# Crystal Structure of N(6)-Methyladeninium Picrate

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The title compound crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a = 11.314(3)$, $b = 5.017(2)$, $c = 26.797(6)$ Å, $\beta = 100.62(2)°$. The structure was determined by X-ray methods and refined to $R = 0.051$ for 1082 observed reflections. The N(6)-methyladeninium ion has H atoms bonded to N(3) and N(7). The two ions are linked together by one bifurcated and one ordinary hydrogen bond. The structure indicates no strong stacking interactions between the ions.

The protonation of the $N(6),N(6)$-dimethyladeninium (DMA) ion has been shown to be different in three different crystalline compounds.[1-3] The $N(6)$ monosubstituted adeninium ions in kinetin picrate [$N(6)$-furfuryladeninium picrate][4] and $N(6)$-methyladeninium (MA) chloride[5] are also protonated differently.

In DMA picrate, the ions are stacked alternately with a considerable overlap and a relatively short interplanar distance, which indicates some charge-transfer contribution to the stacking interactions. No such stacking was observed in kinetin picrate. A possible relationship between protonation and stacking interactions in DMA compounds has been discussed.[3] The purpose of the present investigation was to observe the protonation and possible stacking interactions in MA picrate.

## Experimental

Light yellow, needle-shaped crystals were obtained by very slow evaporation of a solution of equimolar amounts of $N(6)$-methyladenine and picric acid in methanol. The crystal used for data collection had the dimensions $0.15 \times 0.50 \times 0.25$ mm, respectively, approximately along the $a$, $b$- and $c$-axis.

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$^{-1}$. For the structure determination the 1082 reflections with $I > 2\sigma(I)$ were used. Corrections were made for a continous reduction down to 92% of the original intensities of the standard reflections and for Lorentz and polarization effects. No absorption corrections were performed.

*Crystal data.* $N(6)$-Methyladeninium picrate, $C_6H_8N_5^+$ $C_6H_2N_3O_7^-$, $M_f = 378.26$. Space group $P2_1/c$ (No. 13), $a = 11.314(3)$, $b = 5.017(2)$, $c = 26.797(6)$ Å, $\beta = 100.62(2)°$,

