

# Crystal Structure of *N*(6),*N*(6)-Dimethyladeninium Nitrate

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The title compound crystallizes in the monoclinic space group  $P2_1/c$  with cell dimensions  $a = 10.790(2)$ ,  $b = 5.661(2)$ ,  $c = 16.653(3)$  Å,  $\beta = 109.98(2)^\circ$ . The structure was determined by X-ray methods and refined to  $R = 0.051$  for 807 observed reflections. The *N*(6),*N*(6)-dimethyladeninium ions have H atoms bonded to N(3) and N(7). These ions are linked to each other and to nitrate ions by hydrogen bonds. The structure of this and other *N*(6)-substituted adeninium compounds indicate that the reason why N(1) is not protonated in several of these compounds is steric hindrance of hydrogen-bond formation from such an NH group.

The protonation of *N*(6)-substituted adeninium ions is different in different compounds and depends on the anion present. In the chlorides of the *N*(6)-methyladeninium and the *N*(6),*N*(6)-dimethyladeninium (DMA) ions, H atoms are bonded to N(1) and N(9),<sup>1,2</sup> as is also the case for all compounds of the unsubstituted adeninium ion.<sup>3</sup> In DMA tricyanoethenolate dioxane solvate,<sup>4</sup> *N*(6)-furfuryladieninium picrate<sup>5</sup> and *N*(6)-methyladeninium picrate<sup>6</sup> H atoms are bonded to N(3) and N(7), and in DMA picrate<sup>7</sup> to N(3) and N(9). In all picrates the protonation make possible hydrogen bond systems which are very similar and seem to be quite stable. In the DMA compounds not protonated at N(1) there seem to be strong stacking interactions between different ions. The structure of DMA nitrate was investigated in order to elucidate the factors affecting the protonation and the stacking interactions in these compounds.

## Experimental

Crystals of a diprotonated compound were formed by evaporation of a solution of *N*(6),*N*(6)-dimethyladenine in concentrated nitric acid. These crystals were dissolved in methanol and after the addition of an equimolar amount of *N*(6),*N*(6)-dimethyladenine and slow evaporation of the solvent, yellow, plate-shaped crystals of DMA nitrate were formed. The crystal used for data collection had the approximate dimensions 0.1×0.3×0.2 mm along the *a*-, *b*-, and *c*-axes, respectively. The cell parameters and X-ray intensities were measured on an Enraf–Nonius CAD4 diffractometer using Mo- $K_\alpha$  radiation ( $\lambda = 0.71069$  Å). The cell parameters were determined from the setting angles of 25 reflections. The intensities were collected by an  $\omega/2\theta$  scan at a rate in  $\omega$  of 0.9–4.0° min<sup>-1</sup>. For the structure determination the 807 reflections with  $I > 2\sigma(I)$  were used. Corrections were made for a continuous reduction down to 93% of the original intensities of the standard reflections and for Lorentz and polarization effects. No absorption corrections were performed.

**Crystal data.** *N*(6),*N*(6)-Dimethyladeninium nitrate,  $C_7H_{10}N_5^+NO_3^-$ ,  $M_F = 226.20$ . Space group  $P2_1/c$  (No. 13),  $a = 10.790(2)$ ,  $b = 5.661(2)$ ,  $c = 16.653(3)$  Å,  $\beta = 109.98(2)^\circ$ ,  $V = 956.0(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.571$ ,  $D_m = 1.57$  g cm<sup>-3</sup> (floatation),  $\mu(\text{Mo-}K_\alpha) = 1.366$  cm<sup>-1</sup>.

**Structure determination and refinement.** The non-H atoms were located using MULTAN80.<sup>8</sup> All H atoms were found from a difference map, except the methyl-H atoms at C(10). Positions of these atoms which could be used as starting points for refinement were calculated. In the last part of the least-squares refinement positional parameters for all atoms and thermal parameters, anisotropic for non-H atoms and isotropic for H atoms, were refined. The weighting scheme used was

$$w = [44.9 t_1(x) + 63.2 t_2(x) + 22.9 t_3(x)]^{-1}$$

where  $t_n(x)$  is the Chebyshev polynomial and  $x = |F_0|/|F_0(\text{max})|$ .<sup>9</sup> The final  $R = 0.051$  and  $R_w = [\sum w(F_0 - F_c)^2 / \sum wF^2]^{1/2} = 0.039$ . The maximum electron density in the final difference map is 0.23 e Å<sup>-3</sup>. Lists of observed and calculated structure factors and anisotropic temperature factors may be obtained from one of the authors (T.D.) on request. The final positional parameters and  $U_{eq}/U_{iso}$  values are given in Table 1.

