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Crystal Structures of *N*(6),*N*(6)-Dimethyladeninium Trichloroacetate and *N*(6)-Methyladeninium Dinitrate

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N(6),*N*(6)-Dimethyladeninium trichloroacetate crystallizes in the orthorombic space group *Pnma* with cell dimensions $a = 20.008(5)$, $b = 6.738(3)$, $c = 7.291(2)$ Å. The structure was refined to $R = 0.068$ for 549 observed reflections. The adeninium ion has H atoms bonded to N(3) and N(9). This kind of protonation of an adeninium ion has been observed earlier only in *N*(6),*N*(6)-dimethyladeninium picrate.

N(6)-Methyladeninium dinitrate crystallizes in the monoclinicic space group $P2_1/c$ with cell dimensions $a=6.428(2)$, $b=20.269(2)$, $c=16.918(2)$ Å, $\beta=98.56(2)°$. The structure was refined to $R=0.054$ for 3215 observed reflections. There are two crystallographically independent formula units. In both units the adeninium ion has H atoms bonded to N(1), N(3) and N(9), as observed earlier for *N*(6),*N*(6)-dimethyladeninium dichloride. This result indicates that diprotonated *N*(6) substituted adeninium ions do not show a similar kind of tautomerism as that observed for the corresponding monoprotonated ions.

By X-ray structure determinations it has been shown that the bonding of H atoms to ring N atoms in *N*(6)-monosubstituted and *N*(6),*N*(6)-disubstituted adeninium ions, in this and previous papers called the protonation of the ring N atoms, is different in different compounds and depends on the anion present. In some compounds the protonation is at N(1) and N(9),[1–4] as also observed in all compounds of the unsubstituted adeninium ion.[5,6] In several other compounds the protonation is at N(3) and N(7).[7–10] This tautomerism has been explained as results of differences in strength of the possible hydrogen bonds in these compounds.[3] In *N*(6),*N*(6)-dimethyladeninium picrate the protonation is at N(3) and N(9).[11] This has been assumed to be due to the geometry of the picrate ion with three O atoms in such positions that two bifurcated hydrogen bonds may be formed from N(3)–H(3) and N(9)–H(9).

^{15}N NMR spectra show that protonation of *N*(6),*N*(6)-dimethyladenine by trifluoroacetic acid in dimethyl sulfoxide solution results in an equilibrium between different tautomers.[12] As no X-ray studies have been performed so far of *N*(6)-substituted adenines protonated by carboxylic acids, the structure of *N*(6),*N*(6)-dimethyladeninium (DMA) trichloroacetate was determined.

N(6),*N*(6)-Dimethyladeninium dichloride, which is the only diprotonated *N*(6)-substituted adeninium compound which has been studied by X-ray crystallography, is protonated at N(1), N(7) and N(9),[2] as also observed for other diprotonated adeninium compounds.[6] *N*(6)-Dimethyladeninium (MA) dinitrate was studied in order to see if tautomerism may occur also on diprotonation of *N*(6) substituted adeninium compounds.

Experimental

Crystals of DMA trichloroacetate were obtained by slow evaporation of the solvent from a solution in methanol of *N*(6),*N*(6)-dimethyladenine and trichloroacetic acid in the molar ratio 1 : 1. Very poor crystals of MA dinitrate were formed by slow evaporation of a solution of *N*(6)-methyladenine in concentrated nitric acid. By dissolving these crystals in a mixture of methanol and ethanol and subsequent evaporation of the solvent, crystals of a better quality could be obtained. The cell parameters and X-ray intensities were measured on an Enraf-Nonius CAD4 diffractometer. For DMA trichloroacetate the reflections were weak, and exposure to the X-ray beam resulted in a strong reduction of the intensities. There were similar problems, but to a lesser degree, also for MA dinitrate. In order to reduce the radiation damage, the crystals were kept in sealed capillaries, and Cu$K\alpha$ radiation (λ = 1.5418 Å) rather than Mo$K\alpha$ radiation was used. The cell parameters were obtained from the setting angles of 25 reflections. Crystal data and experimental conditions are given in Table 1. Corrections were made for the

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Table 1. Crystal data and experimental conditions.

