

Crystal Structures of *N*(6),*N*(6)-Dimethyladenine Hydrochloride Monohydrate and *N*(6),*N*(6)-Dimethyladenine Dihydrochloride

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Both title compounds crystallize in the monoclinic space group $P2_1/c$. The hydrochloride monohydrate has cell parameters $a=9.661(2)$ Å, $b=14.308(5)$ Å, $c=7.620(1)$ Å, $\beta=103.79(2)^\circ$. The structure was refined to $R=0.067$ for 1434 observed reflections. The dihydrochloride has cell parameters $a=7.445(2)$ Å, $b=19.675(3)$ Å, $c=7.090(1)$ Å, $\beta=98.07(2)^\circ$. The structure was refined to $R=0.034$ for 1778 observed reflections. The protonation of *N*(6),*N*(6)-dimethyladenine is at N(1) in the hydrochloride monohydrate and at N(1) and N(7) in the dihydrochloride, giving a mono- and a di-protonated ion with the H atoms bonded to the rings as observed for other adenine derivatives. For the monoprotonated ion, however, these H positions are different from those recently reported for the same ion in different environments.

It has recently been shown that in the tricyanoethenolate dioxane solvate the *N*(6),*N*(6)-dimethyladeninium ion has H-atoms bonded to N(3) and N(7),¹ not to N(1) and N(9) as in other protonated adenine derivatives.² In order to test the hypothesis that this unusual bonding is a result of interaction between the adeninium derivative and its environments, it was decided to investigate the structure of the chloride of the same adeninium derivative. Crystals, suitable for single crystal X-ray analysis, were obtained of the monohydrate of this compound and during this work also of the dihydrochloride of *N*(6),*N*(6)-dimethyladenine (DMA). As even the latter compound might throw light on the proton affinity of DMA, the crystal structures both of *N*(6),*N*(6)-dimethyladenine hydrochloride

monohydrate (DMA · HCl · H₂O) and of *N*(6),*N*(6)-dimethyladenine dihydrochloride (DMA · 2HCl) were determined.

EXPERIMENTAL

By slow evaporation of a solution of DMA in concentrated hydrochloric acid crystals of DMA · 2HCl were formed, a few of them of a satisfactory quality. By dissolving the crystals in 96 % ethanol and evaporating the solvent, plate-shaped crystals of DMA · HCl · H₂O were obtained. Crystals, probably of the water-free monohydrochloride, were formed by the same procedure using methanol instead of ethanol, but the quality of these crystals was very poor.

For both compounds cell parameters and X-ray intensities were measured on an Enraf-Nonius CAD4 diffractometer using CuK α radiation ($\lambda=1.5418$ Å). The cell parameters were determined from the setting angles of 25 reflections. Crystal data are given in Table 1. The intensities were collected by an $\omega/2\theta$ scan at a rate in ω of $0.5-2.9^\circ \text{ min}^{-1}$. The crystals were kept in sealed capillaries.

During the data collections, the intensities of the standard reflections of DMA · HCl · H₂O decreased continuously down to 90 % of their original values whereas there was no apparent decrease in those of DMA · 2HCl. 1434 reflections for DMA · HCl · H₂O and 1778 for DMA · 2HCl had $I > 2\sigma(I)$ and were used for the structure determination. Lp and absorption corrections were performed for both compounds.

Table 1. Crystal data.

