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Crystal Structure of *N*(6),*N*(6)-Dimethyladeninium Tricyanoethenolate Dioxane Solvate

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The title compound crystallizes with 1/2 dioxane molecule per formula unit in the monoclinic space group *C2/m* with cell parameters a=14.473(2) Å, b=6.862(1) Å, c=17.493(3) Å, β=111.04(1)°. The structure was refined to R=0.069 for 792 observed reflections. The structure is disordered with each ion and molecule in two orientations. The *N*(6),*N*(6)-dimethyladeninium ion has H atoms bonded to N(3) and N(7) which is different from what has been observed in other adeninium derivatives. The two ions are linked by several hydrogen bonds along (010) and are stacked alternately in infinite columns along [010].

Crystal structure investigations [1–5] show that in most molecular complexes of adenine derivatives the partner molecules are hydrogen bonded to each other and, in addition, associated by stacking interactions. Spectroscopic measurements [6,7] indicate charge transfer interactions in complexes of adenine and its derivatives with π^*-acceptors. The intention of the present work was to study the interactions in a crystalline complex with tetracyanoethylene as the acceptor. Unexpected reactions during the crystallization, however, gave the title compound. As there might be hydrogen bonds and stacking interactions of interest even in this compound, the crystal structure was investigated.

EXPERIMENTAL

By evaporation in the atmosphere of a dioxane solution of equimolecular amounts of *N*(6),*N*(6)-dimethyladenine and tetracyanoethylene a brown residue was formed, mainly as a powder, but with a few needle-shaped crystals. Because of instability and difficulties in making a sufficient amount of the crystals, the composition was not found by the usual analytical methods, but as a result of the structure analysis. The formation of the compound may be explained in accordance with what is known from the literature [8] by assuming hydrolysis of tetracyanoethylene, using water from the atmosphere, and subsequent protonation of the adenine derivative. The crystal chosen for data collection had the dimensions 0.12×0.8×0.3 mm in the axial directions.

The cell parameters and X-ray intensities were measured on an Enraf-Nonius CAD4 diffractometer using Cu$K\alpha$ radiation (λ=1.5418 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 0.3–2.9° min^{-1}. Although the crystals were kept in sealed capillaries, there was a continuous reduction of intensity of the standard reflections down to 56 % of their original values and a considerable decrease of the quality of the crystals during the data collection. 793 reflections with $I>1.5\sigma(I)$ were used for the structure determination. Lp and absorption corrections were performed.

CRYSTAL DATA

N(6),*N*(6)-Dimethyladeninium tricyanoethenolate dioxane solvate, $C_7H_{10}N_5^+$ $C_5N_3O^-$ 1/2 $C_4H_8O_2$, F.W.=326.33. Space group *C2/m*, a=14.473(2) Å, b=6.862(1) Å, c=17.493(3) (Å), β=111.04(1)°, V=1621.5 Å^3, Z=4, D_x=1.34 g cm^{-3}, D_m=1.35 g cm^{-3} (by flotation), μ(Cu$K\alpha$)=8.15 cm^{-1}.

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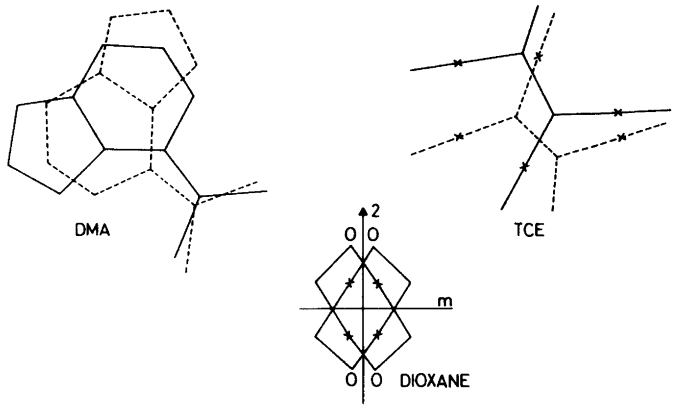

Fig. 1. The disorder of the molecules. Minor orientations with broken lines.