Compound	*N*(6),*N*(6)-Dimethyladeninium trichloroacetate	*N*(6)-Methyladeninium dinitrate
Formula	$C_7N_5H_{10}^+ \cdot CCl_3COO^-$	$C_6N_5H_9^{2+} \cdot 2NO_3^-$
M_r	326.57	275.18
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/c$
a/Å	28.008(5)	6.428(2)
b/Å	6.738(3)	20.269(2)
c/Å	7.291(2)	16.918(2)
β/°		98.56(2)
V/Å^3	1375.9(6)	2179.6(5)
Z	4	8
D_x/g cm^{-3}	1.576	1.677
D_m/g cm^{-3} (flotation)	1.60	1.63
μ(Cu*K*α)/cm^{-1}	60.9	13.3
Absorption correction (max/min)	2.187/0.535	1.770/0.702
Crystal dimensions/mm	0.07 × 0.30 × 0.07	0.35 × 0.30 × 0.22
Scan mode	ω/2Θ	ω/2Θ
Scan speed of ω/° min^{-1}	0.5–2.7	0.5–3.3
Θ range/°	0–75	0–75
Criterion for significance	$I>2\sigma(I)$	$I>3\sigma(I)$
No. of independent reflections measured	1396	4136
No. of reflections used in final refinement	549	3215
$w=1$ for $\lvert F_o\rvert<A$, $(A/F_o)^2$ for $\lvert F_o\rvert>A$, $A=$	34	50
$R=\Sigma\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\Sigma\lvert F\rvert$	0.068	0.054
$R_w=[\Sigma w(F_o-F_c)^2/\Sigma wF^2]^{1/2}$	0.069	0.059
Max Δρ/e Å^{-3}	0.25	0.53

continous reductions of the standard reflections down to 65% and 91% of their original intensities for DMA trichloroacetate and MA dinitrate, respectively, and for Lorentz and polarization effects. The crystals of both compounds had very irregular shapes and the dimensions were difficult to measure. Corrections for absorption were therefore performed by the empirical method of Walker and Stuart[13] during the structure refinement, before merging of equivalent reflections, and before anisotropic temperature factors were introduced.

All computer programs used in the structure determinations and refinements are included in Ref. 14. Scattering factors were taken from Ref. 15. For both structures all non-H atoms were found by direct methods using MULTAN80.[16] For MA dinitrate all H atoms were found from difference maps, and positional parameters for all atoms and thermal parameters, anisotropic for non-H atoms and isotropic for H atoms, were refined in the final least-squares refinement.

For DMA trichloroacetate two space-groups, $Pn2_1a$ and *Pnma*, were possible from the Laue symmetry and the systematic absences. Refinement based on both space groups were therefore performed. Refinements based on $Pn2_1a$ failed to converge and gave unreasonable results. With *Pnma* the structure could be refined satisfactorily. Disorder had to be introduced, with two equivalent orientations of the $-CCl_3$ group, rotated relative to each other around the C–C bond, which is situated in the mirror plane (010). All H atoms could be located from difference maps, except one methyl-H atom. The approximate position of this atom was calculated. In the final least-squares refinement positional paremeters and anisotropic thermal parameters of the disordered Cl atoms were refined separately in alternate cycles. For all other non-H atoms positional parameters and anisotropic thermal parameters were refined simultaneously. For all non-methyl H atoms and one methyl-H atom positional parameters could be refined. Isotropic thermal parameters could be refined for the non-methyl H atoms except that of H(9). The other parameters of the H atoms were kept fixed in the refinements.

The final positional parameters and U_{eq}-values for non-H atoms are given in Table 2. Bond distances and angles not involving H atoms, geometry of the hydrogen bonds and the packing of the ions are shown in Figs. 1 and 2. Lists of observed and calculated structure factors, anisotropic temperature factors, positions and U_{iso}-values for H atoms and bond distances and angles involving H atoms may be obtained from one of the authors (T.D.) on request.

