STRUCTURE OF ADENINUM CHLOROACETATE–CHLOROACETIC ACID SOLVATE $C_5H_6N_5^+$ $ClCH_2COO^-$. $ClCH_2COOH$

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The structure adeninium chloroacetate–chloroacetic acid solvate was solved by direct methods and refined anisotropically to $R = 0.085$ for 1978 unique observed reflections ($I \geq 3\,\sigma(I)$). The title compound is orthorhombic, $a = 24.138(4)$, $b = 15.525(2)$, $c = 7.136(1)$ Å, *Pccn*, $Z = 8$. The adenine molecule, which is protonated at N(1), is almost planar with a dihedral angle of 0.3(2)° between the imidazole and the pyrimidine rings. The chloroacetate is partially disordered. A dimensional net of H-bonds between adenine, chloroacetic acid and chloroacetate is formed.

The crystal and molecular structure of the title compound has been determined as a continuation of our studies concerned with structures containing various protonated adenine[1 – 4]. The preliminary crystal data of this compound named adenine bis monochloroacetate has been presented in Cambridge Crystallographic Database (CCD). Single crystals of this set serve as models for the interpretation of the results obtained by various methods of low-temperature reflection and emission spectroscopy for polynucleotides. For example Raman marker bands characteristic of identical adenine protonation degree were found, that can be applied to the interpretation of spectra of more complex systems in solution[5].

EXPERIMENTAL

Crystals were grown by cooling solution of the title compound in 1 mol l^{-1} chloroacetic saturated at 308 K. (cooling gradient 1 K/day). Crystal seeds were used. Twice recrystallized or sublimed adenine (Lachema) and twice redistilled chloroacetic acid (Lachema) served as starting material. Crystals are colourless needles with maximum dimensions 7 × 1 × 1.5 mm and they are often twinned.

The molecular formula was confirmed by elemental analysis, purity by HPLC method and the crystal density was determined by flotation in toluene–diiodomethane mixture.

Crystal Structure Determination

Orthorhombic, space group *Pccn* (No. 56), a = 24.138(4), b = 15.525(2), c = 7.136(1) Å, V = 2 647.1(7) Å^3, Z = 8, D_0 = 1.59(1), D_x = 1.608(1) g cm^{-3}, $\mu(MoK_\alpha)$ = 5.04 cm^{-1}, M_r = 324.1, $F(000)$ = 1 328. The preliminary values of lattice parameters and space group were determined from Weissenberg photographs recorded with CuK_α radiation. The structure was solved by direct methods and refined anisotropically by the full matrix least-squares method[6]. The $\Delta\rho$ map showed a maximum at the distance 1.56 Å from C11 atom of the chloroacetic acid. A partial disorder has been found on the chloroacetate, where the chlorine atom occupies two positions. For this reason the H-atoms of the chloroacetic acid and the chloroacetate were fixed in calculated positions with fixed U_{iso} values of 1.3 times of the U_{eq} value of the attached atoms. The H-atoms of adenine molecule were found from $\Delta\rho$ map isotropically refined. Lorentz and polarization corrections were made in a usual way. Application of empirical ψ-scan absorption correction slightly increased the R-factor final value and therefore was neglected. Data collection and structure refinement parameters are listed in Table I.

TABLE I
Data collection and structure refinement parameters

Crystal dimension	0.4 × 0.4 × 0.45 mm
Diffractometer and radiation used	Enraf–Nonius CAD4
	$\lambda(MoK_\alpha)$ = 0.71073 Å
Scan technique	$\omega/2\theta$
No. and θ range of reflections for lattice parameter refinement	25, 17 – 18°
Range of h, k and l	0 – 26 0 – 17 0 – 12
Standard reflections	14 0 0, 0 10 0, 4 3 –1
Standard reflections monitored in interval; intensity fluctuation	180 min; –1.2%
Total number of reflections measured, 2θ range	3 846, 1 – 60°
No. of unique observed reflections	1 978
Criterion for observed reflections	$I \geq 3\,\sigma(I)$
Function minimized	$\sum w\,(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme	unit weight
Parameters refined	214
Extinction coefficient	$4.1 \cdot 10^{-7}$
Values of R, wR, and S	0.085, 0.092, 3.15
Ratio of max. least-squares shift to e.s.d. in the last cycle	0.12
Max. and min. heights in final $\Delta\rho$ map	1.97 eÅ^{-3} (1.56 Å away from C(11));
	–0.71 eÅ^{-3}
Source of atomic scattering factors	SDP package
Program used	SDP (ref.[6]), PARST88 (ref.[7])
Computer used	PDP 11/73, PC/AT