STRUCTURE DETERMINATION AND REFINEMENT

Three space groups, *C*2, *Cm* and *C*2/*m*, are possible from the systematic absences. A sharpened Patterson map indicated that most of the atoms are situated in the planes $y=0$ and $y=1/2$. From this, as well as a more detailed analysis of the Patterson map and packing considerations it was possible to conclude that *C*2/*m* is the most probable space group, and also to find a position and orientation of the adenine derivative which could be used as a starting point for the structure determination. The interpretation of the subsequent Fourier maps led to the deduction of the composition of the compound and to the conclusion that both the tricyanoethenolate ion (TCE) and the dioxane molecule are disordered, each with two different orientations. The orientations of TCE are non-equivalent whereas those of dioxane are related by symmetry and therefore equivalent. Least squares refinements performed at this stage could not bring *R* below 12 % and gave unreasonable thermal parameters for some atoms of the *N*(6),*N*(6)-dimethyladeninium ion (DMA). By assuming a second orientation also of this ion the structure was refined to the final *R*-value and the thermal parameters of DMA became reasonable. The disorder of the molecules is shown in Fig. 1.

A difference map (Fig. 2) shows clearly the positions of the non-methyl H atoms of the major orientation of DMA. Surprisingly, two of these are bonded to N(3) and N(7), rather than to N(1) and N(9) as in other adeninium derivatives.[9,10] No H atom bonded to N'(7) in the minor orientation can be seen in the map. As protonation at N'(7) and at N'(1) both seem possible for steric reasons, the possibility that the disorder is accompanied by tautomerism cannot be excluded, and one H position of the minor orientation is therefore regarded as uncertain. All the other H positions not found from the difference map were calculated with C–H distances of 0.95 Å and disorder due to rotation of the methyl groups assumed. The *U* values used for the H atoms were 0.10 $Å^2$ for those bonded directly to the ring system of DMA and 0.13 $Å^2$ for the others. The parameters of these atoms were not refined, but included in the structure factor calculations.

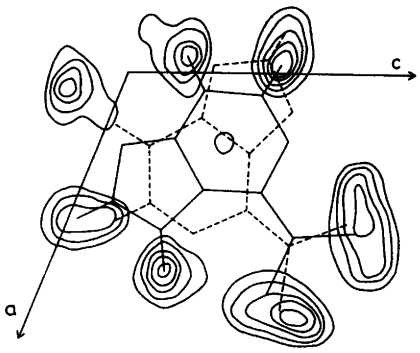

Fig. 2. Section through a difference Fourier map showing the H atoms. Contours are at intervals of 0.05 e $Å^{-3}$, starting at 0.05 e $Å^{-3}$.

Table 1. Positional parameters and equivalent or isotropic temperature factors (Å^2). $U_{eq}=1/3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j\cos a_{ij}$, or $U_{iso}+1/3\Delta U$ for atoms where the method of Kartha and Ahmed [12] has been used. Standard deviations in parentheses. Occupancy factors are 0.70 for N(1)–C(11), 0.30 for N′(1)–C′(11), 0.58 for O(1)–C(16), 0.42 for O′(1)–C′(16) and 0.50 for O(2)–C(18).

	x	*y*	*z*	U_{eq} or U_{iso}
N(1)	0.1193(7)	0	0.2596(5)	0.093
C(2)	0.0408(8)	0	0.1972(8)	0.097
N(3)	0.0322(6)	0	0.1159(5)	0.086
C(4)	0.1194(6)	0	0.1052(6)	0.081
C(5)	0.2120(7)	0	0.1702(6)	0.087
C(6)	0.2134(7)	0	0.2508(6)	0.080
N(6)	0.2924(6)	0	0.3184(5)	0.094
N(7)	0.2795(6)	0	0.1328(6)	0.095
C(8)	0.2305(7)	0	0.0530(7)	0.097
N(9)	0.1345(5)	0	0.0338(5)	0.086
C(10)	0.2853(8)	0	0.4018(6)	0.112
C(11)	0.3926(8)	0	0.3166(6)	0.121
N′(1)	0.2864	0	0.1781	0.062
C′(2)	0.2306	0	0.1015	0.071
N′(3)	0.1292	0	0.0693	0.082
C′(4)	0.0883	0	0.1269	0.077
C′(5)	0.1417	0	0.2117	0.058
C′(6)	0.2448	0	0.2392	0.070
N′(6)	0.3037	0	0.3160	0.074
N′(7)	0.0703	0	0.2465	0.087
C′(8)	–0.0162	0	0.1852	0.062
N′(9)	–0.0095	0	0.1130	0.070
C′(10)	0.4113	0	0.3393	0.075
C′(11)	0.2650	0	0.3823	0.087
O(1)	0.4754(7)	0	0.1644(6)	0.101
N(10)	0.5902(16)	0	0.0327(9)	0.209
N(11)	0.8184(14)	0	0.2168(16)	0.158
N(12)	0.6492(12)	0	0.3874(9)	0.112
C(12)	0.5561(10)	0	0.1675(9)	0.073
C(13)	0.6564(12)	0	0.2391(13)	0.090
C(14)	0.5755(11)	0	0.0895(8)	0.119
C(15)	0.7460(26)	0	0.2252(31)	0.151
C(16)	0.6550(12)	0	0.3207(10)	0.092
O′(1)	0.8222(15)	0	0.2820(11)	0.133
N′(10)	0.6700(18)	0	0.3816(14)	0.110
N′(11)	0.4904(12)	0	0.1873(11)	0.089
N′(12)	0.7291(12)	0	0.0728(11)	0.134
C′(12)	0.7309(20)	0	0.2616(14)	0.085
C′(13)	0.6607(16)	0	0.1871(10)	0.075
C′(14)	0.6923(20)	0	0.3346(16)	0.115
C′(15)	0.5764(20)	0	0.1894(16)	0.082
C′(16)	0.6953(12)	0	0.1223(11)	0.093
O(2)	0.0113(8)	0.2009(10)	0.5156(6)	0.120(3)
C(17)	–0.0249(11)	0.0860(34)	0.5641(8)	0.129
C(18)	0.0724(10)	0.0894(29)	0.4813(9)	0.119

