

Fig. 2. View of molecular packing in the crystal of IV. (Program PLUTO, Motherwell & Clegg, 1978.)

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Structure of 3-Methylcytidinium Nitrate

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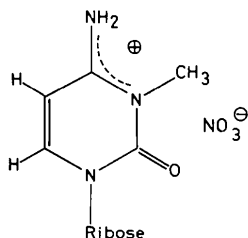
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Abstract. $C_{10}H_{16}N_3O_5^+ \cdot NO_3^-$, $M_r = 320.3$, orthorhombic, $P2_12_12_1$, $a = 10.276$ (2), $b = 6.6950$ (6), $c = 20.244$ (2) Å, $V = 1392.8$ (2) Å³, $Z = 4$, $D_x = 1.53$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.088$ mm⁻¹, $F(000) = 672$, $T = 290$ K, $R = 0.042$ for 1015 observed reflexions. The dimensions and conformation [glycosidic torsion angle $\chi = 50.7$ (4)°, pseudorotation parameters $P = 168.1$ (7) and $\tau_m = 37.0$ (5)°, side-chain orientation $\gamma = 53.6$ (4)°] of the present 3-methylcytidinium cation are similar to those in 3-methylcytidinium chloride. The pyrimidine system shows slight but significant deviations from planarity and is overlapped by the NO_3^- anion. There is a three-dimensional network of weak H bonds in which all available proton donors are utilized and the acceptors are the nitrate O atoms and O(3') and O(5') on the ribose. O(5') is H-bonded to C(6) through a

weak intramolecular C(6)—H(6)···O(5') link [3.279 (6) Å].

Introduction. The present work is part of a series of investigations into the factors influencing dimensions and molecular interactions of nucleosides. In our previous papers we have studied the effects of base modification and protonation in both cytidine (Jaskólski, Krzyżosiak, Sierzputowska-Gracz & Wiewiórowski, 1981; Krzyżosiak, Jaskólski, Sierzputowska-Gracz & Wiewiórowski, 1982; Kozerski, Sierzputowska-Gracz, Krzyżosiak, Bratek-Wiewiórowska, Jaskólski & Wiewiórowski, 1984) and adenosine (Jaskólski, 1982*a,b*, 1984*a*) series. Our recent interest is concentrated on *N*-methylated nucleoside cations (Jaskólski & Alejska, 1985) and on the influence of different counter-anions on the conforma-

tion and molecular interactions of nucleosides (Wiewiórowski, Jaskólski, Rychlewska, Bratek-Wiewiórowska, Alejska, Perkowska & Krzyżosiak, 1986). In this paper we present the X-ray structure of 3-methylcytidinium nitrate (3-MeCyd⁺·NO₃⁻).



Experimental. Suitable crystals from ethanol–acetone, crystal 0.20 × 0.40 × 0.55 mm, Syntex P2₁ diffractometer. Cell parameters from least-squares treatment of setting angles of 15 reflexions (14 < 2θ < 20°). θ:2θ profiles measured for 1451 unique +h+k+l reflexions with 2θ ≤ 50° (h_{max} = 12, k_{max} = 7, l_{max} = 24), profile analysis according to Lehmann & Larsen (1974). No significant intensity variation for two standard reflexions measured every 1.5 h. No absorption or extinction corrections. 1016 observed reflexions with I ≥ 1.96σ(I). Structure solved by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement on F, w = σ⁻²(F). One extinction-affected reflexion (012) excluded from final refinement. C–H hydrogen atoms generated geometrically, O(N)–H hydrogen atoms located in a ΔF map, all H atoms included as fixed isotropic contribution to F_c, orientation of the –CH₃ group optimized in the least-squares refinement. R = 0.042, wR = 0.042, S = 5.4, (Δ/σ)_{max} = 0.5, largest peak in final ΔF map = 0.26, largest trough = –0.19 e Å⁻³. Computer programs: MULTAN80, SHELX76 (Sheldrick, 1976) and local programs, molecular illustrations drawn using PLUTO (Motherwell & Clegg, 1978) and 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-MeCyd⁺ cation are given in Fig. 1, and its thermal-ellipsoid representation is shown in Fig. 2. The dimensions of the present 3-methylcytosinium cation are very close to those found in 3-MeCyd⁺·Cl⁻ (Jaskólski & Alejska, 1985) except for the C(2)–N(3) bond which in the present