	DMA · HCl · H ₂ O	DMA · 2HCl
Formula	C ₇ H ₁₀ N ₅ ⁺ Cl ⁻ H ₂ O	C ₇ H ₁₁ N ₅ ²⁺ 2Cl ⁻
F.W.	217.66	236.11
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.661(2)	7.445(2)
<i>b</i> (Å)	14.307(5)	19.675(3)
<i>c</i> (Å)	7.620(1)	7.090(1)
β (°)	103.79(2)	98.07(2)
<i>V</i> (Å ³)	1022.9	1028.3
<i>Z</i>	4	4
<i>D</i> _x (g cm ⁻³)	1.413	1.525
<i>D</i> _m (flotation) (g cm ⁻³)	1.44	1.54
μ (CuK α) (cm ⁻¹)	31.44	54.24
Crystal dimensions, appr. in axial directions (mm)	0.06×0.36×0.58	0.3×0.1×0.1

STRUCTURE DETERMINATION AND REFINEMENT

For both structures the positions of the Cl atoms were found from Patterson maps. These positions were used as starting points for successive Fourier syntheses which gave the positions of the other non-hydrogen atoms. All the H atoms were located from difference maps.

In the last part of the least squares refinements of both structures all atomic positions and thermal parameters, anisotropic for non-hydrogen

atoms and isotropic for H atoms, were varied. For DMA · 2HCl the effect of extinction turned out to be important and an isotropic extinction parameter was refined in the last cycles.

The weighting scheme used was $w = XY$ with $X=1$ for $\sin \theta > A$, else $X = \sin \theta / A$, $Y=1$ for $|F_o| < B$, else $Y = B / |F_o|$. For DMA · HCl · H₂O the values $A=0.8$ and $B=3.0$ were used, the final $R=0.067$ and $R_w = [\sum w(F_o - F_c)^2 / \sum w F^2]^{1/2} = 0.082$. For DMA · 2HCl $A=0.8$ and $B=7.0$ were used, $R=0.034$ and $R_w=0.044$. Lists of observed and

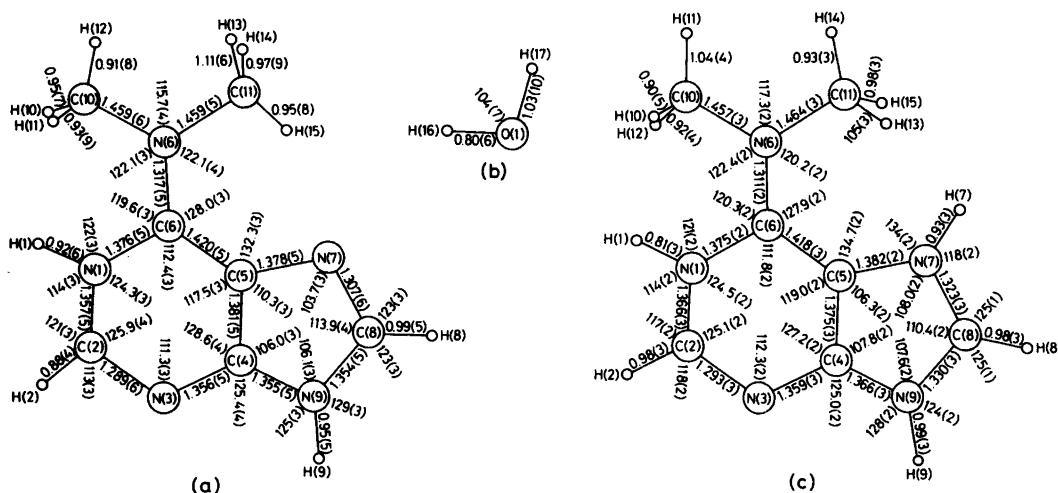


Fig. 1. Bond distances (Å) and angles (°) in monoprotonated DMA (a) and the water molecule (b) in DMA · H₂O · HCl and in diprotonated DMA (c) in DMA · 2HCl.

