Crystal Structure of N(6),N(6)-Dimethyladeninium Picrate

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The title compound crystallized in the triclinic space group $P\bar{1}$ with cell dimensions $a = 6.889(2)$, $b = 10.515(4)$, $c = 11.411(3)$ Å, $\alpha = 80.70(3)$, $\beta = 77.49(3)$, $\gamma = 84.51(3)°$. The structure was refined to $R = 0.058$ for 2372 observed reflections. The N(6),N(6)-dimethyladeninium ion is protonated at N(3), not at N(1) as in the chloride and in most other investigated compounds of adenium derivatives. It is linked to a picrate ion by two bifurcated hydrogen bonds. The ions are stacked alternately in infinite columns with a mean interplanar distance of 3.34 Å.

All H atoms of the N(6),N(6)-dimethyladeninium (DMA) ion are bonded as in other adeninium derivatives in the chloride,[1,2] whereas two H atoms are bonded in an unusual way in the tricyanoethenolate dioxane solvate.[3] There may be a relationship between the unusual H positions and the alternate stacks of planar molecules in the latter compound. As similar stacks were expected in DMA picrate, this compound was investigated to study the H positions in the DMA ion.

Experimental

Light yellow, needle-shaped crystals were obtained by very slow evaporation of a solution of equimolar amounts of N(6),N(6)-dimethyladenine and picric acid in methanol. The crystal used for data collection was cut from a large needle and had the dimensions $0.85 \times 0.60 \times 0.25$ mm in the directions [100], [011] and [0$\bar{1}$1].

The cell parameters and X-ray intensities were measured on an Enraf-Nonius CAD4 diffractometer using $MoK\alpha$ 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 ω of 1.0–4.0° min^{-1}. No intensity reduction of the standard reflections during the data collection was observed. For the structure determination the 2372 reflections with $I > 2\sigma$ (I) were used. Corrections were performed for Lorentz, polarization and absorption effects.

Crystal data

N(6),N(6)-Dimethyladeninium picrate, $C_7H_{10}N_5^+$ $C_6H_2N_3O_7^-$, F.W. = 392.29. Space group $P\bar{1}$, $a = 6.889(2)$, $b = 10.515(4)$, $c = 11.411(3)$ Å, $\alpha = 80.70(3)$, $\beta = 77.49(3)$, $\gamma = 84.51(3)°$, $V = 794.8(4)$ Å, $Z = 2$, $D_x = 1.639$, $D_m = 1.62$ g/cm^{-3} (flotation), $\mu(MoK\alpha) = 1.47$ cm^{-1}.

Structure determination and refinement

The approximate positions and orientations of the ions could be found from a Patterson map, and successive Fourier syntheses were used to locate the non-H atoms. All H atoms could be found from a difference map.

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 $w = XY$ with $X = 1$ for sin $\theta > 0.6$, else $X = \sin\theta/0.6$, $Y = 1$ for $|F_o| < 6$, else $Y = 6/|F_o|$. The final $R = 0.058$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF^2]^{\frac{1}{2}} = 0.071$. The maximum electron density in the final difference map is 0.39 e/Å.^{3} Lists of observed and calculated structure factors and anisotropic temperature factors may be obtained from the author on request. The final positional

