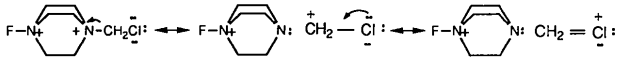
Comparison of cations derived from monoquaternization of mono-substituted 1,4-diazabicyclo-[2.2.2]octane with the diamine, itself in hydrogen-bonded complexes (Takama, Yasui, Harada, Kasai, Tanaka & Toda, 1988; Yasui, Yabuki, Takama, Harada, Kasai, Tanaka & Toda, 1989), shows that while the non-quaternized N-atom environment remains similar to that in the parent diamine, the bonds around the tetrahedrally coordinated N atom have lengthened significantly [1.485 (8)–1.52 (1) Å *cf.* 1.445 (9)–1.454 (9) Å at the amine N atom]. This change is accompanied by a contraction of some of the ring C—C bonds, so that the bridgehead N···N distances of 2.56 (1) and 2.57 (1) Å remain identical to that in 1,4-diazabicyclo[2.2.2]octane. On fluorination all N—C bonds become indistinguishable and the ring C—C distances are uniformly contracted; hence the bridgehead distance shortens to 2.48 (2) Å. The bond contraction that takes place when the amine becomes a dispositive cation is typical, although the bridgehead N···N distance shows some variation, with the value of 2.548 Å for the 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane dication matching that in the neutral non-quaternized amine, and the diprotonated species, like the *N*-fluoro salt (1), possessing a contracted N···N distance [to 2.475 (4) Å].

A further consequence of fluorination is a weakening of the $^{+}$N—CH_2Cl bond [1.53 (2) Å *cf.* 1.491 (7) and 1.48 (1) Å], coupled with a shortening of the C—Cl bond [1.71 (2) Å *cf.* 1.760 (8) and 1.74 (1) Å], implying that partial donation of a Cl-atom lone pair is involved, as indicated by the resonance formulation below.



A decrease in electron density at the C atom of the CH_2Cl group once *N*-fluorination has occurred is revealed by the ^{1}H NMR spectral data: the protons of the CH_2Cl group in the *N*-fluoro compound (1) resonate *ca* 0.5 p.p.m. to lower field than those in the monoquaternary salt (2) (Banks, Fields, Khaffaf & Sharif, 1993).

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Structure of *N*-Acetyl-L-homocarnosine Monohydrate

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Abstract. *N*-(4-Acetamido-1-oxobutyl)-L-histidine monohydrate, $C_{12}H_{18}N_4O_4.H_2O$, $M_r = 300.3$, orthorhombic, $P2_12_12_1$, $a = 7.181$ (1), $b = 13.919$ (1), $c = 14.547$ (1) Å, $V = 1454.1$ Å^3, $Z = 4$, $D_x = 1.37$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 1.01$ cm^{-1}, $F(000) = 640$, $T = 291$ K, final $R = 0.038$ for 1486

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0108-2701/93/030495-03$06.00

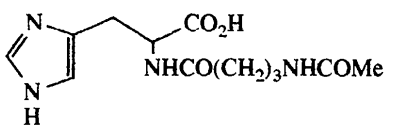
Table 1. *Fractional coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O(1)	0.1392 (3)	0.3376 (1)	0.3521 (1)	0.039
O(2)	0.3214 (3)	0.2223 (1)	0.4077 (1)	0.039
O(3)	0.5081 (3)	0.4900 (1)	0.3361 (1)	0.036
O(4)	0.5844 (3)	0.8946 (2)	0.4207 (1)	0.045
O(100)	−0.0920 (3)	0.7894 (2)	0.3476 (2)	0.057
N(1)	0.3175 (3)	0.4769 (1)	0.4581 (1)	0.028
N(2)	0.5876 (3)	0.3964 (2)	0.6687 (1)	0.029
N(3)	0.4677 (3)	0.5063 (2)	0.7538 (2)	0.034
N(4)	0.3060 (3)	0.8413 (2)	0.3705 (2)	0.036
C(1)	0.2653 (4)	0.3075 (2)	0.4041 (2)	0.028
C(2)	0.3617 (3)	0.3762 (2)	0.4725 (2)	0.025
C(3)	0.3122 (4)	0.3444 (2)	0.5706 (2)	0.031
C(4)	0.4012 (4)	0.4045 (2)	0.6436 (2)	0.028
C(5)	0.6221 (4)	0.4585 (2)	0.7354 (2)	0.033
C(6)	0.3285 (4)	0.4739 (2)	0.6970 (2)	0.034
C(7)	0.3963 (4)	0.5270 (2)	0.3899 (2)	0.027
C(8)	0.3383 (4)	0.6311 (2)	0.3826 (2)	0.035
C(9)	0.4628 (4)	0.6904 (2)	0.3200 (2)	0.038
C(10)	0.3791 (5)	0.7857 (2)	0.2933 (2)	0.039
C(11)	0.4123 (4)	0.8909 (2)	0.4286 (2)	0.037
C(12)	0.3158 (5)	0.9444 (3)	0.5031 (3)	0.063

