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Structure of 1,1'-(5-Methyl-2,4-pyrimidinediyl)dipyridinium Dichloride Dihydrate

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Abstract. $C_{15}H_{14}N_4^{2+} \cdot 2Cl^- \cdot 2H_2O$, $M_r = 357.2$, triclinic, $P\bar{1}$, $a = 9.322$ (1), $b = 14.268$ (2), $c = 7.5902$ (9) Å, $\alpha = 94.22$ (1), $\beta = 113.867$ (8), $\gamma = 109.695$ (9)°, $V = 843.0$ (2) Å³, $Z = 2$, $D_x = 1.407$ g cm⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 36.49$ cm⁻¹, $F(000) = 372$, $T = 291$ K, $R = 0.035$, $wR = 0.038$ for 2092 observed reflexions. The methyl group influences the conformation of the dication. The pyrimidine (I) and two pyridinium (II and III) rings composing the dication are nearly planar but are strongly twisted with respect to each other [I/II 24.7 (4), I/III 53.5 (3), II/III 134.7 (4)°]. The two water molecules are hydrogen bonded to both Cl⁻ anions, forming clusters.

Introduction. Nucleic acid bases such as hypoxanthine, guanine, 1-methyluracil, 1-methylthymine and related *O*-protected nucleosides undergo a quantitative transformation into fluorescent monopyridinium salts when treated with various phosphorylating agents in the presence of pyridine (Adamiak, Biała & Skalski, 1985; Adamiak, Biała, Gdaniec, Mielewczyk & Skalski, 1986). Under analogous conditions xanthine, uracil and thymine are transformed into dipyridinium cations.

Unlike most of the monopyridinium derivatives (Jaskólski, Skalski, Adamiak & Adamiak, 1987) the dipyridinium compounds form crystals stable enough for X-ray analysis. Of particular interest in these structures is the spatial arrangement of the three rings composing the dication. Recently we have

reported the crystallographic structure of uracil-derived dipyridinium dichloride monohydrate which appeared to be nearly planar with only slight deviations from strict planarity for the two pyridinium rings (Jaskólski, Skalski & Adamiak, 1988). In this paper we present the structure of the thymine-derived analog, *i.e.* 1,1'-(5-methyl-2,4-pyrimidinediyl)dipyridinium dichloride dihydrate. It will be shown that the methyl substituent in the 5-position of the pyrimidine moiety of this salt imposes a significant steric hindrance which results in severe distortion from coplanarity of the three-ring system.

Experimental. The synthesis of the title compound is described elsewhere (Skalski, Wenska, Gdaniec & Adamiak, 1991). Suitable crystals were obtained from water. Space group from de Jong–Bouman photographs; crystal size 0.3 × 0.35 × 0.40 mm; Syntex P2₁ diffractometer, graphite monochromator, CuK α radiation. Cell parameters from least-squares treatment of setting angles of 15 reflexions ($40.2 \leq 2\theta \leq 87.5^\circ$). θ - 2θ profiles measured for 2269 unique $+h \pm k \pm l$ reflexions with $2\theta \leq 115^\circ$ [$\max. (\sin\theta/\lambda) = 0.547 \text{ \AA}^{-1}$] and with $0 \leq h \leq 10$, $-15 \leq k \leq 14$, $-8 \leq l \leq 7$; profile analysis according to Lehmann & Larsen (1974). No significant intensity variation for two standard reflexions recorded every 100 reflexions. No absorption correction. 2092 observed reflexions with $I \geq 2\sigma(I)$. Structure solved by direct methods using *SHELXS86* (Sheldrick, 1986). Full-matrix least-squares refinement on F , $w = \sigma^{-2}(F)$. All H atoms located in ΔF map and included in the refinement, anisotropic thermal parameters for

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non-H atoms, isotropic for H atoms, empirical isotropic extinction parameter x refined to $14.1(2) \times 10^{-6}$ and F_c multiplied by $(1 - xF_c^2)/\sin\theta$. $R = 0.035$, $wR = 0.038$, $(\Delta/\sigma)_{\max} = 0.013$, $(\Delta\rho)_{\max} = 0.25$, $(\Delta\rho)_{\min} = -0.18 \text{ e } \text{Å}^{-3}$. Computer programs: *SHELX76* (Sheldrick, 1976), *CSU* (Vickovic, 1988) and local programs (Jaskólski, 1982); molecular illustrations drawn using *ORTEPII* (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Atomic positions and equivalent isotropic temperature factors are listed in Table 1;* an *ORTEP* plot of the molecule with the numbering scheme is shown in Fig. 1. Bond distances and angles in the structure are given in Table 2. The dimensions of the two pyridinium rings are very similar to those found in the other structures of pyridinium salts (Jaskólski, Skalski, Adamiak & Adamiak, 1987; Jaskólski, Skalski & Adamiak, 1988, 1991). In the pyrimidine moiety the endocyclic angles show a characteristic distribution with a very wide N—C—N angle [$128.7(3)^\circ$] and narrow C—N—C angles [$114.2(3)$, $114.3(2)^\circ$]. Corresponding values in the 1,1'-(2,4-pyrimidinediyl)dipyridinium dication are: $129.4(2)$, $113.6(2)$ and $114.7(2)^\circ$ respectively (Jaskólski, Skalski & Adamiak, 1988). The C—N⁺ distances between the pyrimidine and the pyridinium rings are $1.457(2)$ and $1.453(3) \text{ Å}$ and compare well with the corresponding value in the 1-(2-amino-6-puriny)pyridinium cation [$1.454(3) \text{ Å}$] (Jaskólski, Skalski, Adamiak & Adamiak, 1987) and in the 1,1'-(2,4-pyrimidinediyl)dipyridinium dication [$1.459(3)$ and $1.453(3) \text{ Å}$].

