg. Nucl. Chem. Lett.* **14**, 61–64.

Maverick, E., Seiler, P., Schweizer, W. B. & Dunitz, J. D. (1980). *Acta Cryst.* B**36**, 615–620.

Nagano, O. (1979). *Acta Cryst.* B**35**, 465–467.

Nagano, O., Kobayashi, A. & Sasaki, Y. (1978). *Bull. Chem. Soc. Jpn*, **51**, 790–793.

Suh, I.-H. & Saenger, W. (1978). *Angew. Chem. Int. Ed. Engl.* **17**, 534.

Weber, G. & Saenger, W. (1980). *Acta Cryst.* B**36**, 424–428.

Weber, G. & Sheldrick, G. M. (1980). *Acta Cryst.* B**36**, 1978–1980.

Acta Cryst. (1981). B**37**, 2111–2114

5-Nitro-L-histidine Monohydrate

By X. Solans and M. Font-Altaba

Departamento de Cristalografía y Mineralogía, Universidad de Barcelona, Gran Via 585, *Barcelona* 7, *Spain*

(*Received* 18 *March* 1981; *accepted* 18 *May* 1981)

Abstract. $C_6H_8N_4O_4.H_2O$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}519$ (4), $b = 10{\cdot}757$ (3), $c = 6{\cdot}590$ (1) Å, $V = 887{\cdot}5$ (7) Å^3, $Z = 4$, $D_c = 1{\cdot}63$ Mg m^{-3}. The structure was solved with *MULTAN* and refined by full-matrix least squares. The final R is 0·045 for 1127 observed reflections. The torsion angles are similar to those obtained in L-histidine. The nitro substituent modifies the bond distances in the imidazolyl ring.

0567-7408/81/112111-04$01.00

Introduction. The role of histidine in the biological activity of natural peptides is being studied by the Department of Organic Chemistry of the University of Barcelona (Giralt, Ludevid & Pedroso, 1979). In particular, 5-nitro-L-histidine has been used to substitute the L-histidine in hypothalamic peptide hormones in order to study the acidity–activity relationship (Giralt, Ludevid, Albericio & Bassedas, 1979). To determine the structure–activity relationship, the present X-ray analysis has been carried out.

Colourless prismatic crystals were obtained by recrystallization from aqueous solution. A crystal 0·03 × 0·03 × 0·1 mm was selected for crystal measurements on a Phillips PW 1100 four-circle diffractometer. The unit cell was measured by automatically centring 25 independent reflections and refining the orientation matrix and unit-cell parameters by least squares. Intensities were collected with Mo *Kα* radiation, monochromatized by reflection from a graphite crystal. 1162 independent reflections were measured in the range $2\theta \leq 60°$, 1127 of which were considered as observed by the criterion $I \geq 2·5\sigma(I)$.

The structure was solved with *MULTAN* (Main, Woolfson, Hull, Lessinger, Germain & Declercq, 1980). An *E* map computed with the phases from the set with the highest combined figure of merit revealed peaks for all non-hydrogen atoms. The structure was isotropically and anisotropically refined by means of a full-matrix least-squares method with *SHELX* (Sheldrick, 1976). The function minimized was $w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0·00039|F_o|^2]^{-1}$. The scattering factors were from *International Tables for X-ray Crystallography* (1974) and anomalous-scattering factors from Cromer & Liberman (1970). A difference synthesis at $R = 0·065$ revealed the positions of hydrogen atoms, which were refined isotropically.

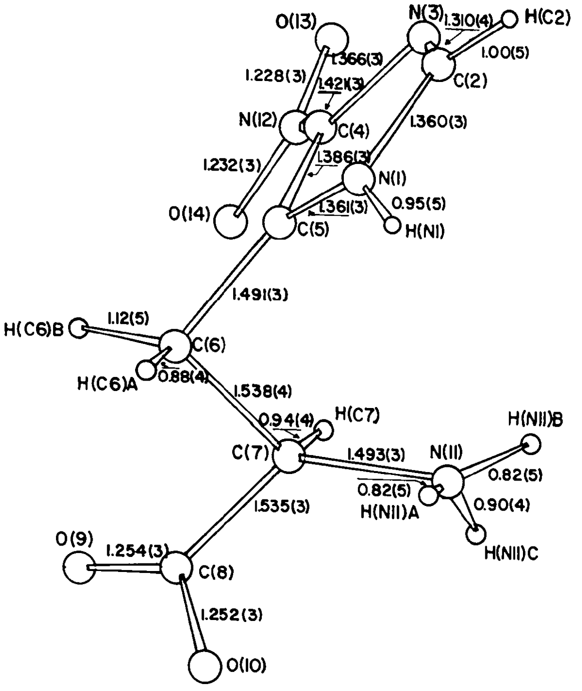

Fig. 1. View of 5-nitro-L-histidine with the numbering of atoms and bond distances in Å.

