

Fig. 1. The molecular conformation of oxmetidine dihydrochloride and atomic numbering.

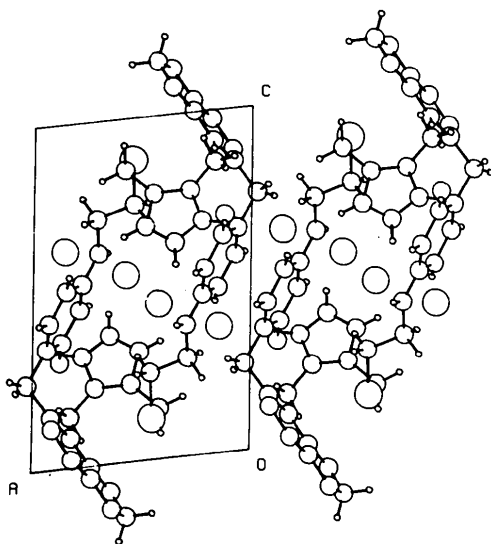


Fig. 2. Crystal structure in projection down *b*.

The aromatic group, 4-methylimidazolyl, is planar, and the methylthioethyl chain has the expected folded conformation with *gauche* linkages (both in the same sense) at C(7)—S(8) and S(8)—C(9). Similar *gauche* linkages at S atoms have been observed for the methylthioethyl chain in all H2 antagonists in the solid state except for cimetidine monohydrate (Kojić-Prodić, Ružić-Toroš, Bresciani-Pahor & Randaccio, 1980) and for famotidine (Yanagisawa, Hirata & Ishii, 1987). The isocytosine residue is planar. In the dication in (1), the isocytosine is protonated on both ring N atoms and the problem of a tautomeric form does not arise. Examination of the Cambridge Structural Database indicates that in six-membered rings, protonated N atoms have endocyclic angles $>120^\circ$ and unprotonated N atoms endocyclic angles $<120^\circ$. Further, N atoms in peptide-like linkages form C—N—C angles of about 124° , significantly $>120^\circ$. Thus the expectation is that the dication should have both endocyclic angles at the N atoms $>120^\circ$. This is observed in (1) (Table 2).

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Structure of 2,3-Naphthalenediamine Dihydrochloride Dihydrate

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Abstract. $C_{10}H_{12}N_2^{2+} \cdot 2Cl^- \cdot 2H_2O$, $M_r = 267.15$, monoclinic, $P2_1/c$, $a = 7.057(2)$, $b = 13.017(3)$, $c = 13.982(3)$ Å, $\beta = 92.57(4)^\circ$, $V = 1283.1(5)$ Å³, $Z =$

4, $D_x = 1.382$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 4.95$ cm⁻¹, $F(000) = 560$, $T = 298$ K, final $R = 0.036$, $wR = 0.026$ for 1814 uniquely observed [$I \geq 2\sigma(I)$]

reflections. Crystals were obtained by dissolving 2,3-diaminonaphthalene in a solution of hydrochloric acid. The organic moiety in the molecule is nearly planar and forms parallel stacks with the dipoles of adjacent molecules pointing in opposite directions to each other. The mean bond lengths and angles for the naphthalene ring are similar to those in the naphthalene molecule, except for the C(9)—C(10) bond which is longer than the corresponding bond in the naphthalene moiety of the 2,3-diaminonaphthalene ion. The structure contains intermolecular hydrogen bonds between the amino groups, the chloride ions and the water molecules.

Introduction. 2,3-Diaminonaphthalene (2,3-DAN) is a potential electron-rich ligand. Because of its complexing properties with Se (Yang, Huang, Feng & Mei, 1986; Tamari, Hirai, Tsuji & Kusaka, 1987), it is also known as a good reagent for the determination of small amounts of Se in biological materials and water. The formation of a transition-metal complex with Co, in which 2,3-DAN acts as a delocalized unsaturated electron-rich ligand, has been reported and a structure determination has been carried out (Liaw, Peng, Chern & Sheu, 1986).

It proved difficult to grow single crystals of the neat 2,3-DAN molecule suitable for X-ray crystallographic study by slowly evaporating a solvent containing 2,3-DAN at room temperature. Therefore, 2,3-DAN was dissolved in hydrochloric acid to form 2,3-DAN hydrochloride and single crystals were grown. Therefore, we report here the molecular and crystal structure of the uncomplexed 2,3-DAN ion.

Experimental. 2,3-Diaminonaphthalene (0.2 g) was added to hydrochloric acid (23%, 10 ml), and the reaction mixture was heated with stirring. Another equal amount of hydrochloric acid was added after a few minutes. The reaction mixture was heated continuously until all of the 2,3-diaminonaphthalene had dissolved. It was then refluxed for about 20 min. The reaction solution was allowed to stand at room temperature overnight. Some tiny yellow crystals were precipitated. In order to obtain suitably sized crystals, the mixture was filtered and the filtrate was left at room temperature for another 2 d. Several yellow crystals of suitable size grew in the bottom of the beaker.