In the last part of the least squares refinement the positions of all non-hydrogen atoms were varied independently, except those of the minor orientation of DMA which were refined as a rigid group with bond distances and angles as those found for the major orientation. Anisotropic thermal parameters were used for all non-hydrogen atoms, except for O(1), N(12), C(12), C(16), N′(10), N′(11), C′(14), C′(15) and O(2) which are close to atoms from other orientations, and for those of the minor orientation of DMA. As the refinement showed that the vibrations in this compound are greatest along [010], all these atoms except O(2) were given additional vibrations in this direction by introducing "half atoms" and refining the y-values.[12] As N(6) and N′(6) of the major and minor orientation of DMA are very close, alternating cycles were performed in which the thermal parameters of N(6) were varied while those of all non-hydrogen atoms of the minor orientation were kept constant, and *vice versa*. The number of variable parameters in these cycles were 193 and 201, respectively. The reflection 404 turned out to have a great systematic error and was left out of the refinement. Occupancy factors of 0.70 and 0.58 for the major orientations of DMA and TCE, respectively, were arrived at after systematic variation of the factors and least squares refinement of the structure with these factors kept constant for each set of values.

The weights used in the refinement were $w=XY$, where $X=1$ for sin $\theta>0.5$, else $X=\sin\theta/0.5$, $Y=1$ for $|F_o|\leq 10$, else $Y=10/|F_o|$. The final $R=0.069$ and $R_w=[\Sigma w(F_o-F_c)^2/\Sigma wF^2]^{1/2}=0.089$. Lists of observed and calculated structure factors and anisotropic thermal parameters may be obtained from the author on request. The final parameters are given in Table 1. Bond distances and angles are shown in Fig. 3, the molecular

