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Structure of 3-Methylcytidinium Chloride, $C_{10}H_{16}N_3O_5^+.Cl^-$

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Abstract. $M_r = 293.7$, orthorhombic, $P2_12_12_1$, $a = 7.225$ (1), $b = 11.639$ (1), $c = 14.921$ (1) Å, $V = 1254.7$ (3) Å^3, $Z = 4$, $D_x = 1.56$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1.54178$ Å, $\mu = 2.79$ mm^{-1}, $F(000) = 616$, $T = 290$ K, $R = 0.030$ for 1959 observed reflexions. The dimensions and conformation of the 3-methyl-cytidinium cation ($\chi = 45.2$, $P = 163.0$, $\tau_m = 40.3$, $\psi = 55.2°$) are very similar to those characterizing the cytidinium cation in cytidine hydrochloride. The pyrimidine ring shows deviations of up to 0.03 Å from planarity and N(4) is 0.118 Å from the pyrimidine plane. There is a two-dimensional network of H bonds in which all available proton donors are utilized: NH···O(2) 2·89, NH···Cl$^-$ 3·20, OH···Cl$^-$ 3·07, 3·25, 3·27 Å.

Introduction. In our previous studies of the factors influencing dimensions and molecular interactions of nucleosides we have investigated the effects of base modification and protonation (Jaskólski, Krzyżosiak, Sierzputowska-Gracz & Wiewiórowski, 1981; Krzyżosiak, Jaskólski, Sierzputowska-Gracz & Wiewiórowski, 1982; Kozerski, Sierzputowska-Gracz, Krzyżosiak, Bratek-Wiewiórowska, Jaskólski & Wiewiórowski, 1984; Jaskólski, 1982*a, b,* 1984*a*). The present paper reports the structure of a cytidinium cation which has a methyl group instead of a proton at the N(3) site. It is of interest to investigate the

differences between the N-protonated and N-methylated cations. There has been a structural report on the 3-methylcytidinium cation in the literature (3-methylcytidine methyl sulphate monohydrate; Shefter, Singh, Brennan & Sackman, 1974) but the accuracy is low and therefore not suitable for detailed comparative studies.
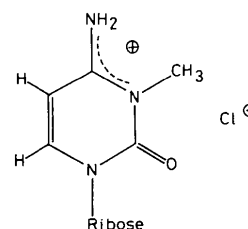
Experimental. Suitable crystals obtained from methanol–ethyl acetate, crystal $0.3 \times 0.4 \times 0.4$ mm, Syntex $P2_1$ diffractometer, cell parameters from least-squares treatment of setting angles of 15 reflexions, $\pm h \pm k \pm l$ measured up to $2\theta = 115°$ and hkl up to $2\theta = 132°$, $\theta:2\theta$ scan, background–peak–background, 8810 reflexions collected, 1981 unique ($R_{int} = 0.030$), 1970 observed with $I \geq 1.96\sigma(I)$, no significant variation for two standard reflexions, no absorption correction; structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain,

Declercq & Woolfson, 1980), full-matrix least squares, $\sum w\Delta^2$ minimized, $\Delta = |F_o| - |F_c|$, $w = 1/\sigma^2(F_o)$ for $|F_o| \geq 3.92\sigma(F_o)$, $w = 0$ for $|F_o| < 3.92\sigma(F_o)$ or $-\Delta > 5.7\sigma(F_o)$, $\sigma^2(F_o) = \sigma_1^2(F_o) + 0.0005F_o^2$, $\sigma_1(F_o)$ based on counting statistics; H atoms located in ΔF map; final refinement: anisotropic non-H atoms, isotropic H atoms, empirical isotropic extinction parameter x used to correct F_c according to $F_c' = F_c \times (1 - xF_c^2/\sin\theta)$, which converged at $x = 35$ (6) $\times 10^{-7}$, $R = 0.030$, $wR = 0.045$, $S = 1.97$, $(\Delta/\sigma)_{max} = 0.6$, largest peak in final ΔF map = 0.44 e Å^{-3}, largest hole = -0.39 e Å^{-3}; chirality of crystal confirmed by procedure outlined by Rogers (1981): $wR^+ = 0.051$, $wR^- = 0.093$; computer programs: *MULTAN*80, *SHELX*76 (Sheldrick, 1976) and local programs by MJ, molecular illustrations drawn using *ORTEP* (Johnson, 1976); atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates are listed in Table 1.* Bond distances and angles in the 3-methylcytidinium (3-MeCyd) cation are given in Fig. 1, and its thermal-ellipsoid representation is shown in Fig. 2. Comparison with Cyd.HCl (Mosset, Bonnet & Galy, 1979) reveals that the dimensional differences between the cytosinium moieties in Cyd.H$^+$ and 3-MeCyd$^+$ are quite small. Therefore, one should not expect any significant differences in the base electronic structure between the two forms of the cytosinium cation. Introduction of —CH$_3$ instead of —H at the N(3) site decreased the C(2)—N(3)—C(4) angle by 1.8 (3)° and slightly increased ($\sim$0.01 Å) the N(3)—C bond lengths. The pyrimidine ring is significantly nonplanar, the maximum deviation from its best plane being 0.030 (2) Å $(\chi^2 = 835)$. C(1'), O(2), C(3) and N(4) show appreciable deviations from the pyrimidine plane, the deviation of N(4) being as large as 0.118 (2) Å.