Results

In DMA trichloroacetate the non-H part of the adeninium ion is restricted to be planar by the space group symmetry. The H positions located from the difference map shows that the ion is protonated at N(3) and N(9). This conclusion is confirmed by the finding that no bond distances or angles in the DMA ion deviate significantly from those observed in DMA picrate,[11] which has the same protonation. Several of the distances and angles are significantly different from those of *N*(1),*N*(9)- and *N*(3),*N*(7)-protonated DMA ions. A sufficient condition for *N*(3),*N*(9)-protonation seems therefore to be that

Table 2. Positional parameters and equivalent temperature factors (in Å^2) for non-H atoms.[a]

Atom	x	y	z	U_{eq}[b]
N(6),*N*(6)-Dimethyladeninium trichloroacetate				
N(1)	0.5659(3)	0.250	0.251(1)	0.068(4)
C(2)	0.5270(5)	0.250	0.351(1)	0.071(5)
N(3)	0.4826(3)	0.250	0.289(1)	0.064(4)
C(4)	0.4788(4)	0.250	0.103(1)	0.052(4)
C(5)	0.5167(4)	0.250	−0.016(2)	0.052(4)
C(6)	0.5625(4)	0.250	0.060(2)	0.058(4)
N(7)	0.5002(3)	0.250	−0.196(1)	0.058(4)
C(8)	0.4538(4)	0.250	−0.175(1)	0.058(4)
N(9)	0.4381(3)	0.250	0.004(1)	0.061(4)
N(6)	0.6037(3)	0.250	−0.029(1)	0.068(4)
C(10)	0.6492(5)	0.250	0.061(2)	0.108(5)
C(11)	0.6050(5)	0.250	−0.227(2)	0.096(8)
Cl(1)[c]	0.3205(1)	0.284(1)	0.7027(6)	0.108(2)
Cl(2)[c]	0.2756(2)	0.429(1)	0.3820(3)	0.132(2)
Cl(3)[c]	0.2851(2)	0.012(1)	0.4424(8)	0.128(3)
O(1)	0.3977(3)	0.250	0.450(1)	0.085(4)
O(2)	0.3552(3)	0.250	0.187(1)	0.088(4)
C(12)	0.3593(4)	0.250	0.356(2)	0.075(5)
C(13)	0.3124(4)	0.250	0.462(2)	0.066(5)
N(6)-Methyladeninium dinitrate				
N(1)	0.5510(4)	0.6319(1)	0.3350(1)	0.033(1)
C(2)	0.5622(5)	0.6965(1)	0.3119(2)	0.036(1)
N(3)	0.5613(4)	0.7172(1)	0.2393(1)	0.037(1)
C(4)	0.5445(4)	0.6673(1)	0.1861(2)	0.033(1)
C(5)	0.5304(4)	0.6012(1)	0.2028(2)	0.031(1)
C(6)	0.5387(4)	0.5806(1)	0.2831(2)	0.031(1)
N(7)	0.5149(4)	0.5676(1)	0.1318(1)	0.037(1)
C(8)	0.5215(5)	0.6113(1)	0.0749(2)	0.043(1)
N(9)	0.5384(4)	0.6719(1)	0.1050(1)	0.039(1)
N(6)	0.5361(4)	0.5192(1)	0.3065(1)	0.037(1)
C(10)	0.5399(5)	0.4978(2)	0.3886(2)	0.043(1)
N(10)	0.5322(4)	0.8276(1)	0.0321(1)	0.039(1)
O(1)	0.5545(4)	0.7743(1)	−0.0028(1)	0.060(1)
O(2)	0.5470(4)	0.8805(1)	−0.0049(1)	0.053(1)
O(3)	0.5028(5)	0.8277(1)	0.1015(1)	0.071(1)
N(11)	0.4966(4)	0.3948(1)	0.1415(2)	0.039(1)
O(4)	0.5087(4)	0.3396(1)	0.1133(1)	0.056(1)
O(5)	0.4283(5)	0.4410(1)	0.0952(2)	0.070(1)
O(6)	0.5432(5)	0.4059(1)	0.2133(2)	0.076(1)
N(1)′	−0.0422(4)	0.2531(1)	0.1971(1)	0.034(1)
C(2)′	−0.0540(5)	0.2213(1)	0.2678(2)	0.037(1)
N(3)′	−0.0471(4)	0.2489(1)	0.3373(2)	0.039(1)
C(4)′	−0.0214(4)	0.3154(1)	0.3332(2)	0.033(1)
C(5)′	0.0003(4)	0.3512(1)	0.2666(2)	0.033(1)
C(6)′	−0.0133(4)	0.3199(1)	0.1916(2)	0.032(1)
N(7)′	0.0282(4)	0.4164(1)	0.2897(2)	0.039(1)
C(8)′	0.0223(5)	0.4188(1)	0.3671(2)	0.042(1)
N(9)′	−0.0082(4)	0.3588(1)	0.3953(1)	0.041(1)
N(6)′	0.0001(4)	0.3491(1)	0.1239(1)	0.039(1)
C(10)′	−0.0183(6)	0.3167(2)	0.0465(2)	0.049(1)
N(10)′	−0.0511(4)	0.3932(1)	0.5861(1)	0.039(1)
O(1)′	−0.0472(4)	0.4395(1)	0.5394(1)	0.054(1)
O(2)′	−0.0620(5)	0.4029(1)	0.6568(1)	0.071(1)
O(3)′	−0.0422(4)	0.3346(1)	0.5605(1)	0.051(1)
N(11)′	0.0070(5)	0.5295(1)	0.1368(2)	0.054(1)
O(4)′	0.0035(5)	0.5856(1)	0.1132(2)	0.085(1)
O(5)′	0.1220(5)	0.5160(2)	0.2012(2)	0.088(1)
O(6)′	−0.1022(5)	0.4843(2)	0.1030(2)	0.094(1)

