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3-Dimethylamino-1-phenyl-1-propanone Hydrochloride Monohydrate

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Abstract. $C_{11}H_{16}NO^+.Cl^-.H_2O$, orthorhombic, *Pbca*, $a = 7.342$ (2), $b = 11.043$ (2), $c = 30.440$ (4) Å, $Z = 8$, $D_x = 1.301$ (1) Mg m^{-3}, $T = 295$ K, Mo $K\alpha$ ($\lambda = 0.7107$ Å). The structure was solved by direct methods and refined by full-matrix least-squares methods to a conventional R of 0.044 for the 1477 reflections with intensities above 2σ. The structure consists of a quarternary ammonium cation, a chloride anion, and a water of hydration. The single H atom on the N atom of the quaternary ammonium ion is hydrogen bonded to the chloride ion. The water of hydration is weakly hydrogen bonded to a symmetry-related water and also hydrogen bonded to the chloride ion. Distances and angles in the quaternary ammonium cation are normal. Except for one methyl C atom on the amine N, the non-H atoms are essentially coplanar.

Introduction. 3-Dimethylamino-1-phenyl-1-propanone hydrochloride monohydrate was prepared from acetophenone *via* the Mannich reaction (Maxwell, 1955). Crystals were obtained from a water–ethanol–acetone mixture. A crystal of approximate dimensions $0.3 \times 0.4 \times 0.4$ mm was chosen for the X-ray studies. The crystal system, cell dimensions and space group were determined using an Enraf–Nonius CAD-4 automated diffractometer.

All computations were performed on a PDP 11/34 computer using the Enraf–Nonius *SDP* software. A total of 2894 reflections were measured to a maximum 2θ of 47° using the θ–2θ step scan technique with a variable speed to enhance the uniformity of the counting statistics from reflection to reflection. Three standard reflections measured after approximately every 150 reflections indicated no crystal decomposition. The data were corrected for background and

Lorentz–polarization effects. The empirical absorption-correction method (ψ scans) was applied giving a range of transmission of 0.948 to 0.998.

Table 1. *Positional and thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}^* (Å^2)
Cl	0.7729 (1)	0.35272 (8)	0.08475 (2)	5.19 (4)
O	0.0153 (3)	−0.0381 (1)	0.32732 (5)	4.55 (9)
O(W)	0.9344 (5)	0.0836 (3)	0.04494 (12)	12.8 (3)
N	0.9145 (3)	0.2148 (2)	0.42569 (6)	3.82 (9)
C(1)	0.8699 (3)	0.0862 (2)	0.26595 (7)	3.12 (9)
C(2)	0.9164 (3)	0.1983 (2)	0.24931 (9)	3.7 (1)
C(3)	0.9256 (4)	0.2166 (2)	0.20450 (9)	4.4 (1)
C(4)	0.8896 (4)	0.1232 (3)	0.17614 (8)	4.6 (1)
C(5)	0.8433 (4)	0.0101 (2)	0.19223 (8)	4.4 (1)
C(6)	0.8344 (3)	−0.0078 (2)	0.23664 (8)	3.8 (1)
C(7)	0.8567 (3)	0.0617 (2)	0.31396 (7)	3.2 (1)
C(8)	0.8924 (3)	0.1640 (2)	0.34577 (8)	3.5 (1)
C(9)	0.8781 (4)	0.1184 (2)	0.39237 (8)	3.9 (1)
C(10)	0.7764 (4)	0.3123 (3)	0.42521 (9)	5.4 (2)
C(11)	0.9280 (5)	0.1601 (3)	0.47044 (9)	6.0 (2)
H(OW)1	0.975 (7)	0.021 (5)	0.0185 (12)	14.3
H(OW)2	0.843 (7)	0.034 (4)	0.0510 (13)	14.3
H(N)	1.027 (4)	0.251 (2)	0.4206 (7)	4.8
H(C2)	0.942 (3)	0.262 (2)	0.2682 (7)	4.7
H(C3)	0.959 (4)	0.285 (2)	0.1925 (8)	5.3
H(C4)	0.890 (4)	0.133 (2)	0.1465 (9)	5.6
H(C5)	0.818 (4)	−0.052 (2)	0.1737 (7)	5.4
H(C6)	0.808 (3)	−0.082 (2)	0.2504 (8)	4.9
H1(C8)	0.802 (3)	0.228 (2)	0.3400 (7)	4.6
H2(C8)	1.007 (3)	0.188 (2)	0.3403 (7)	4.6
H1(C9)	0.974 (4)	0.057 (2)	0.3988 (8)	5.0
H2(C9)	0.750 (3)	0.090 (2)	0.3994 (8)	5.0
H1(C10)	0.663 (4)	0.282 (3)	0.4277 (7)	6.4
H2(C10)	0.771 (4)	0.350 (3)	0.3973 (9)	6.4
H3(C10)	0.813 (4)	0.375 (3)	0.4476 (9)	6.4
H1(C11)	0.954 (4)	0.219 (3)	0.4906 (9)	6.9
H2(C11)	1.028 (4)	0.104 (3)	0.4653 (8)	6.9
H3(C11)	0.804 (4)	0.126 (3)	0.4776 (8)	6.9