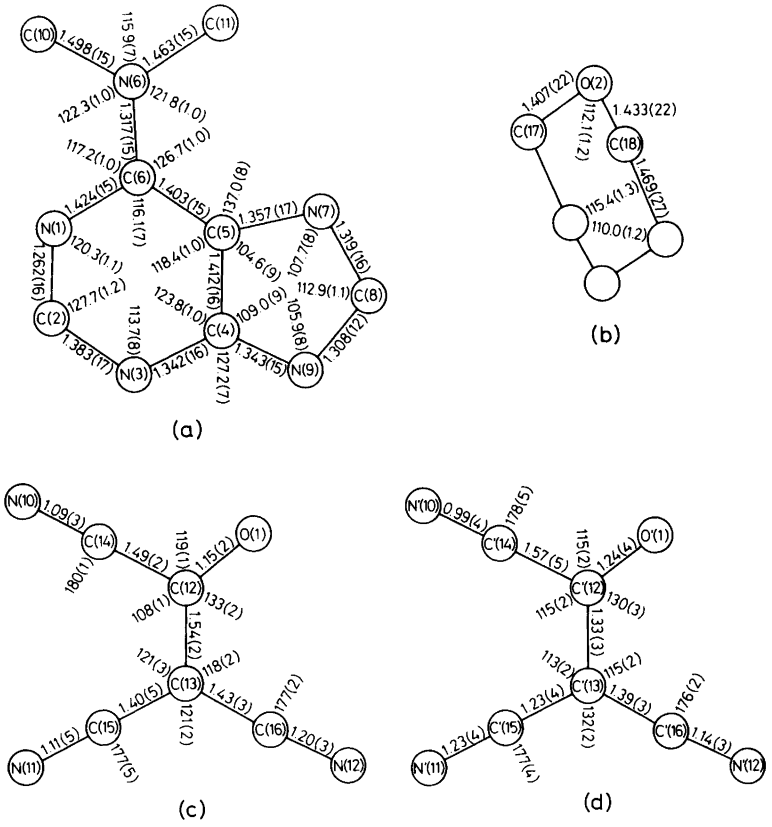

Fig. 3. Bond distances (Å) and angles (°) in DMA, major orientation (a), dioxane (b) and TCE, major orientation (c) and minor orientation (d). Standard deviations in parentheses.

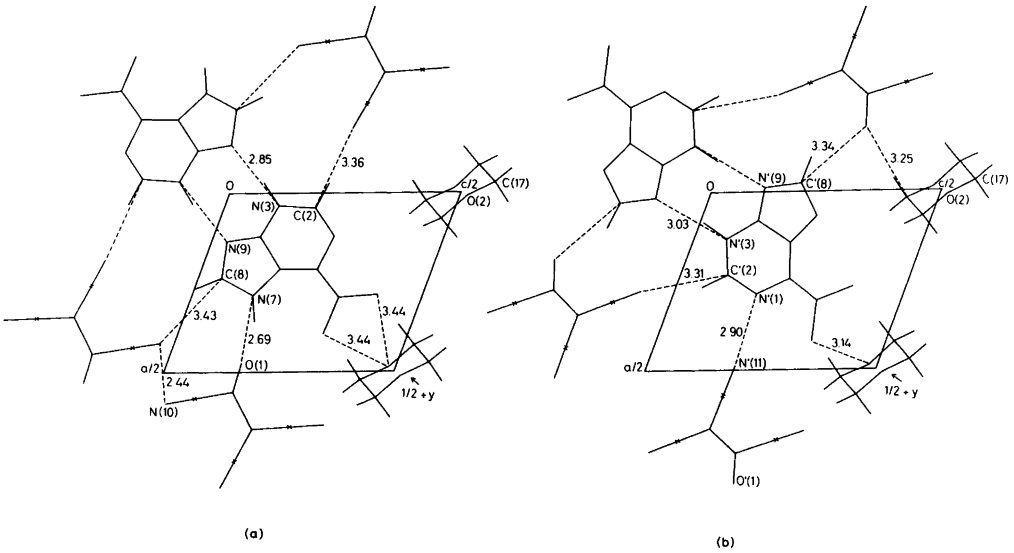

Fig. 4. The packing of the molecules in their major orientations (a) and minor orientations (b) in a layer along (010). One H atom of the DMA ion in the minor orientation, which position is uncertain, and methyl H atoms are not included. Short intermolecular distances (Å) are given.

packing and intermolecular distances in Fig. 4 and the overlap of the molecules in Fig. 5.

Scattering factors for the H atoms are taken from Ref. 13, those used for the other atoms are taken from Ref. 14. All calculations have been performed at the CYBER 171 MP at the University of Tromsø. The computer program used for data reduction has been written at the University of Lund and modified at the University of Tromsø. The other programs used are included in the X-RAY 76 system.[15]

DISCUSSION

The bond distances and angles in DMA deviate significantly from those found in other adeninium derivatives.[9–11] This would be expected from the different H positions, and it appears from the resonance picture in Fig. 6 that there is full agreement between the bond distances and the observed H positions. It also appears from this picture that the N(1)–C(2) bond, which has a very short bond length, is an approximately pure double bond.

It is remarkable that even in the closely related *N*(6)-methyladeninium chloride [9] the H atoms are bonded as in other adeninium derivatives. The unusual bonding in the present compound may thus possibly be a result of interactions between the DMA ion and its environments. This hypothesis will be tested by structure investigations of other DMA-compounds.

Because of large standard deviations and high correlation between parameters of TCE, bond distances and angles of this ion are very uncertain and will not be subject to any further comments.