Table 2. Positional parameters and equivalent or isotropic temperature factors (\AA^2).
 $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cos \alpha_{ij}$. Standard deviations in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U_{iso}
DMA · HCl · H₂O				
Cl(1)	0.40025(10)	0.14739(6)	0.13979(14)	0.0557(3)
O(1)	-0.3795(3)	0.2500(3)	0.4566(5)	0.0703(12)
N(1)	0.1710(3)	0.2856(2)	0.2101(4)	0.0511(9)
C(2)	0.0844(4)	0.2175(3)	0.2473(6)	0.0537(12)
N(3)	-0.0347(3)	0.2304(2)	0.2921(5)	0.0551(10)
C(4)	-0.0657(4)	0.3227(3)	0.2968(5)	0.0469(10)
C(5)	0.0114(4)	0.3983(2)	0.2596(5)	0.0464(10)
C(6)	0.1433(4)	0.3797(2)	0.2150(4)	0.0429(9)
N(6)	0.2356(3)	0.4403(2)	0.1798(4)	0.0513(9)
N(7)	-0.0591(3)	0.4803(2)	0.2760(5)	0.0537(10)
C(8)	-0.1738(4)	0.4526(3)	0.3236(6)	0.0567(12)
N(9)	-0.1834(3)	0.3587(2)	0.3391(5)	0.0540(10)
C(10)	0.3695(5)	0.4111(4)	0.1398(9)	0.0681(16)
C(11)	0.2159(5)	0.5410(3)	0.1923(8)	0.0647(15)
H(1)	0.252(6)	0.263(3)	0.180(7)	0.063(12)
H(2)	0.104(4)	0.158(3)	0.234(6)	0.047(10)
H(8)	-0.246(5)	0.497(3)	0.349(6)	0.064(13)
H(9)	-0.253(5)	0.323(3)	0.378(6)	0.061(12)
H(10)	0.426(8)	0.373(6)	0.230(11)	0.104(24)
H(11)	0.345(8)	0.372(6)	0.041(11)	0.135(27)
H(12)	0.421(8)	0.464(6)	0.141(10)	0.110(24)
H(13)	0.295(8)	0.564(5)	0.317(10)	0.094(24)
H(14)	0.229(8)	0.574(5)	0.086(11)	0.127(24)
H(15)	0.127(8)	0.557(5)	0.216(10)	0.118(24)
H(16)	-0.433(6)	0.280(4)	0.499(8)	0.071(15)
H(17)	-0.446(11)	0.215(7)	0.349(15)	0.163(35)
DMA · 2HCl				
Cl(1)	0.16500(6)	0.12890(2)	0.04023(8)	0.0416(2)
Cl(2)	0.66123(7)	0.07473(2)	0.32095(8)	0.0465(2)
N(1)	0.37544(24)	0.26391(8)	0.15518(24)	0.0359(5)
C(2)	0.53889(29)	0.23731(10)	0.23204(31)	0.0403(6)
N(3)	0.67845(24)	0.27246(9)	0.30466(25)	0.0411(5)
C(4)	0.64504(26)	0.34039(10)	0.29794(26)	0.0358(5)
C(5)	0.48625(25)	0.37222(9)	0.22421(26)	0.0333(5)
C(6)	0.33766(25)	0.33225(9)	0.14026(26)	0.0326(5)
N(6)	0.18005(22)	0.35325(8)	0.05424(23)	0.0363(5)
N(7)	0.51450(23)	0.44093(8)	0.25644(25)	0.0359(5)
C(8)	0.68237(29)	0.44918(11)	0.34310(31)	0.0412(6)
N(9)	0.76577(23)	0.38941(9)	0.36910(25)	0.0395(5)
C(10)	0.03284(29)	0.30655(11)	-0.01260(37)	0.0434(6)
C(11)	0.14222(37)	0.42606(11)	0.03273(41)	0.0511(7)
H(1)	0.299(4)	0.236(2)	0.117(4)	0.054(8)
H(2)	0.552(4)	0.118(1)	0.229(4)	0.052(7)
H(7)	0.443(4)	0.479(2)	0.230(4)	0.067(9)
H(8)	0.736(3)	0.493(1)	0.386(3)	0.043(6)
H(9)	0.891(5)	0.383(2)	0.436(5)	0.077(10)
H(10)	0.012(6)	0.283(2)	0.091(6)	0.106(13)
H(11)	-0.078(5)	0.329(2)	-0.093(5)	0.086(11)
H(12)	0.072(6)	0.273(2)	-0.086(6)	0.099(12)
H(13)	0.254(4)	0.448(2)	-0.018(4)	0.071(9)
H(14)	0.036(5)	0.432(2)	-0.052(5)	0.066(8)
H(15)	0.142(4)	0.447(1)	0.158(4)	0.052(7)