$$* B_{eq} = \tfrac{4}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

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The 2427 nonextinct data were averaged to 1818 independent reflections and, of these, the 1477 reflections with F_o greater than $2\sigma(F_o)$ were used for the structure solution (*MULTAN*, Germain, Main & Woolfson, 1971) and refinement. H atoms were assigned B values about one unit higher than the B_{eq} of the atom to which they are attached, and only their positional parameters were refined. Starting positions were chosen based on a difference Fourier synthesis.

The least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$, $\sigma^2(F_o^2) = \sigma^2$ counting + $(0.05 F_o^2)^2$, and $\sigma^2(F_o) = \sigma^2(F_o^2)/4F_o^2$.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final agreement factors for refinement of the 191 variables were $R(F_o) = 0.044$, $wR(F_o) = 0.069$, and the error of an observation of unit weight = 2.17. The isotropic extinction factor (Zachariasen, 1967) from the least-squares refinement was 6.82×10^{-7}. The $R(F_o)$ including the reflections below $2\sigma(F_o)$ was 0.060 and the largest parameter shift on the last least squares was less than 0.02 times the corresponding e.s.d. A final difference synthesis revealed no electron density greater than 0.4 e Å^{-3}.

The final positional parameters and equivalent isotropic B values are given in Table 1 and selected

bond angles in Table 2.* Fig. 1 shows the molecular geometry, bond distances and proposed hydrogen-bonding scheme.

Discussion. The title compound has been shown to possess some biological activity as an antifertility agent (Rashid, Naqvi, Ashrafi & Quraishi, 1974) and more recently its photochemistry has been examined with the aim of understanding electron-transfer processes (Encinas & Scainano, 1979). The primary goal of this study was to establish the conformation of the saturated chain with respect to the aromatic ring and, in particular, to examine the possibility of interaction of the amine proton with the aromatic ring. At least in the solid state that interaction does not occur but rather the amine H is hydrogen bonded to ionic chloride which in turn is hydrogen bonded to the water of hydration (Fig. 1). A large portion of the organic cation is essentially

Table 2. *Bond angles* (°)

Standard deviations from the least-squares refinement are included in parentheses here and elsewhere in the manuscript.