[a] Standard deviations in parentheses.
[b] $U_{eq}=1/3\Sigma\Sigma U_{ij}a_i^*a_j^*a_ia_j\cos\alpha_{ij}$. [c] Occupancy factor 0.5.

there are two O atoms in the anion in positions suitable for hydrogen bond formation from N(3)–H(3) and N(9)–H(9). The distance O(1)—O(2), 2.255(13) Å, is larger than the O—O distances in the nitrate ion,[10] the sulfate ion[3,4] and the bisulfate ion.[4] The reason why the compounds with the latter ions are not protonated in the same way may be that the geometrical conditions for formation of such hydrogen bonds are less favourable.

The two equivalent orientations of the $-CCl_3$ group in the trichloroacetate ion are rotated 20.0(5)° relative to each other. The geometry of the trichloroacetate ion agrees well with that observed in other compounds,[17] except for the short C(13)–Cl(2) distance. This unreasonable distance may possibly indicate that the model used for the disorder of the $-CCl_3$ group is too simple.

In MA dinitrate there are two crystallographically independent formula units. In both units MA is protonated at N(1), N(7) and N(9), as also observed in DMA dichloride.[2] No tautomerism in the diprotonated *N*(6)-methylated adeninium ion is thus observed. No bond distances or angles in the two independent MA ions are significantly different from each other. The N(1)–C(6) distance of 1.356(4) Å is possibly significantly shorter than the corresponding distance, 1.375(2) Å, in DMA dichloride. Apart from this, no bond distances or angles in the ring systems of the present structure differ significantly from those in DMA dichloride. The non-H part of one of the MA ions [N(1)–C(10)] is planar, except for C(6), N(6) and C(10), which are 0.036(3), 0.099(3) and 0.107(3) Å, respectively, of of the plane. The non-H part of the other MA ion (N(1)′-C(10)′) is planar, except for N(1)′, C(5)′ and C(10)′ which are 0.020(2), -0.033(3) and 0.062(4) Å, respectively, out of the plane. All the nitrate ions are planar. There are significant differences in the bond distances and angles in the nitrate ions, as also observed in other compounds.[10]

