

planar as can be seen in Table 3 which gives the deviation of the atoms from the least-squares plane through the aromatic ring as well as torsion angles along the side chain. The methyl C atom C(10) is the only non-H atom more than 0.27 Å from that plane. There is no obvious reason for this configuration other than crystal-packing efficiency.

Bond distances can be compared with compounds such as 3-(*p*-chlorophenyl)-1,1-dimethylurea (Baughman, Hembre, Helland & Jacobson, 1980). Our average aromatic C—C distance of 1.380 (10) Å compares well with 1.38 (2) Å in that study, and our average C—N distance of 1.488 (3) Å compares with their value of 1.45 (2) Å.

Acta Cryst. (1982). B38, 627–629

N^α-Acetyl-5-nitro-L-histidine

BY X. SOLANS AND M. FONT-ALTABA

Department of Crystallography and Mineralogy, University of Barcelona, Gran Via 585, Barcelona 7, Spain

(Received 14 May 1981; accepted 15 July 1981)

Abstract. C₈H₁₀N₄O₅, orthorhombic, *P*2₁2₁2₁, *a* = 15.425 (3), *b* = 9.756 (2), *c* = 6.822 (1) Å, *V* = 1026.6 (6) Å³, *Z* = 4, *D*_c = 1.56 Mg m⁻³. The structure was solved with the *MULTAN* system and refined by the full-matrix least-squares method. The final *R* value is 0.063 for 1534 observed reflections. The bond distances and angles are similar to those obtained for 5-nitro-L-histidine. Most torsion angles are similar to those in other L-histidine derivatives, but the C(7)—C(8) torsion angle differs by about 90°.

Introduction. The role of histidine in the biological activity of natural peptides is being studied at the Department of Organic Chemistry of the University of Barcelona (Giralt, Ludevid & Pedroso, 1979) — in particular, the influence of the 5-nitro substituent in hypothalamic peptide hormones (Giralt, Ludevid, Albericio & Bessedas, 1979). In order to determine the structure–activity relationship due to the presence of a 5-nitro substituent, the crystal structure determinations of 5-nitro-L-histidine (Solans & Font-Altaba, 1981) and the title compound have been carried out.

Colourless prismatic crystals were obtained from an aqueous solution. A crystal 0.2 × 0.2 × 0.3 mm was selected for measurements on a Philips 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 the least-squares method. Intensities

References

- BAUGHMAN, R. G., HEMBRE, R. I., HELLAND, B. J. & JACOBSON, R. A. (1980). *Cryst. Struct. Commun.* **9**, 749–752.
- ENCINAS, M. V. & SCAINANO, J. C. (1979). *J. Am. Chem. Soc.* **101**, 2146–2152.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MAXWELL, C. E. (1955). *Org. Synth. Collect.* **3**, 305–306.
- RASHID, S., NAQVI, S. N. H., ASHRAFI, S. H. & QURASHI, A. H. (1974). *Pak. J. Zool.* **6** (1–2), 17–24.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

were collected with Mo *K*α radiation, monochromatized by reflection from a graphite crystal. 1549 independent reflections were measured in the range 2θ ≤ 60°; 1534 of these were considered as observed according to the condition *I* > 2.5σ(*I*).

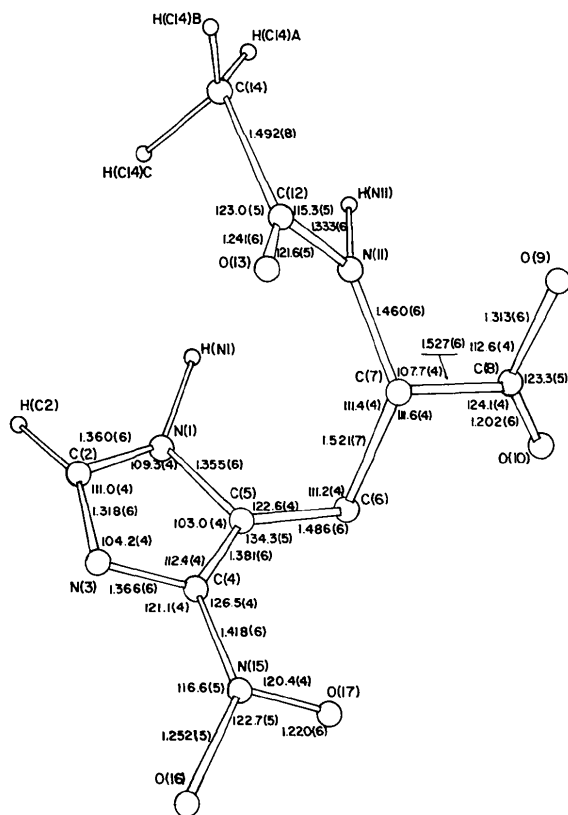
The structure was solved with the *MULTAN* system of computer programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). An *E* map computed with the phases from the set with the highest combined figure of merit revealed peaks for all non-hydrogen atoms. The structure was refined by means of the full-matrix least-squares method with *SHELX* (Sheldrick, 1976). The function minimized was |*F*_o − *F*_c|². A difference synthesis at *R* = 0.070 revealed the positions of six H atoms, while H atoms linked to C(6) and C(7) were given calculated positions. A subsequent refinement with anisotropic thermal parameters for C, N, O and isotropic parameters for H gave a final *R* factor of 0.063 for all observed reflections.*