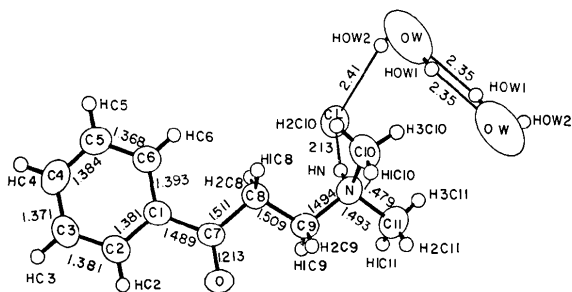|			
C(9)—N—C(10)	112.9 (2)	C(3)—C(4)—C(5)	120.3 (2)
C(9)—N—C(11)	110.1 (2)	C(4)—C(5)—C(6)	119.5 (2)
C(10)—N—C(11)	110.4 (2)	C(1)—C(6)—C(5)	121.1 (2)
C(2)—C(1)—C(6)	118.7 (2)	O—C(7)—C(1)	120.7 (2)
C(2)—C(1)—C(7)	122.6 (2)	O—C(7)—C(8)	120.5 (2)
C(6)—C(1)—C(7)	118.7 (2)	C(1)—C(7)—C(8)	118.8 (2)
C(1)—C(2)—C(3)	120.4 (2)	C(7)—C(8)—C(9)	109.9 (2)
C(2)—C(3)—C(4)	120.2 (2)	N—C(9)—C(8)	112.8 (2)

Fig. 1. Bond distances, atom labelling and thermal ellipsoids for 3-dimethylamino-1-phenyl-1-propanone hydrochloride monohydrate. Standard deviations in bond distances (ignoring H atoms) are 0.002 to 0.003 Å. The C–H distances range from 0.88 to 1.01 Å with standard deviations of 0.02–0.03 Å [av. 0.95 (4) Å]. The N–H distance is 0.93 (2) Å, and O–H distances are 1.11 (4) and 0.89 (5) Å for H(OW)1 and H(OW)2 respectively.

Table 3. *Weighted least-squares plane*

The equation of the plane is of the form: $AX + BY + CZ - D = 0$ where A,B,C and D are constants and X, Y, and Z are orthogalized coordinates.

	A	B	C	D
Plane 1	−0.9662	0.2576	−0.0117	−6.0227

	X	Y	Z	Distance (Å)
Atoms in plane				
C(1)	6.3867	0.9515	8.0955	0.003 (2)
C(2)	6.7281	2.1899	7.5891	−0.002 (2)
C(3)	6.7955	2.3921	6.2250	0.001 (3)
C(4)	6.5312	1.3602	5.3617	0.000 (3)
C(5)	6.1915	0.1113	5.8514	0.001 (3)
C(6)	6.1261	−0.0865	7.2034	−0.003 (3)
Other atoms				
C(7)	6.2898	0.6811	9.5570	0.010 (2)
O	5.9861	−0.4205	9.9636	0.014 (2)
C(8)	6.5518	1.8116	10.5254	0.036 (2)
C(9)	6.4472	1.3073	11.9438	−0.009 (3)
N	6.7140	2.3719	12.9579	−0.004 (2)
C(10)	5.7004	3.4486	12.9435	1.252 (3)
C(11)	6.8130	1.7682	14.3203	−0.271 (4)

Relevant torsion angles (°) (e.s.d.'s ~0.3°)

C(2)—C(1)—C(7)—C(8)	1.1
C(2)—C(1)—C(7)—O	180.0
C(6)—C(1)—C(7)—O	−0.2
C(6)—C(1)—C(7)—C(8)	−179.1
C(1)—C(7)—C(8)—C(9)	−178.1
O—C(7)—C(8)—C(9)	3.1
C(7)—C(8)—C(9)—N	178.2
C(8)—C(9)—N—C(11)	−170.9

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.

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N^α-Acetyl-5-nitro-L-histidine

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Abstract. $C_8H_{10}N_4O_5$, orthorhombic, $P2_12_12_1$, $a = 15·425$ (3), $b = 9·756$ (2), $c = 6·822$ (1) Å, $V = 1026·6$ (6) Å^3, $Z = 4$, $D_c = 1·56$ 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 & Bassedas, 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

were collected with Mo $K\alpha$ radiation, monochromatized by reflection from a graphite crystal. 1549 independent reflections were measured in the range $2\theta \leq 60°$; 1534 of these were considered as observed according to the condition $I > 2·5\sigma(I)$.

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.