DISCUSSION

The final atomic coordinates for non-hydrogen atoms and their equivalent isotropic thermal parameters are listed in Table II, the bond distances and angles in Table III, the results of planarity studies of adenine molecule in Table IV and hydrogen bond contacts in Table V*.

The projection of the title compound structure along the *c*-axis is given in Fig. 1. There is nearly no overlap between adenines.

The adenine molecule is almost planar as indicated by the χ^2 test. It is monoprotonated at N1 and its geometry is in good agreement with previously published structures of above mentioned set with the same protonation[1 - 4] with the exception of distances C(5)–C(6), N(1)–C(6), C(6)–N(6) and angles N(3)–C(4)–N(9) and C(6)–C(5)–N(7). Nevertheless these values are in general agreement with those given by Taylor and Kennard from CCD[8] and with calculated values[9]. The adenine rings are surrounded by two chloroacetic acids and two chloroacetates forming hydrogen bonds net with them (Fig. 2).

It can be readily seen from Fig. 2 that the title compound structure represents a direct experimental evidence for preferable protonation of adenine at N1 position over N7 one. Both hydrogen bond distances N(1)...O(22) and N(7)...O(12) are practically the same, hence both nitrogen atoms have the same chance to receive proton from chloroacetic acid molecules.

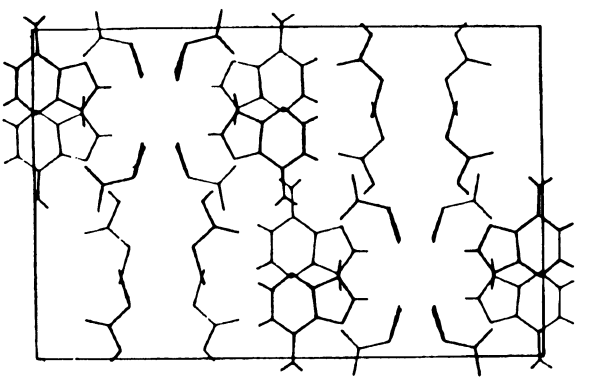

FIG. 1
Molecular packing viewed down *c* axis

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H-atoms may be obtained from authors on request.

At the same time the structure represents the evidence of preferable tautomeric form N(9)–H over N(7)–H, of the N(1)-protonated unsubstituted adenine molecule. Moreover two pairs of cyclic hydrogen bonds with common N(6) atom remind Watson–Crick and Hoogsteen types of base pairing, that occur in a triple helix DNA[10].

The chlorine atom in chloroacetate is disordered with occupancies refined to 0.83(1) and 0.18(1) for Cl(21) and Cl(22), respectively. The type of disorder is a rotational one with the angle of rotation Cl(21)–C(21)–Cl(22) equal to 12.7(4)°. The observed disorder can be explained by tautomerism involving N(1)–H...O and N(1)...H–O

TABLE II

Fractional atomic coordinates for non-H atoms and their equivalent isotropic temperature factors (Å^2) defined as $B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} a_i a_j$ with e.s.d.'s in parentheses