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

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ or $U_{iso}$ |
|---|---|---|---|---|
| N(1) | 0.4803(5) | 0.2740(12) | 0.3453(2) | 0.047(2) |
| C(2) | 0.5328(7) | 0.1033(17) | 0.3790(3) | 0.050(3) |
| N(3) | 0.5143(5) | 0.0689(14) | 0.4264(2) | 0.047(3) |
| C(4) | 0.4323(6) | 0.2373(16) | 0.4412(2) | 0.044(3) |
| C(5) | 0.3742(5) | 0.4233(14) | 0.4082(2) | 0.038(3) |
| C(6) | 0.3994(6) | 0.4476(15) | 0.3590(2) | 0.039(3) |
| N(6) | 0.3490(6) | 0.6290(13) | 0.3254(2) | 0.045(3) |
| C(11) | 0.3745(10) | 0.6554(24) | 0.2741(3) | 0.056(4) |
| N(7) | 0.2984(5) | 0.5503(14) | 0.4345(2) | 0.051(2) |
| C(8) | 0.3134(7) | 0.4339(17) | 0.4804(3) | 0.053(3) |
| N(9) | 0.3956(5) | 0.2446(14) | 0.4864(2) | 0.051(3) |
| H(2) | 0.584(5) | −0.001(15) | 0.370(2) | 0.05(2) |
| H(3) | 0.559(6) | −0.040(16) | 0.453(3) | 0.07(2) |
| H(6) | 0.288(6) | 0.711(14) | 0.334(2) | 0.05(2) |
| H(7) | 0.240(6) | 0.696(16) | 0.425(3) | 0.07(3) |
| H(8) | 0.275(8) | 0.525(21) | 0.507(3) | 0.12(4) |
| H(111) | 0.456(8) | 0.672(17) | 0.279(3) | 0.08(3) |
| H(112) | 0.332(7) | 0.806(19) | 0.253(3) | 0.10(3) |
| H(113) | 0.372(9) | 0.489(24) | 0.260(4) | 0.12(4) |
| C(21) | 0.0796(6) | 0.0608(16) | 0.3729(2) | 0.044(3) |
| O(21) | 0.1705(4) | −0.0862(11) | 0.3764(2) | 0.059(2) |
| C(22) | −0.0010(6) | 0.0550(15) | 0.408602) | 0.044(3) |
| N(22) | 0.0239(9) | −0.1367(15) | 0.4513(2) | 0.069(2) |
| O(22) | 0.1280(7) | −0.1697(18) | 0.4705(2) | 0.132(4) |
| O(23) | −0.0621(7) | −0.2316(12) | 0.4661(2) | 0.094(3) |
| C(23) | −0.1001(7) | 0.2096(15) | 0.4063(2) | 0.043(3) |
| C(24) | −0.1271(6) | 0.3941(14) | 0.3677(2) | 0.039(2) |
| N(24) | −0.2295(5) | 0.5655(15) | 0.3666(2) | 0.054(3) |
| O(24) | −0.2889(4) | 0.5476(12) | 0.4003(2) | 0.064(3) |
| O(25) | −0.2530(5) | 0.7278(14) | 0.3319(2) | 0.084(3) |
| C(25) | −0.0559(6) | 0.4139(16) | 0.3313(2) | 0.042(3) |
| C(26) | 0.0419(5) | 0.2541(14) | 0.3331(2) | 0.035(2) |
| N(26) | 0.1104(5) | 0.2807(13) | 0.2929(2) | 0.040(2) |
| O(26) | 0.0875(4) | 0.4743(12) | 0.2641(2) | 0.060(2) |
| O(27) | 0.1862(5) | 0.1170(12) | 0.2877(2) | 0.059(2) |
| H(23) | −0.150(5) | 0.199(12) | 0.430(2) | 0.03(2) |
| H(25) | −0.069(4) | 0.539(12) | 0.307(2) | 0.02(2) |
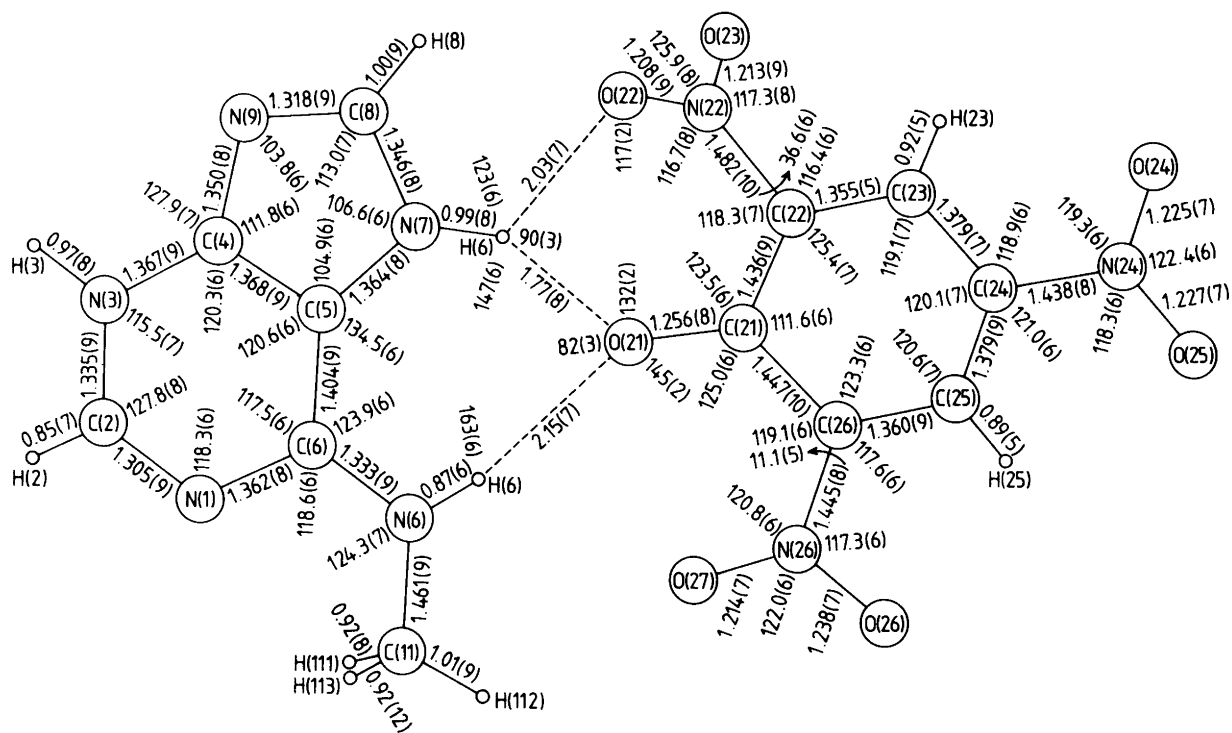
*Fig. 1.* Distances (Å) and angles (°) of the covalent bonds and the hydrogen bonds between the two ions, and the torsion angles (°) of the nitro groups which are significantly twisted relative to the ring plane of the picrate ion. Standard deviations are in parentheses.