The final atomic parameters are listed in Table 1. Fig. 1 shows a view of the molecule, the numbering of the atoms and bond distances and angles.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36302 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$, for H $\times 10^3$) and isotropic thermal parameters (\AA^2)For non-hydrogen atoms $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} / <i>U</i>
N(1)	4796 (3)	2135 (4)	7048 (7)	2.1 (6)
C(2)	5194 (4)	1015 (5)	7825 (9)	2.3 (6)
N(3)	4682 (3)	-66 (4)	7756 (7)	2.2 (6)
C(4)	3946 (3)	404 (5)	6870 (8)	1.7 (6)
C(5)	4002 (3)	1773 (5)	6374 (7)	1.7 (6)
C(6)	3436 (3)	2736 (5)	5273 (8)	1.9 (6)
C(7)	3669 (3)	2756 (5)	3106 (8)	1.7 (6)
C(8)	3109 (3)	3776 (5)	1972 (8)	1.9 (6)
O(9)	3261 (3)	3749 (5)	78 (6)	3.2 (6)
O(10)	2574 (3)	4507 (4)	2714 (6)	2.7 (6)
N(11)	4574 (3)	3138 (4)	2805 (7)	2.0 (6)
C(12)	5203 (4)	2209 (5)	2616 (8)	2.3 (6)
O(13)	5042 (3)	963 (4)	2544 (9)	3.7 (6)
C(14)	6103 (4)	2769 (8)	2610 (14)	3.9 (6)
N(15)	3232 (3)	-479 (4)	6522 (7)	2.4 (6)
O(16)	3298 (3)	-1683 (4)	7140 (7)	3.3 (6)
O(17)	2590 (3)	-60 (5)	5668 (8)	3.6 (6)
H(C6)A	277 (3)	241 (5)	543 (8)	4.9 (7)
H(C6)B	351 (3)	376 (5)	587 (8)	4.9 (7)
H(C7)	356 (3)	173 (5)	256 (8)	4.9 (7)
H(N1)	489 (5)	280 (8)	656 (14)	4.9 (7)
H(C2)	594 (5)	91 (8)	890 (12)	4.9 (7)
H(N11)	485 (5)	380 (8)	282 (15)	4.9 (7)
H(C14)A	604 (5)	360 (8)	226 (15)	4.9 (7)
H(C14)B	648 (5)	230 (8)	251 (14)	4.9 (7)
H(C14)C	622 (5)	261 (9)	456 (13)	4.9 (7)

Fig. 1. View of the molecule with the numbering of the atoms, and bond distances (\AA) and angles ($^\circ$).

Discussion. The bond distances and angles are similar to those obtained by Solans & Font-Altava (1981) for 5-nitro-L-histidine. The main differences are due to electronic localization in the C(8)–O(10) bond, and the electronic delocalization in the *N*^α-acetyl group. The title compound and 5-nitro-L-histidine differ from other L-histidine derivatives (Bennett, Davidson, Harding & Morelle, 1970; Fraser & Harding, 1967; Fuess & Bartunik, 1976; Fuess, Hohlwein & Mason, 1977; Lehmann, Koetzle & Hamilton, 1972; Madden, McGandy & Seeman, 1972) by the presence of the nitro group, which produces the localization of the C–N double bond at C(2)–N(3).

The main torsion angles are shown in Fig. 2. The torsion angle C(6)–C(7)–C(8)–O(10) is -2.7° , while its value is -101.2° in 5-nitro-L-histidine and -94.4° in L-histidine. This difference is due to molecular packing (Fig. 3). A strong hydrogen bond (Table 2) links the carboxylic groups. The other torsion angles are similar to those obtained in the above-mentioned compounds (differences are less than 6.5°).

