

The Crystal and Molecular Structure of 8-Hydroxy-1-methylquinolinium Chloride Hydrate and 1-Methylquinolinium-8-olate Dihydrate

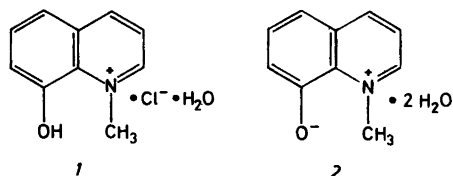
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The structures of the title compounds, $C_{10}H_{10}ClNO \cdot H_2O$ (**1**) and $C_{10}H_9NO \cdot 2H_2O$ (**2**) have been determined by X-ray methods. Full-matrix least-squares refinements led to final conventional R -values of 0.042 for **1** (3443 reflections) and 0.060 for **2** (2214 reflections). Crystals of **1** are triclinic, space group $P\bar{1}$, with (at -150°C) $a=7.765(3)$ Å; $b=7.932(3)$ Å; $c=8.913(3)$ Å; $\alpha=81.95(3)^\circ$; $\beta=72.89(3)^\circ$; $\gamma=70.45(3)^\circ$, $Z=2$. Crystals of **2** are monoclinic, space group $P2_1/c$, with (at -150°C) $a=7.282(2)$ Å; $b=13.643(3)$ Å; $c=10.049(2)$ Å; $\beta=98.69(2)^\circ$, $Z=4$.

The structural changes upon N -methylation of 8-hydroxyquinoline comprise a lengthening of the C–N ring bonds by 0.02 Å and also a weakening of more distant bonds in the molecule. **2** is the conjugate base of the acid **1**. The deprotonation of the oxygen atom leads to a shortening of the C–O bond by 0.06 Å and an increase of the adjacent C–C bond lengths by 0.02 Å.

8-Hydroxyquinoline and its derivatives have been extensively studied, mainly because of their ability to coordinate with a wide range of metal ions and because of their disinfectant effect.¹



Scheme 1.

Although the X-ray structure of the mother compound has been determined in its complex with 1,3,5-trinitrobenzene,² no account of the structure of the N -methylated derivative (**1**) has been found in the literature. There has been some interest in the betaine of the N -methyl derivative (**2**) because of certain peculiarities in its absorption spectrum.³ For comparison we therefore decided to determine this structure as well.

EXPERIMENTAL

Materials. 8-Hydroxy-1-methylquinolinium iodide was prepared according to the method of Saxena *et al.*³ with the exception that the reaction was carried out at room temperature overnight. Compound **2** was obtained from the salt using an anion exchanger (Amberlite®-IRA-400). Treatment of **2** with hydrochloric acid gave **1**.

X-Ray data. The data collection procedure for the two compounds were similar. A SYNTeX $P\bar{1}$ automatic diffractometer was used with graphite crystal monochromated $MoK\alpha$ radiation. The temperature at the crystal site was -150°C . Cell parameters were refined using the diffractometer settings of 15 general reflections with $2\theta > 30^\circ$. Intensities were measured using the θ – 2θ scan technique; the scan speed (2θ) was 2 – 4°min^{-1} depending on the peak intensity, scan width $\pm 1^\circ$. Background counts were taken for 0.35 times the scan time at each of the scan limits. Data were collected up to a $\sin \theta/\lambda$ value of 0.8 \AA^{-1} . The three standard reflections monitored for every 100 data showed no systematic variation. Out of the 3520 unique reflections collected from

compound 1 3443 with $I \geq 2.5\sigma(I)$ were retained for the structure analysis; the corresponding numbers for 2 were 3229 and 2214. The standard deviation of the intensities was calculated as $\sigma(I) = |C_T + (0.02C_N)^{1/2}|$, where C_T is the total number of counts and C_N is the scan count minus background count. Corrections were made for Lorentz and polarization effects but not for absorption.

CRYSTAL DATA

1. 8-Hydroxy-1-methylquinolinium chloride hydrate, $C_{10}H_{10}ClNO \cdot H_2O$, m.p. 250 °C. (dec.) Triclinic, $a = 7.765(3)$ Å; $b = 7.932(3)$ Å; $c = 8.913(3)$ Å; $\alpha = 81.95(3)^\circ$; $\beta = 72.89(3)^\circ$; $\lambda = 70.45(3)^\circ$; $V = 493.9(3)$ Å³; ($t = -150$ °C); $M = 213.66$; $Z = 2$; $F(000) = 224$; $\mu(MoK\alpha) = 3.7$ cm⁻¹; $D_x = 1.436$ gcm⁻³. Space group $P\bar{1}$ (No. 2).