unique observed reflections. The imidazole ring is fully protonated, thus forming a zwitterion. The histidine side chain adopts an 'open' or extended conformation similar to other histidine derivatives, while the acetamidooxobutyl chain bends at the 4-butyl C(10) atom so that it runs parallel to the imidazole ring. There are strong intermolecular hydrogen bonds between the O atoms of the carboxylic acid group and the N atoms of the imidazole ring: O(2)···N(2) 2.605 (3); O(1)···N(3) 2.712 (3) Å.

Introduction. Analysis of the constituents of rat brain has yielded a number of histidine derivatives (O'Dowd, Cairns, Trainor, Robins & Miller, 1990). These were separated by high-performance liquid chromatography. The structure of one of these histidine derivatives was established, by comparison with synthetic material, as *N*-acetyl-L-homocarnosine (1). It was prepared by coupling acetamidobutanoic acid with L-histidine lithium salt by a mixed anhydride method. Although the structure had been established by NMR spectroscopy (O'Dowd *et al.*, 1990) the molecular conformation was thought to be of interest.



(1)

Experimental. Colourless irregular crystals grown from ethanol; crystal *ca* 0.5 × 0.3 × 0.2 mm used for data collection on an Enraf–Nonius CAD-4 diffractometer. Preliminary Weissenberg photographs

Table 2. *Bond lengths* (Å) *and angles* (°)

O(1)—C(1)	1.252 (4)	O(2)—C(1)	1.255 (4)
O(3)—C(7)	1.234 (4)	O(4)—C(11)	1.242 (4)
N(1)—C(2)	1.453 (3)	N(1)—C(7)	1.338 (4)
N(2)—C(4)	1.393 (4)	N(2)—C(5)	1.322 (4)
N(3)—C(5)	1.321 (4)	N(3)—C(6)	1.374 (4)
N(4)—C(10)	1.461 (4)	N(4)—C(11)	1.332 (4)
C(1)—C(2)	1.543 (4)	C(2)—C(3)	1.537 (4)
C(3)—C(4)	1.495 (4)	C(4)—C(6)	1.345 (4)
C(7)—C(8)	1.512 (4)	C(8)—C(9)	1.519 (4)
C(9)—C(10)	1.507 (4)	C(11)—C(12)	1.487 (5)
C(2)—N(1)—C(7)	121.1 (3)	C(4)—N(2)—C(5)	108.7 (3)
C(5)—N(3)—C(6)	108.8 (3)	C(10)—N(4)—C(11)	123.8 (3)
O(1)—C(1)—O(2)	125.0 (3)	O(1)—C(1)—C(2)	120.5 (3)
O(2)—C(1)—C(2)	114.5 (3)	N(1)—C(2)—C(1)	114.0 (2)
N(1)—C(2)—C(3)	111.2 (2)	C(1)—C(2)—C(3)	108.5 (2)
C(2)—C(3)—C(4)	113.5 (3)	N(2)—C(4)—C(3)	123.5 (3)
N(2)—C(4)—C(6)	106.2 (3)	C(3)—C(4)—C(6)	130.3 (3)
N(2)—C(5)—N(3)	108.7 (3)	N(3)—C(6)—C(4)	107.6 (3)
O(3)—C(7)—N(1)	121.9 (3)	O(3)—C(7)—C(8)	122.3 (3)
N(1)—C(7)—C(8)	115.8 (3)	C(7)—C(8)—C(9)	113.6 (3)
C(8)—C(9)—C(10)	113.4 (3)	N(4)—C(10)—C(9)	114.3 (3)
O(4)—C(11)—N(4)	122.2 (3)	O(4)—C(11)—C(12)	120.7 (3)
N(4)—C(11)—C(12)	117.1 (3)		

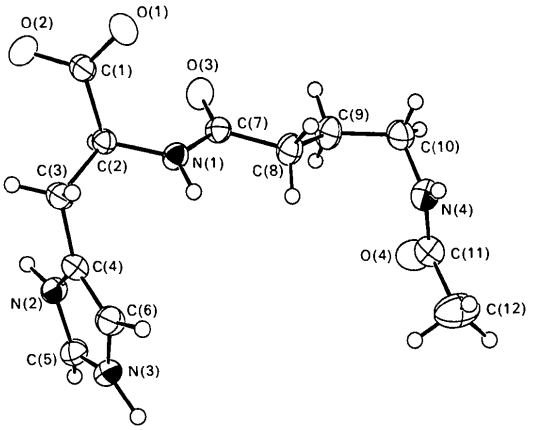


Fig. 1. A perspective view of the title molecule showing the atom-numbering scheme.