$V = 1494.8(8)$ Å, $Z = 4$, $D_x = 1.681$, $D_m = 1.65$ g cm$^{-3}$ (flotation), $\mu$(Mo-$K_\alpha$) = 1.528 cm$^{-1}$.

*Structure determination and refinement.* The non-H atoms were located using MULTAN 80.[6] All H atoms were found from a difference map. In the last part of the least-squares refinement, positional parameters for all atoms and ther-

mal parameters, anisotropic for non-H atoms and isotropic for H atoms, were refined. As secondary extinction turned out to be important, an isotropic extinction parameter was refined. The weighting scheme used was $w = [16.4 \ t_1 \ (x) + 17.8 \ t_2 \ (x) + 1.2 \ t_3 \ (x) - 3.9 \ t_4 \ (x)]^{-1}$ where $t_n (x)$ is the Chebyshev polynominal and $x = |F_o|/|F_o(\text{max})|$.[7] The final $R = 0.051$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F^2]^{\frac{1}{2}} = 0.060$. The
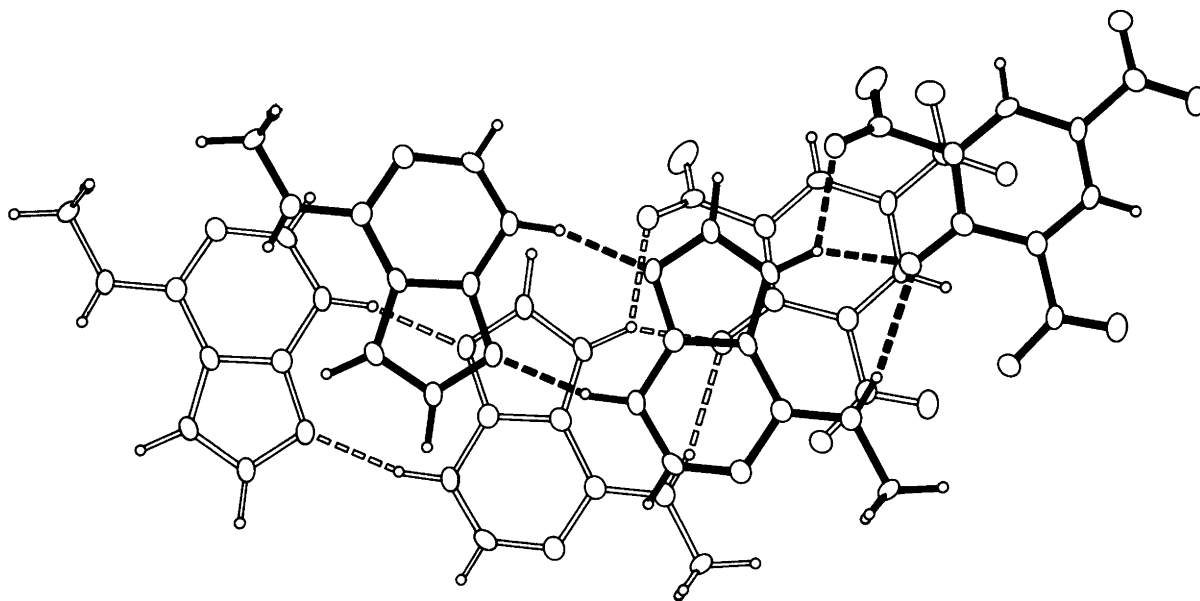