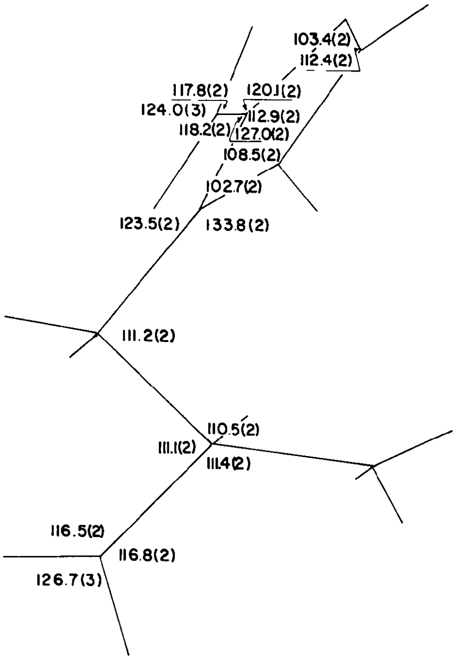

Fig. 2. Bond angles in degrees.

Table 1. *Atomic parameters* ($\times 10^4$; *for* H $\times 10^3$) *and equivalent isotropic temperature coefficients*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq} (Å^2)
N(1)	2668 (2)	3863 (2)	3277 (5)	2·0 (2)
C(2)	1669 (2)	4298 (3)	2882 (6)	2·4 (2)
N(3)	960 (2)	3405 (2)	2774 (4)	2·2 (2)
C(4)	1547 (2)	2356 (2)	3116 (5)	1·6 (2)
C(5)	2621 (2)	2602 (2)	3436 (4)	1·5 (2)
C(6)	3572 (2)	1806 (3)	3840 (5)	1·8 (2)
C(7)	3942 (2)	1138 (2)	1899 (5)	1·6 (2)
C(8)	4849 (2)	219 (3)	2356 (5)	1·8 (2)
O(9)	4582 (2)	−803 (2)	3117 (5)	2·9 (2)
O(10)	5778 (2)	567 (2)	1934 (5)	2·6 (2)
N(11)	4264 (2)	2061 (2)	323 (4)	1·7 (2)
N(12)	1048 (2)	1170 (2)	3065 (4)	2·1 (2)
O(13)	69 (2)	1136 (3)	2985 (6)	3·8 (2)
O(14)	1623 (2)	241 (2)	3098 (4)	2·8 (2)
O(15)	7263 (2)	2564 (2)	1647 (4)	2·9 (2)
H(N1)	331 (3)	432 (4)	302 (8)	3·2 (3)
H(C2)	160 (3)	522 (4)	271 (7)	3·2 (3)
H(C6)*A*	409 (4)	231 (4)	419 (7)	3·2 (3)
H(C6)*B*	338 (3)	101 (4)	490 (8)	3·2 (3)
H(C7)	337 (3)	72 (4)	130 (8)	3·2 (3)
H(N11)*A*	459 (4)	267 (4)	72 (7)	3·2 (3)
H(N11)*B*	370 (4)	227 (5)	−21 (8)	3·2 (3)
H(N11)*C*	480 (3)	181 (4)	−49 (7)	3·2 (3)
H(O15)*A*	686 (3)	205 (4)	123 (8)	3·2 (3)
H(O15)*B*	674 (3)	324 (4)	121 (8)	3·2 (3)

The refinement was terminated at $R = 0{\cdot}045$ for all observed reflections, where R is defined as $\sum||F_o| - |F_c||/\sum|F_o|$.* The final atomic parameters are listed in Table 1. Fig. 1 shows a view of the molecule, the numbering of the atoms and the bond distances, Fig. 2 shows the bond angles.

Discussion. The imidazolyl ring is essentially planar with the largest deviation from the mean plane 0·001 (4) Å. A comparison with other L-histidine compounds (Bennet, Davidson, Harding & Morelle, 1970; Fraser & Harding, 1967; Fuess & Bartunik, 1976; Fuess, Hohlwein & Mason, 1977; Lehmann, Koetzle & Hamilton, 1972; Madden, McGandy & Seeman, 1972) shows differences in the bond distances of the imidazolyl ring (Table 2), so the nitro group produces a localization of the C—N double bond at C(2)—N(3), and an electronic delocalization of the C(4)=C(5) bond in the N(3)—C(4)=C(5)—N(1) group.