2. 1-Methylquinolinium-8-olate dihydrate, $C_{10}H_9NO \cdot 2H_2O$, m.p. 130 °C. (dec.) Monoclinic, $a = 7.282(2)$ Å; $b = 13.643(3)$ Å; $c = 10.049(2)$ Å; $\beta = 98.69(2)^\circ$; $V = 986.9(3)$ Å³; ($t = -150$ °C); $M = 195.22$; $Z = 4$; $F(000) = 416$; $\mu(MoK\alpha) = 1.1$ cm⁻¹; $D_x = 1.314$ gcm⁻³. Absent reflections: (h 0 l) for l odd, (0 k 0) for k odd. Space group $P2_1/c$ (No. 14).

STRUCTURE DETERMINATIONS

The computer programs used for the structure analyses are described in Ref. 4. The atomic scattering factors for Cl⁻, O, N, and C are given by Doyle and Turner⁵ and for H by Stewart, Davidson and Simpson.⁶

Both structures were solved using the program assembly MULTAN.⁷ The usual sequence of isotropic and anisotropic refinements was followed; hydrogen positions were calculated and refined, isotropic thermal parameters were applied. In order to avoid the influence of bonding electrons on the atomic positions only reflections with $\sin \theta/\lambda$ larger than 0.45 Å⁻¹ were used during the last refinement cycles.

The refinements converged to conventional R factors of 0.042 (1) and 0.060 (2), the R_w values were 0.042 (1) and 0.052 (2) and goodness of fit, $[\sum w\Delta F^2/(m-n)]^{1/2}$, 2.03 (1) and 1.45 (2). Difference Fourier syntheses were calculated, giving only minor peaks mainly attributable to valence electrons.

Final atomic coordinates are given in Table 1. Lists of structure factors and thermal parameters are available from the authors.

Table 1. Fractional atomic coordinates.

Atom.	<i>x</i>	<i>y</i>	<i>z</i>
Compound 1			
C1	0.1641(1)	0.3601(1)	-0.3767(1)
C2	0.1744(1)	0.5343(1)	-0.4176(1)
C3	0.0447(1)	0.6713(1)	-0.3274(1)
C4	-0.0906(1)	0.6349(1)	-0.1916(1)
C5	-0.2186(1)	0.7756(1)	-0.0950(1)
C6	-0.3472(1)	0.7393(1)	0.0377(1)
C7	-0.3510(1)	0.5624(1)	0.0786(1)
C8	-0.2278(1)	0.4195(1)	-0.0117(1)
C9	-0.0943(1)	0.4550(1)	-0.1519(1)
C10	0.0324(1)	0.1343(1)	-0.2311(1)
N	0.0345(1)	0.3226(1)	-0.2521(1)
O	-0.2301(1)	0.2502(1)	0.0322(1)
Cl	-0.33565(4)	0.09450(4)	0.59858(3)
WO	-0.4792(1)	0.2215(1)	0.3002(1)
H1	0.2485	0.2602	-0.4373
H2	0.2723	0.5594	-0.5143
H3	0.0390	0.7905	-0.3509
H5	-0.2152	0.8946	-0.1249
H6	-0.4276	0.8313	0.0993
H7	-0.4463	0.5383	0.1767
H10A	0.1241	0.0786	-0.3188
H10B	0.0656	0.0824	-0.1337
H10C	-0.0959	0.1351	-0.2324
HO	-0.3168	0.2492	0.1152
WH1	-0.4264	0.1969	0.3725
WH2	-0.5298	0.1461	0.3042
Compound 2			
C1	0.3561(3)	-0.1390(1)	0.5717(2)
C2	0.3975(3)	-0.0798(2)	0.6862(1)
C3	0.3521(3)	0.0164(2)	0.6781(1)
C4	0.2623(3)	0.0577(1)	0.5557(2)
C5	0.2205(3)	0.1591(1)	0.5455(2)
C6	0.1368(4)	0.1971(1)	0.4255(3)
C7	0.0876(3)	0.1365(1)	0.3132(2)
C8	0.1238(2)	0.0352(1)	0.3138(1)
C9	0.2182(2)	-0.0046(1)	0.4408(1)
C10	0.2417(3)	-0.1726(1)	0.3404(2)
N	0.2709(2)	-0.1022(1)	0.4543(1)
O	0.0762(2)	-0.0192(1)	0.2092(1)
WO1	0.2232(2)	0.0264(1)	-0.0130(1)
WO2	0.5392(2)	0.1374(1)	-0.0273(1)
WH1	0.1789	0.0085	0.0598
WH2	0.1294	0.0247	-0.0772
WH3	0.4248	0.1073	-0.0240
WH4	0.6149	0.0913	-0.0059
H1	0.3799	-0.2099	0.5610
H2	0.4552	-0.1140	0.7568
H3	0.3870	0.0488	0.7525
H5	0.2519	0.1952	0.6332
H6	0.1141	0.2610	0.4186
H7	0.0242	0.1585	0.2259
H10A	0.2958	-0.2337	0.3841
H10B	0.3004	-0.1425	0.2674
H10C	0.1025	-0.1781	0.3090

Table 2. Structural data.