A yellow transparent single crystal with approximate shape of a rectangular parallelepiped, with dimensions $0.3 \times 0.3 \times 0.6$ mm, was selected for study by X-ray diffraction. A modified Picker FACS-I four-circle automated diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used for data collection. 27 strong reflections with their Friedel pairs, in the 2θ range $29\text{--}39^\circ$, were used in a least-squares refinement of the unit-cell parameters.

Intensity data were collected in the 2θ range $3\text{--}50^\circ$ with $0 \leq h \leq 8$, $0 \leq k \leq 15$, $-16 \leq l \leq 16$, at 293 (2) K. A θ - 2θ automated scan mode was employed. Three standard reflections were monitored after every 47 reflections. Standard reflections did not show significant variation. A total of 2272 independent reflections was recorded. Of these, 1814 reflections showed $I \geq 2\sigma(I)$ and were therefore considered as observed and used in the subsequent structural study. Lorentz and polarization corrections were calculated. Absorption corrections were not considered necessary.

The structure was solved by direct methods and Fourier syntheses and refined on F by full-matrix least squares with $\sigma^{-2}(F)$ weights. The $\sigma(F)$ were determined from counting statistics plus a contribution calculated from the excess scatter of the standard reflections. The E map based on the best solution obtained from direct methods gave all of the 16 non-H atoms except for the two water O atoms. Several cycles of full-matrix least-squares refinement with isotropic temperature factors were carried out on the known 14 non-H-atom positions. A difference map revealed the two O atoms. After several more cycles of least-squares refinements using anisotropic temperature factors for the non-H atoms, all of the H atoms were located on a difference map. The non-H atoms were refined anisotropically and the H atoms were refined isotropically until the average shift/e.s.d. and maximum shift/e.s.d. were 1.3×10^{-3} and 1.7×10^{-2} respectively, giving final R and wR values of 0.036 and 0.026. The final electron-density difference map had a maximum peak of $0.4 \text{ e } \text{\AA}^{-3}$, which was considered insignificant. Atomic scattering factors were taken from Cromer & Mann (1968) as given in the *Xtal2.4* (Hall & Stewart, 1988) system. All computations were carried out on a VAX 6320 computer with the *Xtal2.4* system of crystallographic programs.

Discussion. The atomic coordinates of the non-H atoms and equivalent isotropic temperature factors are listed in Table 1. Bond lengths and angles and hydrogen-bond geometry are presented in Table 2.*

A stereodiagram of the molecule, with atomic labels and showing the hydrogen bonds, is illustrated in Fig. 1. A least-squares plane calculated through atoms C(1) to C(10) shows that the C-atom skeleton is almost planar; the largest deviation from the mean plane is 0.011 (3) Å. The distances of the N atoms to

* Lists of structure factors, anisotropic temperature factors, H-atom parameters and bond distances and angles including H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55411 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD0059]

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^2$)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Cl(1)	-0.04146 (10)	0.10217 (5)	-0.18229 (5)	4.79
Cl(2)	0.53242 (10)	0.36646 (5)	-0.35415 (5)	4.14
O(1)	-0.0044 (4)	0.1419 (2)	0.1550 (2)	5.3
O(2)	0.5211 (4)	0.1040 (2)	-0.1359 (2)	7.0
N(1)	0.1989 (4)	0.1851 (2)	-0.0077 (2)	3.8
N(2)	0.2989 (4)	0.2646 (2)	-0.1928 (2)	3.9
C(1)	0.1978 (4)	0.3610 (2)	0.0508 (2)	3.2
C(2)	0.2220 (3)	0.2955 (2)	-0.0225 (2)	2.9
C(3)	0.2739 (3)	0.3342 (2)	-0.1123 (2)	3.0
C(4)	0.2970 (4)	0.4365 (2)	-0.1252 (2)	3.1
C(5)	0.2997 (4)	0.6134 (2)	-0.0605 (2)	3.6
C(6)	0.2766 (4)	0.6776 (2)	0.0142 (2)	3.9
C(7)	0.2269 (4)	0.6392 (2)	0.1041 (2)	4.0
C(8)	0.2012 (4)	0.5369 (2)	0.1173 (2)	3.6
C(9)	0.2229 (3)	0.4678 (2)	0.0409 (2)	3.0
C(10)	0.2742 (3)	0.5062 (2)	-0.0496 (2)	3.0

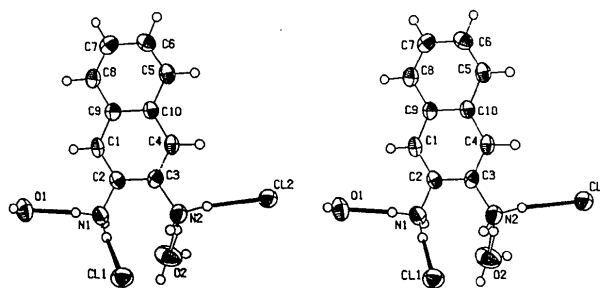


Fig. 1. Stereoscopic view of the molecule and atomic numbering scheme.