Rigid-body-motion analysis showed that all non-H atoms of the DMA ion and all atoms of the nitrate ion vibrate approximately as rigid groups.<sup>10</sup> For the DMA ion corrections of bond distances for librational motion are smaller than the standard deviations. Uncorrected bond distances for this ion, uncorrected and corrected bond distances for the nitrate ion, bond angles for both ions and the geometry of the hydrogen bond between the two ions are shown in Fig. 1. The molecular packing is shown in Fig. 2.

Scattering factors were taken from Ref. 11. With the exception of MULTAN80, all computer programs used are included in the Oxford CRYSTALS package.<sup>12</sup>

Table 1. Positional parameters and equivalent or isotropic temperature factors ( $\text{\AA}^2$ ).<sup>a</sup>

Atom	x	y	z	$U_{\text{eq}}^b$ or $U_{\text{iso}}$
N(1)	0.8194(4)	0.5248(7)	0.2217(3)	0.034(2)
C(2)	0.7323(5)	0.5244(10)	0.2592(4)	0.038(2)
N(3)	0.6329(4)	0.3699(8)	0.2454(3)	0.035(2)
C(4)	0.6261(5)	0.1984(10)	0.1870(3)	0.029(2)
C(5)	0.7113(5)	0.1894(9)	0.1429(3)	0.029(2)
C(6)	0.8154(5)	0.3583(10)	0.1612(3)	0.031(2)
N(6)	0.9094(4)	0.3680(7)	0.1272(3)	0.032(2)
C(10)	1.0131(7)	0.5479(13)	0.1555(6)	0.056(3)
C(11)	0.9163(8)	0.2067(14)	0.0611(6)	0.049(3)
N(7)	0.6727(4)	-0.0080(8)	0.0901(3)	0.033(3)
C(8)	0.5684(5)	-0.0987(10)	0.1070(3)	0.034(2)
N(9)	0.5362(4)	0.0166(8)	0.1657(3)	0.035(2)
H(2)	0.738(6)	0.636(11)	0.309(3)	0.07(2)
H(3)	0.574(4)	0.377(8)	0.280(3)	0.02(1)
H(7)	0.699(4)	-0.059(8)	0.044(3)	0.04(1)
H(8)	0.521(5)	-0.248(9)	0.070(3)	0.05(2)
H(101)	1.030(8)	0.585(15)	0.203(5)	0.13(4)
H(102)	1.111(12)	0.480(19)	0.160(6)	0.22(5)
H(103)	1.021(10)	0.595(19)	0.100(6)	0.16(4)
H(111)	1.005(6)	0.247(12)	0.044(3)	0.11(2)
H(112)	0.836(7)	0.219(12)	0.010(4)	0.11(3)
H(113)	0.916(7)	0.070(12)	0.076(4)	0.07(3)
N(21)	0.3121(5)	0.3178(8)	0.0622(3)	0.036(2)
O(21)	0.2313(4)	0.2190(7)	0.0340(3)	0.056(2)
O(22)	0.3832(4)	0.4439(7)	0.0221(2)	0.055(2)
O(23)	0.3154(4)	0.4850(7)	0.1286(2)	0.056(2)

<sup>a</sup> Standard deviations in parentheses. <sup>b</sup>  $U_{\text{eq}} = 1/3 \sum \sum U_{ij} a_i^* a_j^* a_i a_j \cos \alpha_{ij}$ .