The parameters describing the conformation of the 3-MeCyd$^+$ cation are given in Table 2. It is interesting to note that the conformation of the present 3-MeCyd$^+$ cation is almost identical with that characterizing the cytidinium cation in Cyd.HCl (Table 2). It must therefore be the conformation preferred by the cytidinium cation since it is retained in quite different intermolecular situations [by blocking the N(3)—H proton-donor group, the methyl substituent drastically changes the H-bond scheme — see below]. This statement is further supported by the conformation of the 3-MeCyd$^+$ cation in the structure of 3-MeCyd$^+$.CH$_3$OSO$_3^-$.H$_2$O, which is also very similar (Table 2).

Table 1. *Final fractional coordinates and isotropic temperature factors* (Å^2)

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

|	x	y	z	U_{eq}
Cl	−0.22710 (8)	−0.01310 (4)	−0.88387 (4)	0.0392 (2)
C(2)	−0.2378 (2)	−0.0988 (1)	−0.1101 (1)	0.0230 (5)
O(2)	−0.0805 (2)	−0.1345 (1)	−0.1023 (1)	0.0300 (5)
N(3)	−0.3879 (2)	−0.1740 (1)	−0.1143 (1)	0.0245 (5)
C(3)	−0.3472 (3)	−0.2976 (2)	−0.1126 (2)	0.0329 (8)
C(4)	−0.5662 (3)	−0.1378 (2)	−0.1225 (1)	0.0239 (5)
N(4)	−0.7021 (2)	−0.2126 (1)	−0.1200 (1)	0.0283 (6)
C(5)	−0.5998 (3)	−0.0184 (2)	−0.1334 (1)	0.0273 (6)
C(6)	−0.4556 (3)	0.0543 (2)	−0.1293 (1)	0.0264 (6)
N(1)	−0.2801 (2)	0.0160 (1)	−0.1156 (1)	0.0222 (5)
C(1')	−0.1275 (3)	0.1001 (2)	−0.1077 (1)	0.0232 (5)
C(2')	−0.0809 (2)	0.1567 (2)	−0.1966 (1)	0.0243 (5)
O(2')	−0.0300 (2)	0.0876 (1)	−0.2515 (1)	0.0352 (4)
C(3')	0.0108 (3)	0.2666 (2)	−0.1646 (1)	0.0266 (6)
O(3')	0.1961 (2)	0.2381 (2)	−0.1410 (1)	0.0372 (6)
C(4')	−0.1051 (3)	0.2971 (1)	−0.0819 (1)	0.0268 (6)
O(4')	−0.1839 (2)	0.1886 (1)	−0.05047 (8)	0.0290 (4)
C(5')	−0.2568 (3)	0.3831 (2)	−0.0943 (1)	0.0355 (7)
O(5')	−0.3787 (3)	0.3478 (2)	−0.1639 (1)	0.0500 (6)
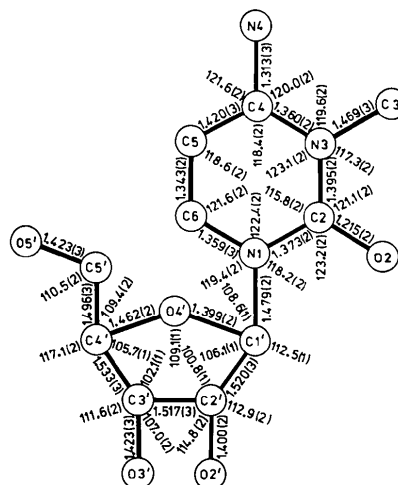
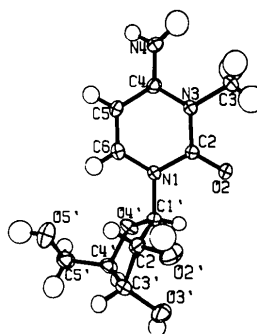Fig. 1. Bond distances (Å) and angles (°) in the 3-MeCyd$^+$ cation.