Atom	*x*	*y*	*z*	B_{eq}, Å^2
Cl(11)	0.83388(9)	0.7295(1)	0.0856(4)	4.72(5)
Cl(21)[a]	0.2842(1)	0.8469(2)	0.0744(8)	10.3(1)
Cl(22)[a]	0.2822(3)	0.8561(6)	0.124(1)	3.4(2)
O(11)	0.9015(2)	0.8818(3)	−0.0436(9)	4.0(1)
O(12)	0.8318(2)	0.9751(3)	−0.18(1)	5.0(1)
O(21)	0.3981(2)	0.9180(3)	0.1187(8)	3.5(1)
O(22)	0.3743(2)	1.0527(3)	0.049(1)	5.0(1)
N(1)	0.5324(2)	0.6181(3)	0.3303(9)	3.0(1)
N(3)	0.4942(2)	0.7571(4)	0.2768(9)	3.0(1)
N(6)	0.4933(2)	0.4871(3)	0.249(1)	3.5(1)
N(7)	0.3957(2)	0.6020(3)	0.112(1)	3.2(1)
N(9)	0.4033(2)	0.7450(3)	0.1365(9)	3.1(1)
C(2)	0.5330(3)	0.7065(4)	0.336(1)	3.2(1)
C(4)	0.4516(3)	0.7118(4)	0.208(1)	2.4(1)
C(5)	0.4458(3)	0.6226(4)	0.193(1)	2.5(1)
C(6)	0.4904(3)	0.5716(4)	0.255(1)	2.7(1)
C(8)	0.3720(3)	0.6771(4)	0.081(1)	3.4(1)
C(11)	0.8128(3)	0.8380(4)	0.086(1)	4.4(2)
C(12)	0.8550(3)	0.8993(4)	−0.000(1)	3.2(1)
C(21)	0.3043(3)	0.9527(4)	0.027(2)	4.8(2)
C(22)	0.3644(3)	0.9740(4)	0.070(1)	3.2(1)

[a] The occupancy factors of Cl(21) and Cl(22) are 0.83(1) and 0.18(1), respectively.

structures[11]. It is interesting that the Raman spectrum of the single crystal also showed at least 80% of adenine molecules to be protonated at N(1) position.

We can concluded that the crystal of adeninium chloroacetate chloroacetic acid solvate is a promising model system for the study of proton transfer phenomena.

TABLE III
Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Atoms	Distance, Å	Atoms	Distance, Å
N(1)–C(2)	1.373(8)	C(5)–C(6)	1.407(10)
N(1)–C(6)	1.355(9)	C(5)–N(7)	1.378(9)
N(3)–C(2)	1.292(9)	N(7)–C(8)	1.317(8)
N(3)–C(4)	1.339(9)	C(8)–N(9)	1.355(8)
C(4)–C(5)	1.396(9)	N(9)–C(4)	1.373(9)
N(6)–C(6)	1.314(8)		
Cl(11)–O(11)	1.760(7)	Cl(21)–C(21)	1.746(7)
C(11)–C(12)	1.524(10)	Cl(22)–C(21)	1.737(12)
C(12)–O(11)	1.196(9)	C(21)–C(22)	1.520(10)
C(12)–O(12)	1.309(8)	C(22)–O(21)	1.239(8)
O(12)–H(12)	0.85(8)	C(22)–O(22)	1.254(8)
Atoms	**Angle, °**	**Atoms**	**Angle, °**
C(2)–N(1)–C(6)	123.5(5)	N(7)–C(5)–C(4)	110.5(5)
C(2)–N(3)–C(4)	110.9(5)	N(7)–C(5)–C(6)	132.2(6)
C(5)–N(7)–C(8)	104.2(5)	C(4)–C(5)–C(6)	117.3(5)
C(4)–N(9)–C(8)	106.8(5)	N(1)–C(6)–C(5)	113.4(6)
N(1)–C(2)–N(3)	126.3(6)	N(1)–C(6)–N(6)	120.4(5)
N(3)–C(4)–N(9)	126.3(5)	C(5)–C(6)–N(6)	126.3(5)
N(3)–C(4)–C(5)	128.7(5)	N(7)–C(8)–N(9)	113.5(6)
N(9)–C(4)–C(5)	105.0(5)		
Cl(11)–O(11)–C(12)	113.8(5)	Cl(21)–C(21)–C(22)	115.5(5)
C(11)–C(12)–O(11)	126.2(5)	Cl(22)–C(21)–C(22)	113.5(6)
C(11)–C(12)–O(12)	108.3(5)	C(21)–C(22)–O(21)	122.0(5)
O(11)–C(12)–O(12)	125.5(5)	C(21)–C(22)–O(22)	111.6(6)
C(12)–O(12)–H(12)	109.6(6)	O(21)–C(22)–O(22)	126.4(5)