*Fig. 2.* The molecular packing viewed perpendicular to the planar part of the MA ion.

maximum electron density in the final difference map is 0.25 e $Å^{-3}$. Lists of observed and calculated structure 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 MA ion and all such atoms of the picrate ion except O(22) and O(23) vibrate approximately as rigid groups.[8] The corrections of bond distances for librational motion are not significant and only uncorrected distances are shown in Fig. 1. This figure also shows the valence angles, the torsion angles of the two nitro groups which are significantly twisted, and the geometry of the hydrogen bonds between the MA ion and the picrate ion. The molecular packing is shown in Fig. 2.

Scattering factors were taken from Ref. 9. With the exception of MULTAN 80 all computer programs used are included in the Oxford CRYSTALS package.[10]

## Discussion

No bond distances or angles of the picrate ion deviate significantly from those observed in other picrates.[3,11,12] All atoms of the six-membered ring as well as N(22) and N(24) are coplanar. O(21) and N(26) are $-0.041(6)$ and $0.044$ (7) Å, respectively, out of this plane. A considerable degree of twisting of one or both nitro groups in a position *ortho* to O(21) has been observed in many other picrates.[3,11,12]

All non-H atoms of the MA ion are coplanar except N(1) which is 0.044(6) Å out of the plane. The ion has H atoms bonded to N(3) and N(7) as is observed also in kinetin picrate, not to N(1) and N(9) as in MA chloride. In DMA picrate the H atoms are bonded to N(3) and N(9). No bond distances and angles of the DMA ion deviate significantly from the corresponding distances and angles in kinetin picrate, but as a result of the different protonations there are several significant deviations from those observed in MA chloride.

Two MA ions are linked together by two equivalent N(3)–H(3)$\cdots$N(9) hydrogen bonds (Fig. 2). The N(3)$\cdots$N(9) distance is 2.848(8) Å, H(3)–N(9) = 1.91(8) Å, and the angle N(3)–H(3) $\cdots$ N(9) = 163(6)°. The hydrogen bonds to the picrate ion from H(6) and H(7) are quite similar to those from the corresponding atoms in kinetin picrate and from H(9) and H(3) in DMA picrate. In the last two compounds this hydrogen-bond system also includes a weak bond to O(27) so that both H atoms take part in bifurcated hydrogen bonds. The H(6)–O(27) distance in the present compound, 2.54(7) Å, is close to the van der

Waals distance and thus only H(7) is involved in a bifurcated hydrogen bond. The similarity indicates that the hydrogen bond systems linking different ions together in these compounds are relatively stable. No such system could have been formed in DMA picrate if the DMA ion had the H atoms bonded to N(3) and N(7) and this may be one important reason for the different protonation of this compound.

Sheets of hydrogen-bonded ions are stacked along the *b*-axis, but there is very little overlap of either different ions or equal ions (Fig. 2). The intermolecular distances between the sheets are all well outside the van der Waals distances. Moreover, the angle of 16.8(3)° between the planar parts of the two ions indicates that there is no strong stacking interaction between different ions.

This work thus seems to confirm that there is a relationship between protonation and stacking interactions in substituted adeninium compounds. A possible explanation for the stronger interactions in DMA picrate may be that an adeninium ion with H atoms bonded to N(3) and N(9) is a stronger electron donor than is one with H atoms bonded to N(3) and N(7).

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