In DMA trichloroacetate the DMA ions are stacked in infinite columns with a considerable overlap (Fig. 1b). The interplanar distance in the stack is 3.369(3) Å. The packing was analyzed by atom-to-atom lattice energy calculations, using the computer program PCK83.[18] The parameters A_{jk}, B_{jk} and C_{jk} in the energy expression

$$E=\sum_j\sum_k -A_{jk}r_{jk}^{-6}+B_{jk}\exp(-C_{jk}r_{jk})+q_jq_kr_{jk}^{-1}$$

are those by Williams *et al.*,[19–21] and the net atomic charges q were calculated by the AM1 method,[22] using the computer program GAUSSIAN 86.[23] For hydrogen-bonding H-atoms $A_{jk}=0$, and B_{jk} was reduced to 25% of the value used for other H atoms in order to reproduce the experimental hydrogen bond distances. If there were intermolecular interactions in the crystals in addition to hydrogen bonds and the ordinary van der Waals interactions described by the analytical potentials, a minimization of the calculated lattice energy, starting with the experimental structure, should result in an increase in intermolecular distances. In order to keep the overlap

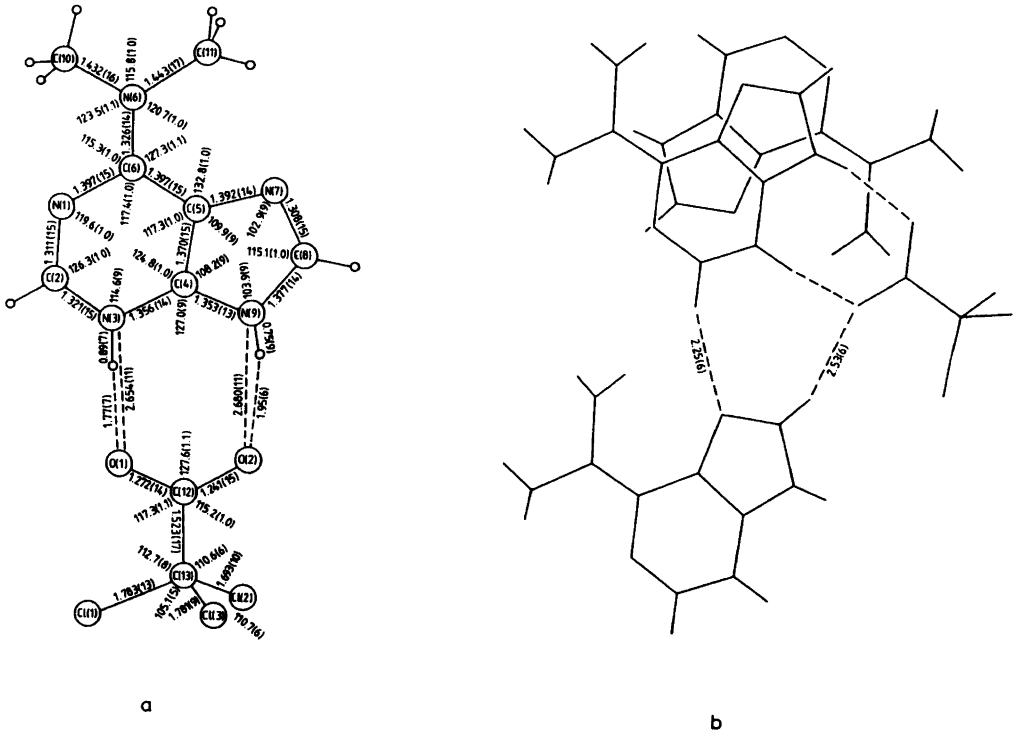

Fig. 1. Bond distances (in Å) and angles (in °) in *N*(6),*N*(6)-dimethyladeninium trichloroacetate (a) and the packing of the ions in this compound (b). The angles C(12)–C(13)–Cl(3) and Cl(1)–C(13)–Cl(2), which are not shown in the figure, are 108.9(4) and 108.6(4)°, respectively. Only one of the equivalent orientations of the $-CCl_3$ group is shown.