Table 2. Bond lengths (\AA), bond angles ($^\circ$) and hydrogen-bond geometry (\AA , $^\circ$)

N(1)—C(2)	1.462 (4)	N(2)—C(3)	1.462 (4)	
C(1)—C(2)	1.349 (4)	C(1)—C(9)	1.409 (4)	
C(2)—C(3)	1.416 (4)	C(3)—C(4)	1.354 (4)	
C(4)—C(10)	1.408 (4)	C(5)—C(6)	1.353 (4)	
C(5)—C(10)	1.416 (4)	C(6)—C(7)	1.411 (4)	
C(7)—C(8)	1.358 (4)	C(8)—C(9)	1.411 (4)	
C(9)—C(10)	1.422 (4)			
C(2)—C(1)—C(9)	121.8 (2)	N(1)—C(2)—C(1)	119.6 (2)	
N(1)—C(2)—C(3)	120.6 (2)	C(1)—C(2)—C(3)	119.7 (2)	
N(2)—C(3)—C(2)	120.4 (2)	N(2)—C(3)—C(4)	119.2 (23)	
C(2)—C(3)—C(4)	120.3 (2)	C(3)—C(4)—C(10)	121.0 (2)	
C(6)—C(5)—C(10)	120.4 (3)	C(5)—C(6)—C(7)	120.8 (3)	
C(6)—C(7)—C(8)	120.6 (3)	C(7)—C(8)—C(9)	120.2 (3)	
C(1)—C(9)—C(8)	122.5 (2)	C(1)—C(9)—C(10)	118.2 (2)	
C(8)—C(9)—C(10)	119.3 (2)	C(4)—C(10)—C(5)	122.3 (2)	
C(4)—C(10)—C(9)	118.9 (2)	C(5)—C(10)—C(9)	118.8 (2)	
D—H...A	D—H	H...A	D...A	D—H...A
N(1)—H(01)...Cl(1)	0.93 (3)	2.20 (3)	3.103 (3)	164 (2)
N(1)—H(02)...O(1)	0.93 (3)	1.87 (3)	2.800 (4)	176 (2)
N(1)—H(03)...Cl(2)	0.93 (3)	2.45 (3)	3.186 (3)	137 (2)
N(2)—H(04)...O(2)	0.98 (3)	1.74 (3)	2.711 (4)	170 (3)
N(2)—H(05)...Cl(2)	0.96 (3)	2.21 (3)	3.146 (3)	163 (2)
N(2)—H(06)...Cl(1)	0.89 (3)	2.46 (3)	3.208 (3)	142 (2)
O(1)—H(101)...Cl(1)	0.88 (4)	2.36 (4)	3.214 (3)	165 (4)
O(1)—H(102)...Cl(2)	0.78 (3)	2.52 (3)	3.267 (3)	162 (3)
O(2)—H(201)...Cl(2)	0.83 (4)	2.29 (4)	3.117 (3)	173 (3)
O(2)—H(202)...Cl(1)	0.82 (4)	2.37 (4)	3.183 (3)	172 (4)

the plane through C(1)—C(10) are 0.036 (4) and 0.001 (4) \AA .

In the naphthalene moiety, the C—C bond distances do not show any significant deviations of the ring system from *mmm* symmetry. The mean bond lengths and angles for the naphthalene ring are similar to those in the naphthalene molecule (Ponomarev, Filipenko & Atovmyan, 1976) except for the C(9)—C(10) bond which is longer than the corresponding bond in naphthalene but is similar to the length of the corresponding bond in the complex of Co^{II} with the 2,3-naphthoquinone diimine anion (Liaw, Peng, Chern & Sheu, 1986). The bond length is also the longest bond in the naphthalene moiety of the 2,3-DAN ion. This is similar to the

situation observed for 3-methyl-2-oxobenzoquinoxaline, which is the condensation product of 2,3-diaminonaphthalene with pyruvic acid (Bertrand, Maltais, Brisse & Olivier, 1985). The lengthening of the C(9)—C(10) bond is assumed to result from the presence of the amino cations in the 2 and 3 positions of the naphthalene ring. The interaction between the positive charges on the N atoms and the conjugated π -bond system of the naphthalene ring causes a redistribution of charge throughout the N atoms and the ring system. Consequently, it results in the lengthening of the C(9)—C(10) bond and a shortening of the N(1)—C(2) and N(2)—C(3) bonds.

The six H atoms on the amino N atoms and the four water H atoms form hydrogen bonds. The two Cl ions accept four hydrogen bonds each, and each water molecule accepts one hydrogen bond. The planar 2,3-diaminonaphthalene cations form parallel stacks along the [100] direction with an interplanar spacing of 3.38 (2) \AA . The normal to the mean molecular plane is inclined at approximately 14° to the stacking direction.

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