Fig. 2. Thermal-ellipsoid view of the 3-MeCyd$^+$ cation. H-atom ellipsoids have been put on an arbitrary scale.

Table 2. *Conformational data for the cytidinium cation in* 3-MeCyd⁺Cl⁻, CydH⁺Cl⁻ *and* 3-MeCyd⁺-CH₃OSO₃⁻.H₂O $(\chi, P, \tau_m$ and ψ in degrees)

	Glycosyl χ	Ribose pucker	Pseudorotation parameters*		Side chain ψ
			P	τ_m	
3-MeCyd⁺Cl⁻†	45·2 (2) (anti)	^2E	163·0 (8)	40·3 (6)	55·2 (2) (g⁺)
CydH⁺Cl⁻‡	45·7 (4)	^2E	162·5 (8)	40·3 (6)	53·5 (4)
3-MeCyd⁺-CH₃OSO₃⁻.H₂O§	46 (1)	$^2T_3$	169·4 (9)	38·4 (6)	62 (1)

* The pseudorotation parameters (Altona & Sundaralingam, 1972) and their standard deviations have been calculated according to Jaskólski (1984b).
† This work.
‡ Mosset, Bonnet & Galy (1979).
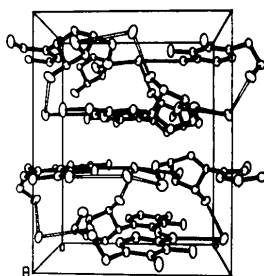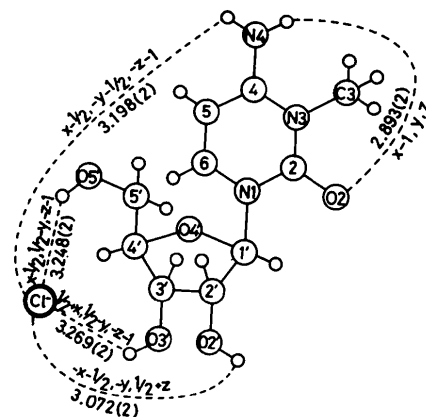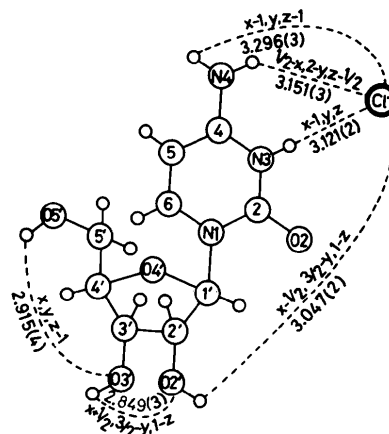§ Shefter, Singh, Brennan & Sackman (1974).

Fig. 3. View of the unit-cell contents. H bonds are indicated by open lines.

(a)

(b)

Fig. 4. Schematic representation of H-bond networks in (a) 3-MeCyd⁺Cl⁻ and (b) CydH⁺Cl⁻. For each H bond (broken line) the $D \cdots A$ distance (Å) and the symmetry code of the acceptor are given.

The packing diagram (Fig. 3) indicates that the 3-methylcytosinium moieties are nearly parallel to the *ab* plane. The structure contains sheets composed of anions and cations. Within a sheet the cations are linked directly by N(4)—H(42)$\cdots$O(2) hydrogen bonds, and indirectly *via* the Cl⁻ anions [N(4)—H(41)$\cdots$Cl⁻, O(3')—H(3'O)$\cdots$Cl⁻, O(5')—H(5'O)$\cdots$Cl⁻]. The sheets are combined into pairs by means of O(2')—H(2'O)$\cdots$Cl⁻ hydrogen bonds forming layers perpendicular to **c**. There are no H bonds between the layers. Fig. 3 shows that the Cl⁻ anion is located between two parallel 3-methylcytosinium moieties: one within 'its' layer (complementary sheet) and one in the adjacent layer. Comparison of the present structure with Cyd.HCl reveals that the packing arrangements of the two structures are somewhat similar [compare Fig. 3 with Fig. 2 of Mosset, Bonnet & Galy (1979)]. However, it should be stressed that the H-bonding situations in these two structures are completely different (Fig. 4). In Cyd.HCl the Cl⁻ anion binds primarily to the base moiety (three of four D—H$\cdots$Cl⁻ bonds) and the base is bound exclusively to the Cl⁻ ions. In the present structure the Cl⁻ anion is mostly involved in H bonding with the sugar residue (three of four D—H$\cdots$Cl⁻ bonds) and the sugar is bound exclusively to the Cl⁻ ions.