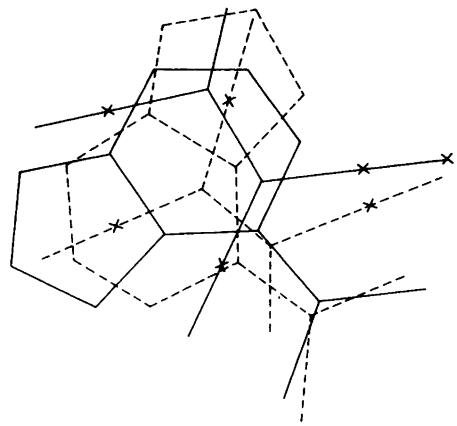

Fig. 5. The overlap of the molecules. Minor orientations with broken lines.

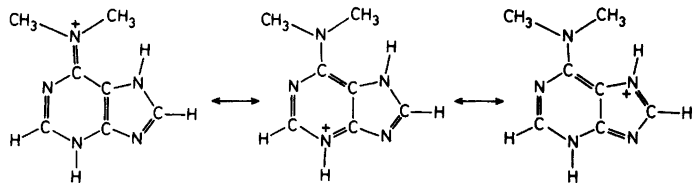

Fig. 6. Resonance structures of the DMA ion.

If the orientations of neighbouring DMA and TCE ions are independent of each other, two unreasonably short C–H···N bonds with C–N distances of 2.47 and 2.64 Å would have to exist. It is therefore believed that in layers along (010) the contacts are mainly between the major orientations and between the minor orientations, although this assumption cannot be strictly correct as the occupancy factors are not equal for the two ions. The two ways of molecular packing are shown in Fig. 4. In both cases DMA forms dimers held together by hydrogen bonds, and there are also many hydrogen bonds along (010) between DMA and TCE. The short distance of 2.44 Å between two equivalent positions of N(10) in the major orientation is hard to explain.

Despite the large number of hydrogen bonds along (010) the crystals are elongated in the [010]-direction, along which the ions are stacked alternately in infinite columns. The interplanar distance, 3.431 Å, is greater than expected if charge transfer interactions had been present. The overlap (Fig. 5) gives no clear indication of an important influence of electrostatic forces. The close contact and nearly parallel orientation of the double bonds N(1)–C(2) and C(12)–C(13) in the major orientations are worth noticing and may be an effect of dispersion or polarization forces.

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REFERENCES

1. Voet, D. and Rich, A. *Proc. Natl. Acad. Sci. U.S.A. 68* (1971) 1151.
2. Shieh, H.-S. and Voet, D. *Acta Crystallogr. B 31* (1975) 2192.
3. Scarbrough, F. E., Shieh, H.-S. and Voet, D. *Proc. Natl. Acad. Sci. U.S.A. 73* (1976) 3807.
4. Fuji, S., Kawasaki, K., Sato, A., Fujiwara, T. and Tomita, K.-I. *Arch. Biochem. Biophys. 181* (1977) 363.
5. Takenaka, A. and Sasada, Y. *Bull. Chem. Soc. Jpn. 55* (1982) 680.
6. Slifkin, M. A. In Ratajczak, H. and Orville-Thomas, W. J., Eds., *Molecular Interactions*, Wiley, New York 1980, Vol. 2, Chapter 6.
7. Sheina, G. G., Radchenko, E. D., Egupov, S. A., Blagoy, Yu. P. and Orlov, V. M. *Int. J. Quantum Chem. 16* (1979) 387.
8. Middleton, W. J., Little, E. L., Coffman, D. D. and Engelhardt, V. A. *J. Am. Chem. Soc. 80* (1958) 2795.
9. Sternglanz, H. and Bugg, C. E. . *Cryst. Mol. Struct. 8* (1978) 263.
10. Hingerty, B. E., Einstein, J. R. and Wei, C. H. *Acta Crystallogr. B 37* (1981) 140.
11. Taylor, R. and Kennard, O. *J. Mol. Struct. 78* (1982) 1.
12. Kartha, G. and Ahmed, F. R. *Acta Crystallogr. 13* (1960) 532.
13. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
14. Cromer, D. and Mann, J. *Acta Crystallogr. A 24* (1968) 321.
15. Stewart, J. M., Machin, P. A., Dickinson, C., Ammon, H. L., Heck, H. and Flack, H. *The X-Ray System, Version of 1976,* Technical Report TR-446, Computer Science Center, University of Maryland, College Park 1976.

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