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

	x	y	z	U_{eq} or U_{iso}
N(1)	0.4658(3)	0.3918(2)	0.1439(2)	0.0396(6)
C(2)	0.5493(4)	0.3264(2)	0.0566(2)	0.0407(7)
N(3)	0.5869(3)	0.1987(2)	0.0691(2)	0.0370(6)
C(4)	0.5335(3)	0.1343(2)	0.1823(2)	0.0327(7)
C(5)	0.4448(3)	0.1941(2)	0.2813(2)	0.0345(7)
C(6)	0.4099(3)	0.3304(2)	0.2607(2)	0.0342(7)
N(6)	0.3310(3)	0.4042(2)	0.3443(2)	0.0424(7)
N(7)	0.4122(3)	0.1016(2)	0.3835(2)	0.0434(7)
C(8)	0.4794(4)	−0.0066(3)	0.3436(2)	0.0460(9)
N(9)	0.5547(3)	0.0077(2)	0.2214(2)	0.0386(6)
C(10)	0.3064(7)	0.5436(3)	0.3114(3)	0.0635(12)
C(11)	0.2693(6)	0.3532(3)	0.4720(3)	0.0547(11)
H(2)	0.581(4)	0.371(3)	−0.019(3)	0.037(7)
H(3)	0.627(5)	0.160(3)	0.010(3)	0.054(9)
H(8)	0.466(5)	−0.089(4)	0.392(3)	0.058(9)
H(9)	0.584(6)	−0.048(4)	0.175(4)	0.068(11)
H(101)	0.436(10)	0.577(6)	0.272(6)	0.119(19)
H(102)	0.283(7)	0.578(5)	0.376(5)	0.094(15)
H(103)	0.214(7)	0.571(5)	0.254(5)	0.092(15)
H(111)	0.359(9)	0.375(5)	0.513(5)	0.110(18)
H(112)	0.247(6)	0.269(5)	0.481(4)	0.078(12)
H(113)	0.143(9)	0.391(6)	0.502(6)	0.117(19)
C(21)	0.1368(3)	0.0817(2)	0.0822(2)	0.0361(7)
C(22)	0.0618(4)	0.0220(2)	0.2048(2)	0.0374(7)
C(23)	−0.0333(4)	0.0876(3)	0.2974(2)	0.0412(8)
C(24)	−0.0633(4)	0.2196(3)	0.2734(2)	0.0423(8)
C(25)	−0.0069(4)	0.2861(2)	0.1583(2)	0.0413(8)
C(26)	0.0888(4)	0.2189(2)	0.0666(2)	0.0391(8)
N(22)	0.0824(4)	−0.1171(2)	0.2341(2)	0.0466(7)
N(24)	−0.1596(4)	0.2903(3)	0.3716(2)	0.0551(9)
N(26)	0.1389(4)	0.2926(2)	−0.0538(2)	0.0488(8)
O(21)	0.2237(3)	0.0214(2)	−0.0013(2)	0.0507(7)
O(22)	0.2209(4)	−0.1774(2)	0.1772(2)	0.0775(9)
O(23)	−0.0414(5)	−0.1701(2)	0.3142(3)	0.0857(11)
O(24)	−0.2111(4)	0.2293(3)	0.4727(2)	0.0811(11)
O(25)	−0.1852(5)	0.4066(3)	0.3491(3)	0.0820(11)
O(26)	0.0289(5)	0.3872(3)	−0.0778(3)	0.0840(11)
O(27)	0.2831(4)	0.2575(2)	−0.1265(2)	0.0703(8)
H(23)	−0.077(5)	0.045(3)	0.377(3)	0.054(9)
H(25)	−0.028(5)	0.377(3)	0.144(3)	0.054(9)

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 picrate ion except the O atoms of the nitro groups vibrate approximately as rigid groups. The corrections of bond distances for vibrational motion are not significant and only uncorrected distances are shown in Fig. 1. This figure also shows valance angles, torsion angles of the two nitro groups which are significantly twisted, and the geometry of the two bifurcated hydrogen bonds which were observed.

Scattering factors for the H atoms are taken from Ref. 4, while those used for the other atoms are taken from Ref. 5. All calculations were performed at the CYBER 171 MP at the University of Tromsø. The computer program used for rigid-
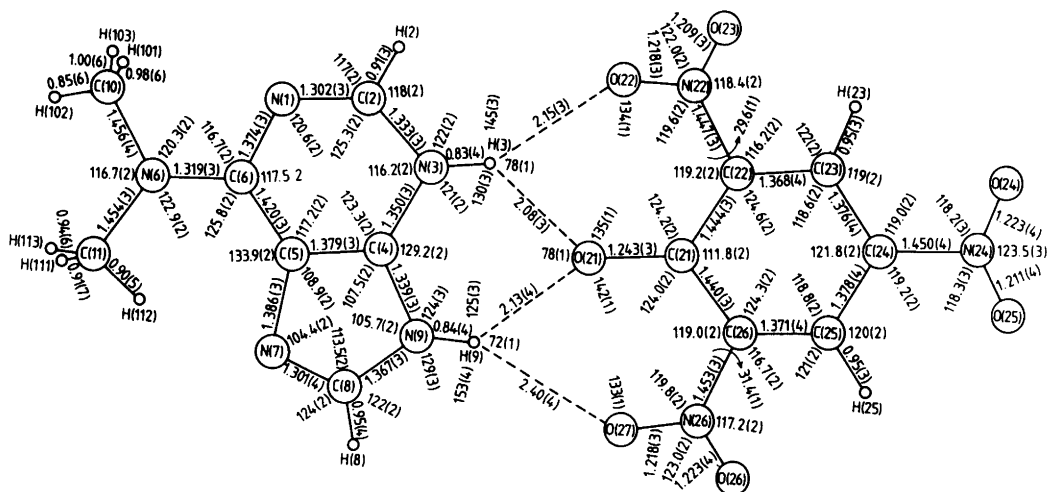
Fig. 1. Distances (Å) and angles (°) of the covalent bonds and the bifurcated hydrogen bonds, and the torsion angles (°) of the nitro groups which are significantly twisted relatively to the planar part of the picrate ion. Standard deviations in parentheses.