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Structure of (2R,3R,4S)-3,4-Dihydroxy-2-hydroxymethyl-8-methyl-6-phenyl-1-oxa-6,8-diazaspiro[4.4]nonane-7-thione, C₁₄H₁₈N₂O₄S

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Abstract. $M_r = 310.37$, tetragonal, $P4_12_12$, $a = 11.255$ (2), $c = 24.829$ (4) Å, $V = 3145.2$ (9) Å³, $Z = 8$, $D_x = 1.31$, $D_m = 1.33$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.23$ mm⁻¹, $F(000) = 1312$, $T = 293$ (2) K, $R = 0.077$ for 2023 observed reflections. The molecule consists of three rings: a tetrahydrofuran and an imidazolidine joined by a common spiro C atom and a phenyl group. The furanose ring displays a conformation intermediate between ^3_2T and ^3E forms. The imidazolidine ring, significantly non-planar, forms dihedral angles of 90.7 (2)° with the furanose ring and 86.3 (2)° with the phenyl ring. Packing is governed by hydrogen bonds and van der Waals contacts.

Introduction. The title compound (III) has recently been synthesized by Fernandez-Bolaños, Fuentes-Mota, Cert-Ventula & Trujillo (1984) at the Organic Chemistry Department of the University of Seville, Spain, by cyclization of 1,3-dihydro-1-methyl-3-phenyl-4-(D-*lyxo*-tetritol-yl)-2-imidazolethione (II) obtained by reaction of 1-deoxy-1-methylamino-D-*lyxo*-hexulose (I) and phenyl isothiocyanate.
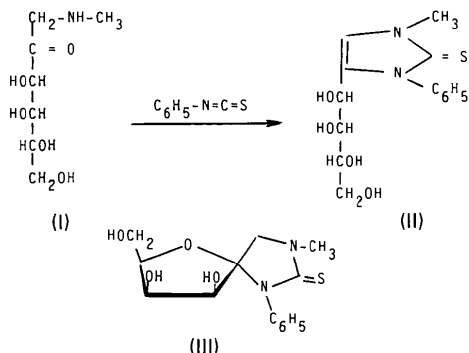
In the attempt to establish the possible correlations between NMR spectroscopy data and X-ray single-crystal diffractometry information the crystal structure of the title compound has been determined. The resolution of the structure confirms the spiranic conformation and the presence of three OH groups as the NMR spectra showed.

Experimental. Sample kindly provided by Professor Fernandez-Bolaños, Organic Chemistry Department, Seville University. Crystal *ca* 0.3 × 0.3 × 0.5 mm. D_m measured by flotation. Enraf–Nonius CAD-4 diffractometer. Cell dimensions from 2θ angles for 25 reflections (6 < θ < 12°). $h \le 15$, $k \le 15$, $l \le 35$. $2\theta_{max} = 12°$. 2714 unique reflections, 2023 intensities $\ge 2\sigma(I)$. Intensities of two standard reflections (008 and 00$\bar{8}$) did not vary significantly. No absorption correction. Structure solved with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Trial structure refined with *XRAY* system (Stewart, Kundell & Baldwin, 1970); final cycles of refinement based on F included one scale factor and positional and anisotropic thermal parameters for non-hydrogen atoms; H atoms located in difference electron density map included in refinement with isotropic thermal parameters equal to those of the bonded atoms. Weighting scheme $w = 1/\sigma^2(F)$. Final $R = 0.077$ and $wR = 0.072$ for the observed reflections only. Max. and average Δ/σ in the last refinement cycle 0.033 and 0.006 respectively. Final difference Fourier synthesis showed $\Delta\rho = \pm0.3$ e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1962). The absolute configuration was assigned on the basis of the configurations of the products used in the synthesis.