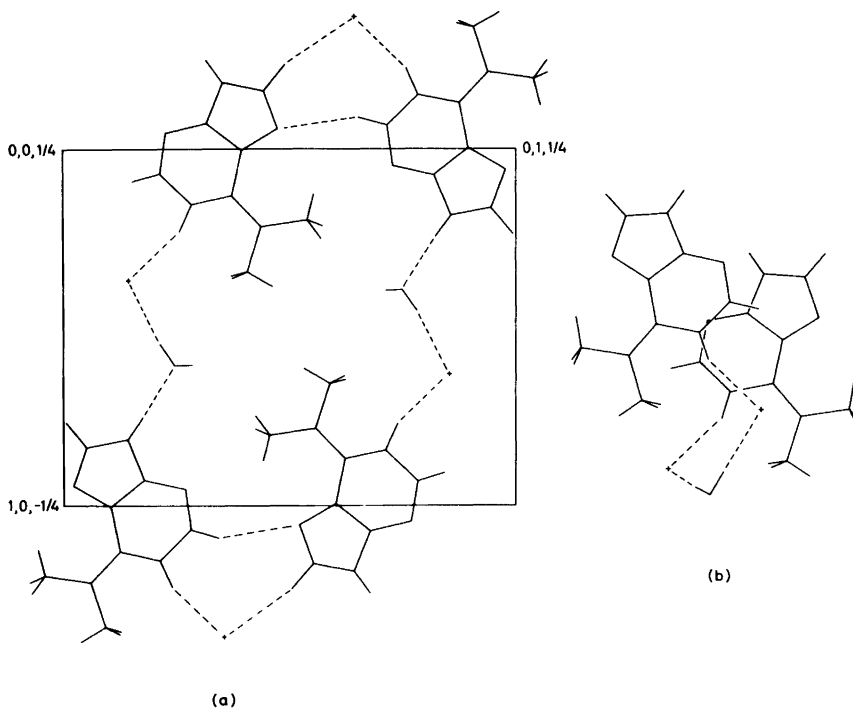


Fig. 2. The molecular packing in $\text{DMA} \cdot \text{HCl} \cdot \text{H}_2\text{O}$ along $(10\bar{2})$, viewed perpendicular to this plane (a), and along the stack, viewed perpendicular to the average molecular plane (b). Broken lines indicate hydrogen bonds and + marks show the Cl^- ions.