Bond lengths (Å)				Bond angles (°)			
1		2		1		2	
	corr.		corr.				
C1–C2	1.402(2)	1.405	1.401(4)	1.406	C1–C2–C3	118.6(1)	119.3(4)
C2–C3	1.370(2)	1.372	1.353(4)	1.357	C2–C3–C4	120.2(1)	120.9(4)
C3–C4	1.418(2)	1.420	1.420(4)	1.423	C3–C4–C9	119.4(1)	118.8(4)
C4–C5	1.413(2)	1.415	1.416(4)	1.421	C4–C9–N	117.7(1)	117.8(4)
C4–C9	1.430(2)	1.433	1.431(4)	1.435	C9–N–C1	121.4(1)	121.9(4)
C5–C6	1.372(2)	1.374	1.368(4)	1.372	N–C1–C2	122.5(1)	121.2(4)
C6–C7	1.407(2)	1.410	1.401(4)	1.406	C4–C5–C6	119.8(1)	119.8(4)
C7–C8	1.387(2)	1.389	1.407(4)	1.411	C5–C6–C7	120.2(1)	120.8(4)
C8–C9	1.431(1)	1.433	1.459(4)	1.463	C6–C7–C8	122.2(1)	123.4(4)
C8–O	1.350(1)	1.353	1.290(4)	1.295	C7–C8–C9	118.4(1)	115.6(4)
C9–N	1.391(1)	1.393	1.387(4)	1.391	C8–C9–C4	118.9(1)	120.3(4)
N–C1	1.335(1)	1.337	1.345(4)	1.348	C9–C4–C5	120.4(1)	120.1(4)
N–C10	1.485(2)	1.488	1.484(4)	1.489	O–C8–C7	121.2(1)	122.3(4)
Hydrogen bond lengths(Å) and angles(°)							
Structure 1							
O–HO...WO	2.631	172.4					
WO–WH1...Cl	3.094	166.0					
WO–WH2...Cl ^a	3.191	161.0					
Structure 2							
O...WH1–WO1	2.691	174.7					
O ^b ...WH2–WO1	2.712	178.0					
WO1...WH3–WO2	2.777	169.3					
WO1 ^c ...WH4–WO2	2.817	169.8					
Equivalent positions							
^a (–1–x, –y, 1–z)							
^b (–x, –y, –z)							
^c (1–x, –y, –z)							

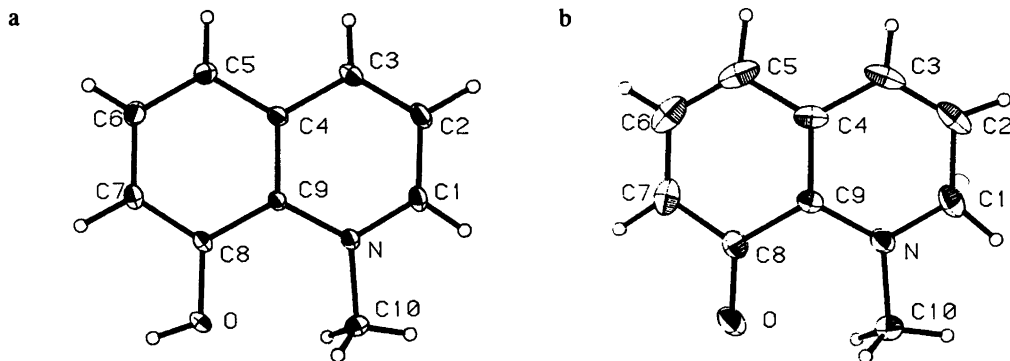


Fig. 1. ORTEP plots of 8-hydroxy-1-methylquinolinium cation (a) and of 1-methylquinolinium-8-olate zwitterion (b).

In Table 2 are listed various structural data. Estimated standard deviations are calculated from the variance-covariance matrices. Analyses of the rigid body motion were carried out; bond lengths corrected for librational motion are given in Table 2.

ORTEP drawings with the numbering schemes for the molecules are shown in Fig. 1.

DISCUSSION

Molecular structure, compound 1. Prout *et al.* have determined the structure of the 1:1 complex of 8-hydroxyquinoline with 1,3,5-trinitrobenzene.² The pattern of long and short C—C bonds is nearly identical to that of *1* in spite of the complex formation. The difference between the two is the methyl group attached to the nitrogen atom of the present compound. In order to obtain information of the effect of *N*-methylation of 8-hydroxyquinoline a simple Hückel calculation was performed. The results showed that the positive charge is roughly equally shared among the atoms N, C1, C3 and C9. A weakening of the N—C1 and N—C9 bonds results in a lengthening of these bonds; this is also what the experimental structural data indicate. More unexpected, however, is the observation that there is an increase in the C2—C3 and C8—C9 bond lengths and a decrease in the C6—C7 bond upon the *N*-methylation. The change in all five bond lengths mentioned is close to 0.02 Å, which seems to be significant. The other bonds are unaffected by the methylation.