body-motion analysis is that of Schomaker and Trueblood[6] and that used for data reduction was written at the University of Lund. These programs were adapted at the University of Tromsø.

Fig. 2. The molecular packing viewed perpendicular to the average molecular plane, showing intermolecular contacts between different stacks (a) and the molecular overlap in the stacks (b). Intermolecular distances (Å) shorter than the van der Waals distance are shown with dotted lines. Standard deviations in (a) are 0.03 Å, in (b) 0.004 Å.

The other programs used are included in the X-Ray 76 system.[7]

Discussion

No bond distances and angles of the picrate ion are significantly different from those observed in other picrates.[8,9] Four atoms of the sixmembered ring of this ion are coplanar whereas C(21) and C(24) (Fig. 1) are 0.040(2) and 0.026(3) Å out of this plane. O(21), N(22), N(24) and N(26) are 0.043(2), −0.081(3), 0.062(3) and −0.076(3) Å out of the same plane. Various kinds of non-planarity of the ring and twisting of one or two nitro groups of the picrate ion have also been observed in other compounds.[8,9]

Each of the two rings of the DMA ion are planar, but the two planes make an angle of 0.76(9)° with each other. N(6), C(10) and C(11) are 0.032(2), 0.056(5) and 0.074(4) Å out of the plane of the pyrimidine ring. The ion is protonated at N(3) as in DMA tricyanoethenolate dioxane solvate, not at N(1) as in DMA chloride and in all compounds investigated so far of other adeninium derivatives.[2] The other N–H bond, however, is at N(9), which is normal, not at N(7) as in DMA tricyanoethenolate dioxane solvate. As a result of the different H positions several bond distances and angles of the DMA ion are
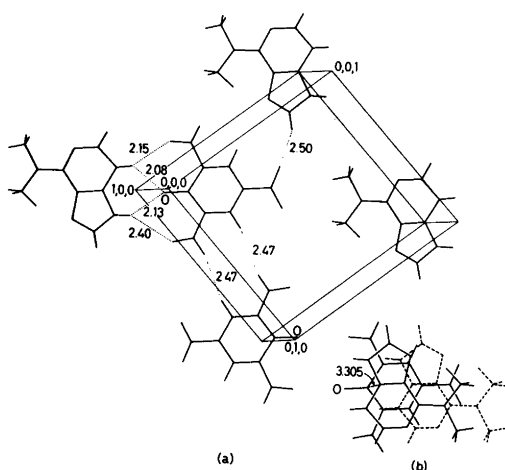
different from those observed in the chloride as well as in the tricyanoethenolate dioxane solvate.

The two ions form pairs linked together by two bifurcated hydrogen bonds, and these are linked to neighbouring pairs by a few weak hydrogen bonds (Fig. 2(a)). Along the needle axis the ions are stacked alternately in infinite columns. The overlap is shown in Fig. 2(b). The angles between the planar part of the picrate ion and the pyrimidine and the imidazole planes of the DMA ion are $2.6(1)°$ and $3.0(1)°$. The average interplanar distances between the ions are approximately 3.34 Å on both sides of the ions. These short distances and the C---C distance of 3.305 Å shown in Fig. 2(b) indicate rather strong interactions between the ions along the stack. As the picrate ion is a relatively strong electron acceptor,[10] there is probably an important contribution of charge-transfer to these interactions.

In the three DMA-compounds investigated so far the H atoms are bonded differently. This bonding must therefore be very sensitive to environmental changes. The results of the present investigation seem to support the idea that the differences are related to the stacking interactions. It is, however, also possible that the stability of the two bifurcated hydrogen bonds is the main reason for the unusual H position in this compound.

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