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43250 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates and equivalent isotropic thermal parameters (Å²)

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

	x	y	z	U _{eq}
N(10)	0.0916 (5)	0.0827 (9)	0.8574 (2)	0.048 (2)
O(11)	0.1936 (4)	0.1128 (8)	0.8875 (2)	0.074 (2)
O(12)	0.0499 (4)	0.2047 (8)	0.8176 (2)	0.090 (2)
O(13)	0.0333 (5)	–0.0754 (8)	0.8660 (3)	0.096 (2)
C(2)	0.6063 (5)	0.4755 (8)	0.7089 (3)	0.036 (2)
O(2)	0.5868 (4)	0.6418 (6)	0.7305 (2)	0.047 (1)
N(3)	0.7019 (4)	0.3504 (7)	0.7380 (2)	0.035 (1)
C(3)	0.7731 (5)	0.4327 (9)	0.7958 (2)	0.048 (2)
C(4)	0.7307 (5)	0.1643 (8)	0.7147 (2)	0.038 (2)
N(4)	0.8241 (4)	0.0583 (7)	0.7415 (2)	0.050 (2)
C(5)	0.6558 (5)	0.0875 (8)	0.6610 (2)	0.036 (2)
C(6)	0.5641 (5)	0.2044 (7)	0.6337 (2)	0.033 (2)
N(1)	0.5424 (4)	0.3947 (6)	0.6556 (2)	0.029 (1)
C(1')	0.4432 (4)	0.5186 (8)	0.6228 (2)	0.033 (2)
C(2')	0.4773 (4)	0.5723 (7)	0.5505 (2)	0.030 (2)
O(2')	0.5500 (3)	0.7528 (5)	0.5475 (2)	0.040 (1)
C(3')	0.3414 (5)	0.5943 (7)	0.5211 (2)	0.034 (2)
O(3')	0.2853 (3)	0.7842 (5)	0.5370 (2)	0.042 (1)
C(4')	0.2628 (5)	0.4374 (7)	0.5567 (3)	0.039 (2)
O(4')	0.3278 (3)	0.4050 (5)	0.6196 (2)	0.039 (1)
C(5')	0.2518 (6)	0.2410 (8)	0.5205 (3)	0.049 (2)
O(5')	0.3778 (4)	0.1642 (5)	0.5029 (2)	0.053 (1)

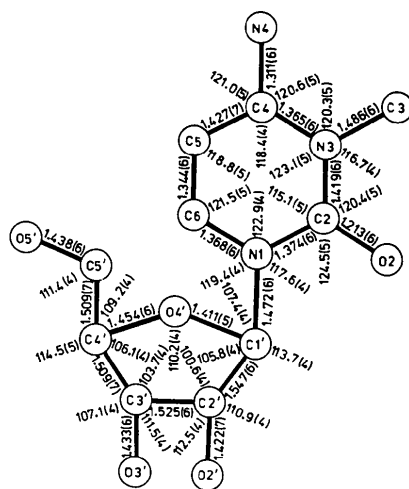


Fig. 1. Bond distances (Å) and angles (°) in the 3-MeCyd⁺ cation.

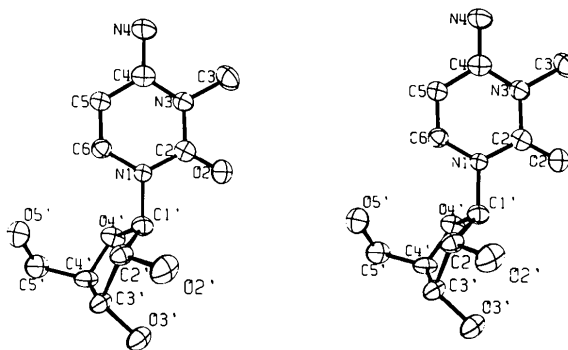


Fig. 2. Stereoscopic thermal-ellipsoid view of the 3-MeCyd⁺ cation. H atoms have been omitted.