The C—O bond length in *1* is 1.353 Å which is typical in hydrogen bonded phenols.^{8,9} The nitrogen—methyl carbon bond length of 1.488 Å is within the range of literature values in *N*-methylpyridinium salts (1.46–1.51 Å^{10,11}).

The oxygen—methyl carbon atoms are separated by 2.65 Å; the two nearest methyl hydrogen atoms are at van der Waals' distance from the oxygen atom, 2.40 and 2.44 Å, respectively. The hydroxyl hydrogen atom is pointing away from the methyl group in the molecular plane and forms a hydrogen bond to a water molecule (*cf.* Table 2).

The 8-hydroxy-1-methylquinolinium ion is, with the obvious exception of two methyl hydrogen atoms, essentially planar. The oxygen and methyl carbon atoms are slightly out on each side

of the least squares plane, 0.08 and 0.12 Å, respectively.

Molecular structure, compound 2. 1-Methylquinolinium-8-olate, *2*, is derived from the 8-hydroxy-1-methylquinolinium ion, *1*, by deprotonation of the hydroxy substituent. In terms of simple bond theory this leads to a shortening of the C—O bond owing to an enhanced double bond character and an accompanying increase of the C7—C8 and C8—C9 bond lengths. Our data are in complete agreement with these predictions, the C—O bond is by 0.06 Å shorter in *2* than in *1*, the neighbouring C—C bonds by 0.02–0.03 Å longer. An analogous situation is observed for the picric acid—picrate system with a slightly larger effect.^{8,12}

The zwitterion is also nearly planar, the oxygen and methyl carbon atoms being situated 0.06 and 0.09 Å, respectively, out on each side of the least squares plane.

Crystal packing. The crystal forces, apart from Coulomb forces in *1*, are dominated in both compounds by hydrogen bonds and interactions between aromatic molecular pairs.

In structure *1* the oxygen atom of the quinolinium ion acts as hydrogen donor in a hydrogen bond to the water molecule. The water molecule is hydrogen bonded to two chloride ions as indicated in Table 2. In structure *2* pairs of centrosymmetrically related molecules are linked together by pairs of water molecules through hydrogen bonds; the oxygen atom of the zwitterion is thus an acceptor for two hydrogen bonds. Each water molecule is hydrogen bonded to two other water molecules as described in Table 2.

In both compounds the aromatic moieties are arranged in centrosymmetrical pairs as indicated in Fig. 2, which shows the overlap diagrams as seen along the normal to the parallel molecular planes. The interplanar spacing is 3.35 Å in both compounds.

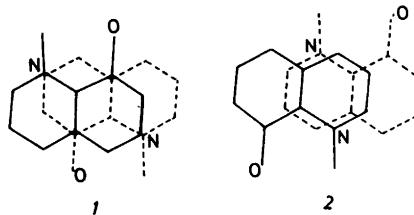


Fig. 2. π - π interaction overlap diagrams of the structures *1* and *2*.

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REFERENCES

1. Hollingshead, R. G. W. *Oxine and Its Derivatives*, Butterworth, London 1954/56.
2. Castellano, E. and Prout, C. K. *J. Chem. Soc. A* (1971) 550.
3. a. Saxema, J. P., Stafford, W. H. and Stafford, W. L. *J. Chem. Soc.* (1959) 1579. b. Tandon, S. P., Bhutra, M. P., Mehta, P. C., Saxena, J. P. and Tandon, K. *Indian J. Pure Appl. Phys.* 6 (1968) 694.
4. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
5. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* 24 (1968) 390.
6. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
7. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
8. Srikrishnan, T., Soriano-Garcia, M. and Parthasarathy, R. *Z. Kristallogr.* 151 (1980) 317.
9. Lechat, J. R., de Almeida Santos, R. H. and Bueno, W. A. *Acta Crystallogr. B* 37 (1981) 1468.
10. Lalancette, R. A., Furey, W., Costanzo, J. N., Hemmes, P. R. and Jordan F. *Acta Crystallogr. B* 34 (1978) 2950.
11. Tafeenko, V. A. and Aslanov, L. A. *Zh. Strukt. Khim.* 21(6) (1980) 79.
12. Jones, C. L., Milburn, G. H. and Sawyer, L. *Acta Crystallogr. B* 37 (1981) 1548.

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