Table 2. *Comparative study of the bond distances* (Å) *in the imidazolyl group*

	This work	Other L-histidines	
		Mean	Range
N(1)–C(2)	1·360	1·324	1·309–1·343
C(2)–N(3)	1·310	1·337	1·314–1·349
N(3)–C(4)	1·366	1·371	1·359–1·379
C(4)–C(5)	1·386	1·369	1·358–1·389
C(5)–N(1)	1·361	1·385	1·376–1·392

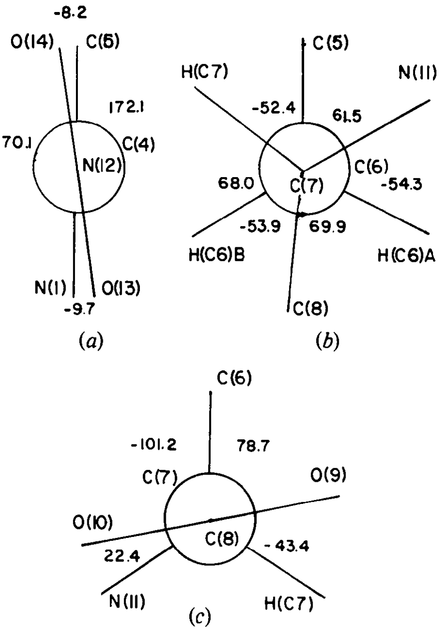

Fig. 3. Newman projections along (*a*) C(4)–N(12), (*b*) C(6)–C(7) and (*c*) C(7)–C(8) (e.s.d.'s are less than 0·4°).

The main torsion angles are shown in Fig. 3. The title compound has the open form typical of uncomplexed L-histidine. The torsion angles are similar to those in L-histidine (Madden, McGandy & Seeman, 1972). [There are differences of −6·8° in C(7)–C(8) and of −4·3° in C(6)–C(7).]

The hydrogen bonds determine the packing of the structure (Table 3 and Fig. 4). A strong hydrogen bond [N(5)–H(N5)···O(10)] links two molecules related by a twofold screw axis parallel to **b**, while weak hydrogen bonds link a molecule with the water molecules O(15) or with the molecules related by a twofold screw axis parallel to **a**. Other short intermolecular distances are N(11)···O(14^{i}) 3·084 (5) Å, and N(11)···O(13^{ii}) 3·087 (5) Å, where (i) is $0{\cdot}5 - x, -y, z - 0{\cdot}5$ and (ii) is $0{\cdot}5 + x, 0{\cdot}5 - y, -z$.

Table 3. *Hydrogen-bond distances in* Å

E.s.d.'s: *AB* less than 0·005 Å and H*B* less than 0·05 Å.

A–H···*B*	*AB*	H*B*
N(11)–H(N11)*C*···N(3^{i})	2·987	2·10
N(11)–H(N11)*A*···O(9^{ii})	2·903	2·09
N(11)–H(N11)*B*···O(15^{iii})	2·850	2·04
O(15)–H(O15)*A*···O(10^{iv})	2·848	2·14
O(15)–H(O15)*B*···O(9^{ii})	2·907	2·00
N(5)–H(N5)···O(10^{ii})	2·677	1·77

Symmetry code

(i) $0{\cdot}5 + x, 0{\cdot}5 - y, -z$
(ii) $1 - x, 0{\cdot}5 + y, 0{\cdot}5 - z$
(iii) $x - 0{\cdot}5, 0{\cdot}5 - y, -z$
(iv) x,y,z

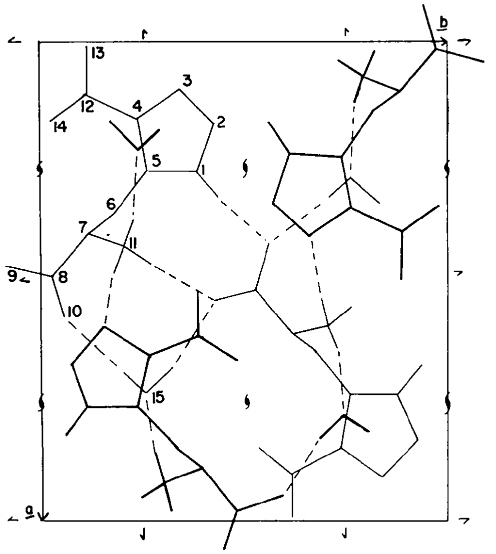

Fig. 4. Projection of unit-cell contents down the *c* axis.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36183 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

We thank Dr J. L. Briansó (Universidad Autonoma de Barcelona) for the use of computer facilities at this University and Dr E. Giralt for providing the samples and for discussions. This work was sponsored by the University of Barcelona.