Table 2. Conformational data for three 3-MeCyd⁺ cations and for CydH⁺.Cl⁻ (χ , P , τ_m and γ in degrees)

	Glycosyl χ	Ribose pucker	Pseudorotation parameters*		Side chain γ
			P	τ_m	
3-MeCyd ⁺ .NO ₃ [†]	50.7 (4) (anti)	² T ₃	168.1 (7)	37.0 (5)	53.6 (4) (g ⁺)
3-MeCyd ⁺ .Cl [‡]	45.2 (2)	² E	163.0 (8)	40.3 (6)	55.2 (2)
3-MeCyd ⁺ . CH ₃ OSO ₃ ⁻ .H ₂ O [§]	46 (1)	² T ₃	169.4 (9)	38.4 (6)	62 (1)
CydH ⁺ .Cl ^{-¶}	45.7 (4)	² E	162.5 (8)	40.3 (6)	53.5 (4)

* The pseudorotation parameters (Altona & Sundaralingam, 1972) and their standard deviations have been calculated according to Jaskólski (1984b).

† This work.

‡ Jaskólski & Alejska (1985).

§ Shefter, Singh, Brennan & Sackman (1974).

¶ Mosset, Bonnet & Galy (1979).

case is slightly longer [by 0.024 (6) Å]. In particular, the C(2)—N(3)—C(4) angles are identical (123.1°), *i.e.* smaller by 1.8° than the corresponding angle in N(3)-protonated cytidinium cation (Cyd.HCl; Mosset, Bonnet & Galy, 1979). The pyrimidine ring shows slight but significant deviations from planarity ($\chi^2 = 80.8$), the maximum deviation from its best plane being 0.028 (5) Å [C(4)]. The exocyclic substituents, particularly C(1'), C(3) and N(4), deviate appreciably from the pyrimidine plane, the deviation of N(4) being as large as 0.086 (4) Å. Similar distortions of the nucleobase moiety were observed in the chloride salt of the 3-methylcytidinium cation (Jaskólski & Alejska, 1985). The exocyclic N(4)H₂ amino group makes an angle of 2° with the pyrimidine ring.

Table 2 shows that the parameters describing the conformation of the present 3-MeCyd⁺ cation are very similar to those reported for two other 3-MeCyd⁺ cations (3-MeCyd⁺.Cl⁻, Jaskólski & Alejska, 1985; 3-MeCyd⁺.CH₃OSO₃⁻.H₂O, Shefter, Singh, Brennan & Sackman, 1974) and for CydH⁺.Cl⁻ (Mosset, Bonnet & Galy, 1979).

The nitrate anion is planar within experimental error ($\chi^2 = 6.62$). It has almost exact trigonal symmetry, the N—O distances being 1.228 (6), 1.225 (6), 1.229 (7) Å and the O—N—O angles 121.0 (6), 119.2 (6), 119.8 (6)°. There is appreciable overlap between the nitrate anion (symmetry code: 1-x, y+0.5, 1.5-z) and the 3-methylcytosinium system. The planes of these two overlapping entities make an angle of 11.8 (4)°, the interplanar distance in the region of overlap being *ca* 3.1 Å. The N—O bonds of the NO₃⁻ anion overlap the three bonds around N(1). It is interesting to note that an overlap between the anion and cation also exists in the structure of CydH⁺.NO₃⁻ (Guy, Nassimbeni, Sheldrick & Taylor, 1976) but in that case the nitrate anion overlaps the C(5)—C(6)—N(1) region of the cytosinium cation.