## Discussion

The DMA ion has H atoms bonded to N(3) and N(7). No bond distances or angles of this ion deviate significantly

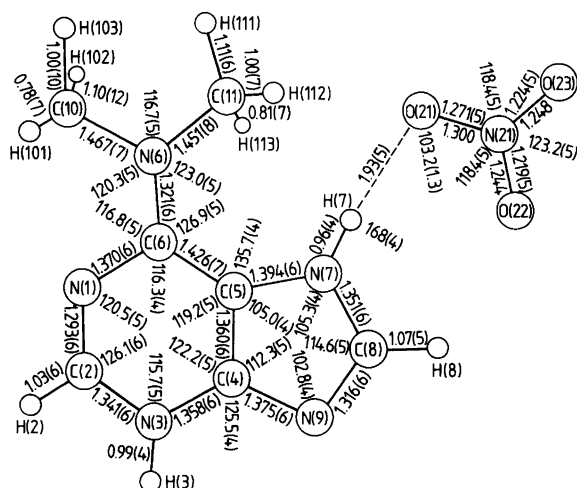


Fig. 1. Distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) of the covalent bonds and the hydrogen bond between the two ions. Standard deviations in parentheses. Distances in the nitrate ion corrected for librational motion are shown underneath the uncorrected distances.

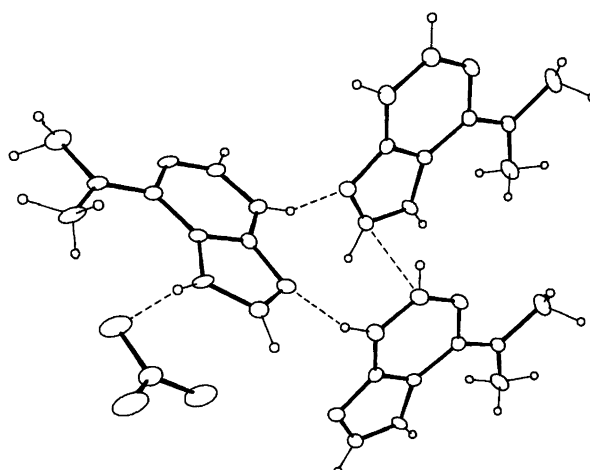


Fig. 2. The molecular packing. The hydrogen bonds and the short intermolecular distance between C atoms are shown with broken lines.

from the corresponding distances and angles in other compounds with the same protonation.<sup>4-6</sup> The significant differences between the bond distances and the bond angles of the nitrate ion indicate that the geometry is influenced by the hydrogen bond to O(21). The corrected N(21)-O(21) distance is longer than the bond distances usually observed in nitrate ions.<sup>3</sup>

No atoms of the ring system of the DMA ion deviate significantly from planarity, except C(8) and N(9) which are 0.047(6) and 0.065(5)  $\text{\AA}$ , respectively, out of this plane. N(6) is 0.034(4)  $\text{\AA}$  out of the same plane, and the planar group C(6), N(6), C(10), C(11) is twisted 2.8(4) $^\circ$  relative to it. No atoms of the nitrate ion deviate significantly from planarity.

DMA ions related by a twofold screw axis are linked together by hydrogen bonds (Fig. 2) with distances H(3)---N(9) = 1.90(4)  $\text{\AA}$ , N(3)---N(9) = 2.839(5)  $\text{\AA}$  and angle N(3)-H(3)-N(9) = 158(4) $^\circ$ . The nitrate ion is linked to the DMA ion by a hydrogen bond and, in addition, each of the O atoms is involved in a C-H---O contact with a H---O distance of 2.3–2.4  $\text{\AA}$ . The only intermolecular distance between non-H atoms shorter than the van der Waals distance is that of 3.322(7)  $\text{\AA}$  between C(2) and C(8) which is indicated in Fig. 2. These are the only overlapping atoms of DMA ions stacked along the *b*-axis. The structure indicates no stacking interactions between the DMA ion and the nitrate ion.

There seems to be little similarity between this compound and other related compounds not protonated at N(1), either in the hydrogen-bond system, or in the packing of the ions. However, in the N(6)-substituted adeninium compounds investigated so far all NH groups participate in hydrogen bonds. The reason why compounds with anions larger than chloride are not protonated at N(1) may be that a hydrogen bond from N(1) would be sterically hindered by a substituent at N(6). If so, the difference in energy between the N(1),N(9)- and the N(3),N(7)-tautomeric form

of N(6)-substituted adeninium ions must be smaller than the energy of a single hydrogen bond.

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