References

Bennet, I., Davidson, A. G. H., Harding, M. M. & Morelle, I. (1970). *Acta Cryst.* B**26**, 1722–1729.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Fraser, K. A. & Harding, M. M. (1967). *J. Chem. Soc. A*, pp. 415–420.

Fuess, H. & Bartunik, H. D. (1976). *Acta Cryst.* B**32**, 2803–2806.

Fuess, H., Hohlwein, D. & Mason, S. A. (1977). *Acta Cryst.* B**33**, 654–659.

Giralt, E., Ludevid, M. D., Albericio, F. & Bassedas, M. (1979). *Bioorg. Chem.* **8**, 59–67.

Giralt, E., Ludevid, M. D. & Pedroso, E. (1979). *Peptides* 1978, pp. 485–488. Wrocław Univ. Press.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 99. Birmingham: Kynoch Press.

Lehmann, M. S., Koetzle, T. F. & Hamilton, W. C. (1972). *Int. J. Pept. Protein Res.* **4**, 229–239.

Madden, J. J., McGandy, E. L. & Seeman, N. C. (1972). *Acta Cryst.* B**28**, 2377–2382.

Main, P., Woolfson M. M., Hull, S. E., Lessinger, L., Germain, G. & Declercq, J. P. (1980). *MULTAN. A System of Computer Programs for Crystal Structure Determination from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Sheldrick, G. M. (1976). *SHELX.* Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1981). B**37**, 2114–2117

18$\langle O_5$(2,6-Pyridino)1$\cdot 2_4 \cdot$1-coronand-6$\rangle$2,16-dione Dihydrate[*]

By George R. Newkome,[†] Frank R. Fronczek and Dalip K. Kohli

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, *USA*

(*Received* 23 *January* 1981; *accepted* 18 *May* 1981)

Abstract. $C_{15}H_{19}NO_7.2H_2O$, monoclinic, $P2_1/n$, a = 9·622 (3), b = 8·791 (6), c = 21·353 (3) Å, β = 96·40 (2)°, Z = 4, d_c = 1·339 Mg m^{-3}, R = 0·055 for 994 observations measured by diffractometer. The macrocyclic polyethereal bis-lactone exists in a nearly flat conformation, in which six potential hydrogen-bond acceptor atoms (N and O) approximate a circle of radius 2·8 Å. A water molecule lies beneath this circle, 1·49 (1) Å from its center, and forms its best hydrogen bond *not* with the N atom, but with the polyethereal O atom most distant from the N atom. A second water molecule is hydrogen bonded to the first with an O···O distance of 3·01 (1) Å.

Introduction. Crown ethers and substituted analogs have been shown to play an active role in the catalysis of organic reactions and the dissolution of inorganic cations (Lehn, 1979; Izatt & Christensen, 1979; Bradshaw, Maas, Izatt & Christensen, 1979; Newkome, Sauer, Roper & Hager, 1977). Application of these macrocycles, *e.g.* (I), to catalyze the decomposition of aryldiazonium salts (Bartsch & Juri, 1980, and references cited therein; Kuokkanen & Virtanen, 1979) prompted us to ascertain the molecular geometry of (I) prior to inclusion of the diazonium moiety. Force-field calculations (Gandour, 1980) on a simple model, dimethyl 2,6-pyridinedicarboxylate (II), support the favored orientation to be (II*a*) by *ca* 13 kJ mol^{-1}. Thus, the question of whether (I) should possess a similar geometry (III) in the crystalline state was addressed. We herein report the crystal structure of the unexpected dihydrate of (I), which exhibits the conformation given in (II*b*), and from the results suggest the possible necessity of inclusion of water (or solvent) in the cavity to ensure the anticipated circular orientation (Lehn, 1978) as a prerequisite to inclusion of a larger guest.

The bis-lactone (I), prepared by known procedures (Frensch & Vögtle, 1977), was shown by satisfactory elemental analysis to exist as a hydrate (m.p. 338–339 K), which can be liberated of the water molecule(s) by warming (333 K) *in vacuo* to give the free molecule (m.p. 356–357 K) as an anhydrous, ill-defined microcrystalline solid. In order to obtain a suitable single crystal, (I) was recrystallized from hexane to regenerate the unexpected dihydrate.

---

[*] IUPAC nomenclature: 3,6,9,12,15-pentaoxa-21-azabicyclo[15.3.1]henicosa-1(21),17,19-triene-2,16-dione dihydrate.

[†] To whom correspondence should be addressed.

0567-7408/81/112114-04$01.00