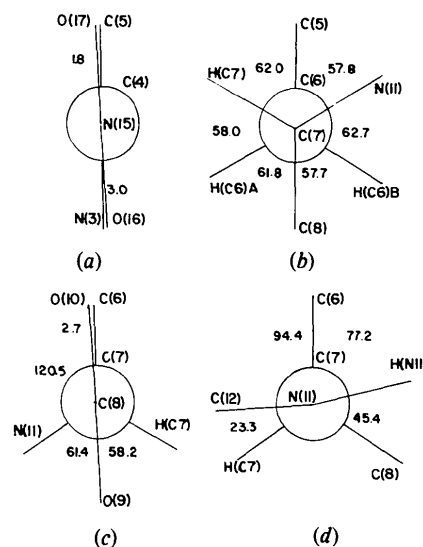
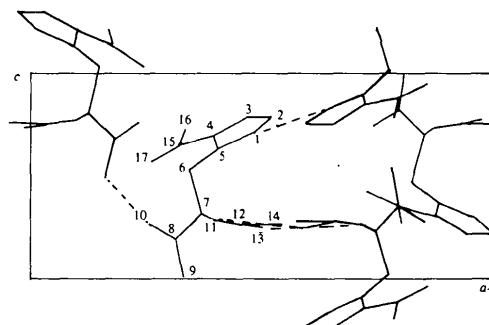
Fig. 2. Projections down (a) C(4)–N(15), (b) C(6)–C(7), (c) C(7)–C(8), and (d) C(7)–N(11). E.s.d.'s are $\leq 0.2^\circ$.Fig. 3. The unit-cell contents projected down the *b* axis.

Table 2. *Hydrogen-bond distances* (Å)

A-B...C	AC	BC
N(1)–H(N1)···N(3) ⁱ	2.850 (6)	2.23 (8)
O(9)–H(O9)···O(10) ⁱⁱ	2.676 (6)	
N(11)–H(N11)···O(13) ⁱⁱⁱ	2.829 (6)	2.13 (8)

Symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

As in L-histidine and 5-nitro-L-histidine, short intermolecular distances are present in the title compound. These are O(16)···O(10)ⁱ = 3.091 (6) and O(17)···N(15)ⁱⁱ = 3.143 (6) Å [(i) = $\frac{1}{2} - x, y, \frac{1}{2} + z$; (ii) = $\frac{1}{2} - x, \bar{y}, z - \frac{1}{2}$].

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

References

BENNETT, I., DAVIDSON, A. G. H., HARDING, M. M. & MORELLE, J. (1970). *Acta Cryst.* **B26**, 1722–1729.

FRASER, K. A. & HARDING, M. M. (1967). *J. Chem. Soc. A*, pp. 415–420.
 FUESS, H. & BARTUNIK, H. D. (1976). *Acta Cryst.* **B32**, 2803–2806.
 FUESS, H., HOHLWEIN, D. & MASON, S. A. (1977). *Acta Cryst.* **B33**, 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. 485–486. Wroclaw Univ. 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.* **B28**, 2377–2382.
 MAIN, P., FISKE, S., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1980). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 SHELDRIK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.
 SOLANS, X. & FONT-ALTABA, M. (1981). *Acta Cryst.* **B37**, 2111–2114.

Acta Cryst. (1982). **B38**, 629–632

A 2:1 Complex of 4-Nitro-1,2-benzenediamine and 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6)

BY GABRIELA WEBER

Anorganisch-Chemisches Institut der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

(Received 1 June 1981; accepted 15 July 1981)

Abstract. $2C_6H_7N_3O_2 \cdot C_{12}H_{24}O_6$, $M_r = 570.60$, monoclinic, $P2_1/c$, $a = 9.740$ (2), $b = 10.178$ (3), $c = 14.615$ (3) Å, $\beta = 95.12$ (5)°, $Z = 2$, $d_c = 1.313$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.096$ mm⁻¹; $R = 0.047$, $R_w = 0.054$ for 2101 independent data. The two 4-nitro-1,2-benzenediamine molecules, related by a centre of inversion, are inclined with dihedral angles 120 (1)° 'above' and 'below' the plane formed by the six O atoms of the crown ether. They are linked to the latter via H bridges, none of which is bifurcated: six H atoms of the four NH₂ groups in the complex serve as e⁻ acceptors from only four O atoms, i.e. two O atoms receive two H bonds each, two receive one H bond each, and two O atoms remain without strong interactions. This pattern causes the macrocycle to adopt a conformation with a sequence of unique torsion angles $ag^+a ag^+a g^+g^+a$ which differs from the approximate D_{3d} symmetry normally found.

Introduction. A number of crystalline adducts of 18-crown-6 (or its derivatives) with H-bond donors have been prepared during the last decade (Pedersen, 1971; Gokel, Cram, Liotta, Harris & Cook, 1974; el Basyony, Klimes, Knöchel, Oehler & Rudolph, 1976; Vögtle & Müller, 1980, 1981). In these compounds, as in the well known complexes with 'fitting' metal ions (e.g. Dunitz, Dobler, Seiler & Phizackerley, 1974), the ligand usually adopts a conformation with approximate D_{3d} symmetry, e.g. with dimethyl acetylenedicarboxylate (Goldberg, 1975), malononitrile (Kaufmann, Knöchel, Kopf, Oehler & Rudolph, 1977), NH₄⁺ (Nagano, Kobayashi & Sasaki, 1978), benzylammonium (Bovill, Chadwick, Sutherland & Watkin, 1980), 2,4-dinitrophenylhydrazine (Hilgenfeldt & Saenger, 1981) and *p*-nitroaniline (Weber, 1981). Recently reported structures of adducts with urea (Harkema, van Hummel, Daasvatn & Reinhoudt,