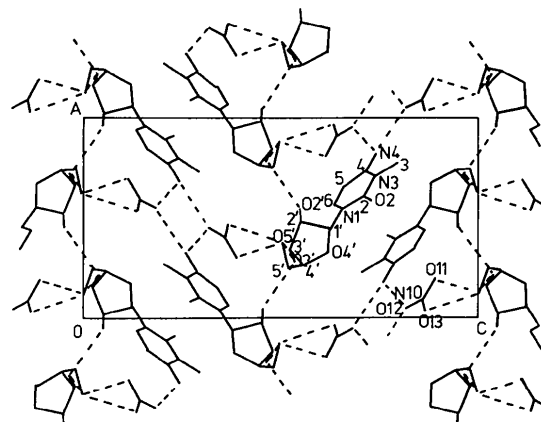


Fig. 3. Crystal packing viewed along *b*. H bonds are indicated by broken lines.

The packing diagram with H bonds is shown in Fig. 3. The exoamino NH₂ group forms two H bonds with O(12) of two different NO₃⁻ anions resulting in H-bonded helical columns running parallel to *b*. The remaining two O atoms of the NO₃⁻ anion [O(11) and O(13)] are H-bonded to the same O(5')—H(5'O) donor (bifurcated H bond) in the adjacent column. There are also two intercationic H bonds involving only ribose moieties: O(3')—H(3'O)...O(5') and O(2')—H(2'O)...O(3'). In this way all available proton donors on the cation are utilized in H-bonding and the acceptors are the three NO₃⁻ oxygen atoms plus O(3') and O(5') on the ribose. All the above H bonds can be classified as weak. There is also a weak intramolecular H bond between C(6)—H(6) and O(5') [C(6)...O(5') 3.279 (6) Å]. It is remarkable that no such bond has been reported for the remaining cations listed in Table 2.

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Structure of Two Modifications of 1,1-Diethyl-3-thiobenzoylthiourea

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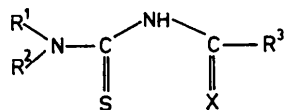
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Abstract. The title compound crystallizes in two polymorphic modifications (I and II). (I) $C_{12}H_{16}N_2S_2$, $M_r = 252.4$, monoclinic, $P2_1/n$, $a = 8.154(1)$, $b = 7.900(1)$, $c = 21.134(1)$ Å, $\beta = 98.92(1)^\circ$, $V = 1344.9(5)$ Å³, $Z = 4$, $D_x = 1.25$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.2$ cm⁻¹, $F(000) = 536$, room temperature. Final $R = 0.056$ for 1286 unique observed reflections. (II) $C_{12}H_{16}N_2S_2$, $M_r = 252.4$, monoclinic, $P2_1$, $a = 8.316(1)$, $b = 14.294(1)$, $c = 11.931(2)$ Å, $\beta = 103.67(1)^\circ$, $V = 1378.1(6)$ Å³, $Z = 4$, $D_x = 1.22$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.2$ cm⁻¹, $F(000) = 536$, room temperature. Final $R = 0.045$ for 1727 unique observed reflections. There are two independent molecules per asymmetric unit. The molecules in both modifications exist as NH tautomers and do not differ significantly in their bond distances and angles. The molecules of (I) as well as the two independent molecules of (II) adopt conformations approximately halfway between E, Z' and Z, Z' . The molecules in both modifications are connected by N–H···S interactions forming dimers, with H···S distances 2.41–2.52 Å.

Introduction. *N*-Chalcogenoacylthioureas are of great interest as chelating ligands in complex chemistry. Whereas the structures of *N*-chalcogenoacylthiourea complexes of transition-metal ions (Fitzl, Beyer, Sieler, Richter, Kaiser & Hoyer, 1977; Knuuttila, Knuuttila, Hennig & Beyer, 1982; Sieler, Richter, Braun, Beyer, Lindqvist & Andersen, 1985) have been described, the structures of the corresponding ligands are generally unknown. We now report the crystal structure of the title compound ($R^1 = R^2 = C_2H_5$, $R^3 = C_6H_5$, $X = S$).



$X = \text{Se, S, O, NR}$

There are three tautomeric forms possible in which the H atom is bonded to the *meso* N atom (dithio keto form), to the S atom of the thiourea moiety and to the S atom of the thiobenzoyl group (thio keto–thiol forms),