TABLE IV
Least squares planes and the deviation of individual atoms from these planes, e.s.d.'s in parentheses

Atom	Deviation, Å	Atom	Deviation, Å
1. The five-atom plane of the imidazole ring			
$(0.419X + 0.034Y - 0.907Z = 3.592)$			
C(4)	0.005(7)	C(8)	0.001(8)
C(5)	−0.005(7)	N(9)	−0.003(6)
N(7)	0.002(7)		
$\chi^2 = 1$			
2. The six-atom plane of the pyrimidine ring			
$(0.424X + 0.030Y - 0.905Z = 3.612$			
N(1)	−0.012(6)	C(5)	−0.011(7)
C(2)	0.001(8)	C(6)	0.022(7)
N(3)	0.008(6)	N(6)[a]	0.053(7)
C(4)	−0.005(7)		
$\chi^2 = 17$			
3. The nine-atom plane of the adenine ring			
$(0.420X + 0.032Y - 0.907Z = 3.581)$			
N(1)	−0.017(6)	C(6)	0.020(7)
C(2)	0.001(8)	N(7)	0.016(7)
N(3)	0.011(6)	C(8)	−0.002(8)
C(4)	0.003(9)	N(9)	−0.007(6)
C(5)	−0.006(7)	N(6)[a]	0.049(7)
$\chi^2 = 22$			

[a] Atoms were given zero weight in calculating the planes; the atoms used to define the planes were equally weighted.

TABLE V
Distances (Å) and angles (°) for the possible intermolecular hydrogen bond contacts, e.s.d.'s in parentheses

D–H...A	D...A	D...H	H...A	D...H...A
N(1)–H(1) ...O(22) [$-x+1, y-1/2, -z+1/2$]	2.618(5)	0.77(6)	1.85(6)	175(2)
N(6)–H(61) ...O(21) [$-x+1, y-1/2, -z+1/2$]	2.989(7)	0.74(6)	2.28(6)	164(2)
N(6)–H(62) ...O(21) [$x-1/2, y-1/2, -z$]	3.118(5)	0.72(6)	2.42(6)	165(2)
N(9)–H(9) ...O(21) [x, y, z]	2.690(7)	0.78(6)	1.92(6)	169(2)
O(12)–H(12)...N(7) [$x+1/2, y+1/2, -z$]	2.598(7)	0.75(6)	1.87(6)	162(2)

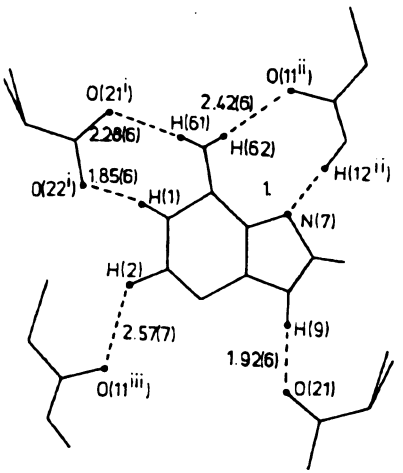

FIG. 2
The three-dimensional network of hydrogen bonds

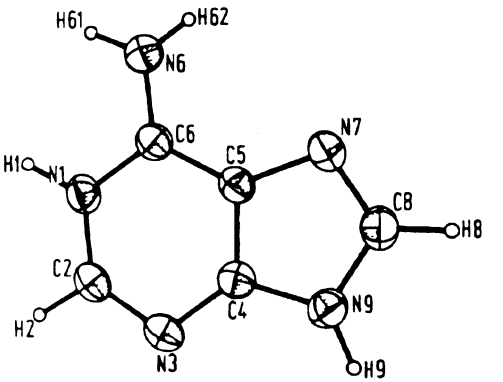

FIG. 3
A perspective view of adenine molecule. Thermal ellipsoids are drawn at the 50% probability level

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