indicated crystals to be orthorhombic, space group $P2_12_12_1$. Density not measured. Least-squares techniques based on 25 reflections, $\theta > 20°$, used to refine lattice parameters. h 0 to 8, k 0 to 16, l 0 to 17. 1597 independent intensities, θ limit 70°, $\omega/2\theta$ scan. Two standard intensities (04$\bar{5}$, 145) used to monitor variations in intensity data: <3% variation observed. Structure solution by direct methods with *MITHRIL* (Gilmore, 1984). Full-matrix least-squares refinement on F of coordinates and anisotropic thermal parameters for all non-H atoms converged with R and wR equal to 0.038 and 0.056, respectively, with $w = 1/\sigma^2(F_o)$. H-atom coordinates, located from difference Fourier maps, included in structure-factor calculations but not refined. 1486 reflections, $I \geq 3.0\sigma_I$, used. Max. $\Delta/\sigma = 0.33$, $S = 3.04$; max. and min. heights in final difference Fourier map 0.13 and −0.26 e $Å^{-3}$. Scattering factors from *International*

Tables for X-ray Crystallography (1974, Vol. IV). Final positional and equivalent isotropic thermal parameters are given in Table 1,* while bond lengths and angles with their e.s.d.'s are given in Table 2. An *ORTEP* (Johnson, 1976) diagram, Fig. 1, illustrates the numbering scheme used in the analysis. All calculations on a VAX 3600 using Glasgow *GX* package (Mallinson & Muir, 1985).

Discussion. The imidazole ring is fully protonated, thus forming a zwitterion. The atoms of the imidazole ring are coplanar, within experimental error, with atom C(3) deviating only 0.014 Å from this plane. Valence angles around N(2), C(5) and N(3) are typical of the protonated form, all being close to 109°.

The histidine side chain adopts an 'open' or extended conformation (Kistenmacher & Marsh, 1971) as in crystals of DL-histidine (Bennett, Davidson, Harding & Morelle, 1970) and in the two modifications of L-histidine (Madden, McGandy & Seeman, 1972; Madden, McGandy, Seeman, Harding & Hoy, 1972). This particular conformation is characterized by the large torsion angle, 179.0 (3)°, about the C(2)—C(3) bond, with the imidazole *gauche* only to the amino group and *trans* to the carboxyl. There also appears to be a rotation of the imidazole ring about the C(3)—C(4) bond whereby N(2) is directed away from N(1) with the loss of the stabilizing N(2)···H(N1)—N(1) intramolecular hydrogen-bond observed in other histidine structures.

An unexpected feature of the molecule is that the acetamidooxobutyl chain is not fully extended, but bends at atom C(10), with a C(9)—C(10)—N(4) bond angle of 114.3 (3)°, so that the acetamido group lies parallel to the imidazole ring. The dihedral angle between the plane of the imidazole ring and the plane of the terminal atoms of the *N*-acetylhomocarnosine chain, N(4), C(11), C(12) and O(4), is 21°. Whether this is a prerequisite for efficient crystal packing or a juxtaposition to accommodate subtle conformational interactions is unclear since neither O(4) nor N(4) appear to interact significantly with other atoms or groups. Bond lengths and angles are in close agreement with values for other histidine molecules (Kistenmacher, Hunt & Marsh, 1972).

There are strong intermolecular hydrogen bonds O(2)···N(2) 2.605 (3) Å [O(2)···H(N2) 1.62 Å] and O(1)···N(3) 2.712 (3) Å [O(1)···H(N3) 1.68 Å], subtending hydrogen valence angles of 174 and 167°, respectively. There are also weaker intermolecular hydrogen bonds between O(1) and O(4) and the interstitial water molecule.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters and geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55665 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1013]

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Structure of 2-Phenyl-2-dehydrosparteine

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Abstract. 1,7,7a,8,9,10,11,13,14,14a-Decahydro-4-phenyl-7,14-methano-2*H*,6*H*-dipyrido[1,2-*a*:1′,2′-*e*]-[1,5]diazocine, $C_{21}H_{28}N_2$, $M_r = 308.47$, monoclinic, $P2_1$, $a = 7.570$ (1), $b = 9.4313$ (7), $c = 12.485$ (1) Å, $\beta = 102.21$ (1)°, $V = 871.2$ (2) Å^3, $Z = 2$, $D_x = 1.176$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu =$

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