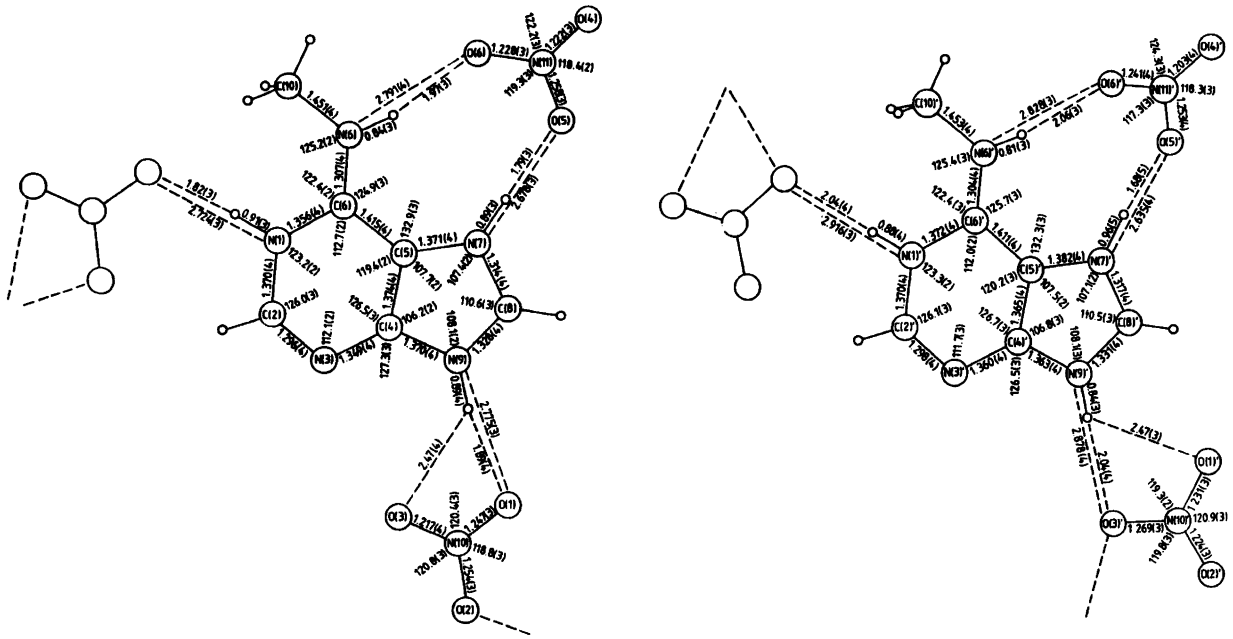

Fig. 2. Bond distances (in Å) and angles (in °) in *N*(6)-methyladeninium dinitrate.

identical to that of the experimental structure, only the crystallographic axes were varied. The interplanar distance obtained for the minimum-energy structure is 0.041 Å shorter than that of the experimental structure. The experimental interplanar distance thus indicates no unexpected strong stacking interaction in the structure.

In the two independent formula units in MA dinitrate the chains of hydrogen-bonded ions are slightly different (Fig. 2). In one chain N(1)–H(1) is bonded to O(2) in one nitrate ion, and N(9)–H(9) is bonded to O(1) in another nitrate ion. In the other chain N(1)′–H(1)′ and N(9)′–H(9)′ are bonded to O(3)′ in two different nitrate

ions. Although the O(3)—H(9) and O(1)′—H(9)′ distances are slightly shorter than the van der Waals distances, the geometries indicate that the bonds to H(9) and H(9)′ should not be regarded as bifurcated hydrogen bonds. The two chains are stacked alternately along the *a*-axis. There are no overlap and no interatomic distances below the van der Waals distances between the stacked ions.

In conlusion, this work indicates that *N*(6)-substituted adeninium ions are *N*(3),*N*(9) protonated when the anion has a geometry which is sufficiently suitable for hydrogen bond formation from both N(3)–H(3) and N(9)–H(9), and that carboxylate ions, like the picrate ion, have such a geometry. These compounds are therefore exceptions to the general rules which seem to determine the protonation in other *N*(6)-substituted adeninium compounds.[3] The work also indicates that there is no tautomerism in diprotonated adeninium ions.

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