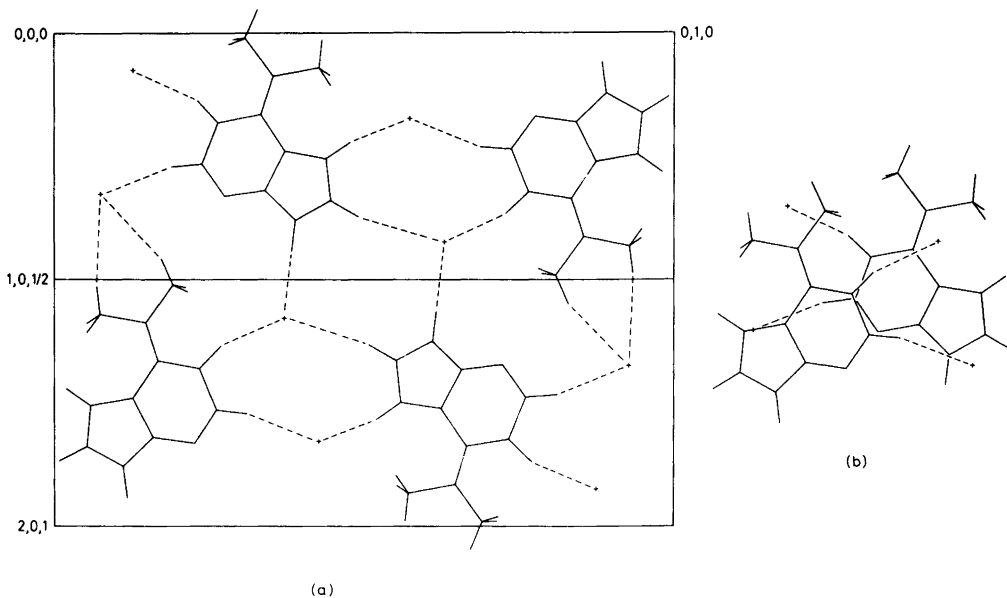


Fig. 3. The molecular packing in $\text{DMA} \cdot 2\text{HCl}$ along $(10\bar{2})$ viewed perpendicular to this plane (a), and along the stack, viewed perpendicular to the average molecular plane (b). Broken lines indicate hydrogen bonds and + marks show the Cl^- ions.

calculated structure factors and anisotropic temperature factors may be obtained from the author on request. The final positional parameters and U_{eq}/U_{iso} values are given in Table 2.

Rigid-body-motion analysis and correction of bond distances for librational motion was performed for both compounds. All the corrections are far from significant, however, and only uncorrected distances are shown in Fig. 1.

Scattering factors for the H atoms are taken from Ref. 3, those used for the other atoms are taken from Ref. 4. All calculations have been performed at the CYBER 171 MP at the University of Tromsø. The computer program used for rigid-body-motion analysis is that of Schomaker and Trueblood⁵ and that used for data reduction has been written at the University of Lund. These programs have been adapted at the University of Tromsø. The other programs used are included in the X-Ray 76 system.⁶

DISCUSSION

DMA is protonated at N(1) in DMA·HCl·H₂O and at N(1) and N(7) in DMA·2HCl, and the positions of all H atoms bonded to the rings are as observed in other mono- and di-protonated adenine derivatives.^{2,7} Even the bond distances and angles (Fig. 1) agree well with those found earlier in such ions.^{2,7} The protonation of DMA thus normally seems to occur as for other adenine derivatives. The unusual H positions and corresponding bond distances and angles observed in monoprotonated DMA in the tricyanoethenolate dioxane solvate¹ are therefore probably results of unusual intermolecular interactions in this compound.

As observed in many other neutral and protonated adenine derivatives,⁷ the C and N atoms in both ions deviate significantly from coplanarity. However, within the limits of error, one part of each ion is planar. For the monoprotonated ion the planar part includes both rings apart from C(6), and for the diprotonated ion the imidazole ring and C(6).

The molecular packing is shown in Figs. 2 and 3. In both compounds the ions and molecules are linked by hydrogen bonds in a nearly planar network, along (102) in DMA·HCl·H₂O and along (10 $\bar{2}$) in DMA·2HCl. These planes are held together through stacks along [001] and in

DMA·Cl·H₂O also by one hydrogen bond per asymmetric unit.

Tables showing the geometry of the hydrogen bonds and deviations from least squares planes through the molecules may be obtained from the author on request.

In DMA·HCl·H₂O the angle between the planar parts of adjacent ions in the stack is 5.3° and the average interplanar distance is 3.33 Å. In DMA·2HCl the corresponding angle and distance is 9.7° and 3.36 Å. It appears from Figs. 2 and 3 that there is little or no overlap of the ions. It is worth noticing that in both structures the distances between Cl⁻ and C(6), 3.60 Å in DMA·HCl·H₂O and 3.36 Å in DMA·2HCl, are the shortest along the stacks between Cl⁻ and a non-hydrogen atom. This remarkably close contact in DMA·2HCl and the hydrogen bond in DMA·HCl·H₂O are the only intermolecular contacts along the stacks shorter than the van der Waals distances.

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