The most significant feature in the present structure is the influence of the methyl group on the planarity of the pyrimidinediylpyridinium dication. The three rings composing the cation (Fig. 1) are nearly planar (χ^2 : I 77.1, II 3.8, III 11.2). The N substituents at the pyrimidine ring deviate from the pyrimidine plane [N(21) by $0.070(2)$, N(41) by $0.036(3) \text{ Å}$] and C(51) of the methyl group deviates by $0.082(4) \text{ Å}$. The dihedral angles, I/II $24.7(4)$ and I/III $53.5(3)^\circ$, show strong twisting between the 5-substituted pyrimidine ring and both pyridinium rings. In the 1,1'-(2,4-pyrimidinediyl)dipyridinium dication these values are $6.2(3)$ and $6.1(3)^\circ$ respectively. As we can see the influence of steric hindrance caused by the methyl group is significant. However,

* Lists of structure factors, anisotropic thermal parameters, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54532 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters (Å^2)*

$$U_{eq} = (1/3)\sum_i U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq}
C(1)	1.0146 (3)	0.3854 (2)	0.3307 (3)	0.0404 (5)
C(2)	1.0541 (3)	0.3511 (2)	0.4933 (3)	0.0343 (6)
N(3)	1.0016 (2)	0.2564 (1)	0.5106 (3)	0.0329 (5)
C(4)	0.8893 (3)	0.1874 (2)	0.3403 (3)	0.0317 (5)
C(5)	0.8307 (3)	0.2087 (2)	0.1564 (3)	0.0350 (6)
C(6)	0.9044 (3)	0.3124 (2)	0.1638 (4)	0.0403 (6)
N(21)	1.1710 (3)	0.4288 (1)	0.6796 (3)	0.0353 (5)
C(22)	1.1669 (4)	0.4086 (2)	0.8491 (4)	0.0454 (7)
C(23)	1.2745 (4)	0.4819 (2)	1.0238 (4)	0.0544 (8)
C(24)	1.3861 (4)	0.5746 (2)	1.0255 (4)	0.0517 (7)
C(25)	1.3878 (4)	0.5934 (2)	0.8510 (4)	0.0523 (7)
C(26)	1.2782 (4)	0.5194 (2)	0.6778 (4)	0.0446 (7)
N(41)	0.8282 (2)	0.0839 (1)	0.3663 (3)	0.0323 (4)
C(42)	0.7659 (3)	0.0685 (2)	0.4998 (4)	0.0417 (6)
C(43)	0.7111 (4)	-0.0270 (2)	0.5315 (4)	0.0492 (7)
C(44)	0.7210 (4)	-0.1071 (2)	0.4295 (4)	0.0485 (7)
C(45)	0.7868 (3)	-0.0897 (2)	0.2963 (4)	0.0428 (6)
C(46)	0.8403 (3)	0.0069 (2)	0.2652 (4)	0.0376 (6)
C(51)	0.6984 (4)	0.1320 (2)	-0.0358 (4)	0.0489 (7)
O(W1)	0.4780 (4)	0.1462 (2)	0.2064 (4)	0.0624 (6)
O(W2)	0.3697 (4)	0.3571 (2)	0.4636 (5)	0.0755 (7)
Cl(1)	0.70946 (9)	0.30844 (5)	0.62232 (9)	0.0504 (2)
Cl(2)	0.1321 (1)	0.17753 (7)	0.0708 (1)	0.0749 (3)

Table 2. *Bond distances (Å) and angles ($^\circ$) in the dication*

C(2)—N(1)	1.320 (3)	C(2)—N(3)	1.309 (3)
N(1)—C(6)	1.333 (3)	N(3)—C(4)	1.326 (2)
C(6)—C(5)	1.391 (4)	C(4)—C(5)	1.377 (3)
C(2)—N(21)	1.457 (2)	C(4)—N(41)	1.453 (3)
N(21)—C(22)	1.351 (4)	N(41)—C(42)	1.355 (4)
C(22)—C(23)	1.368 (3)	C(42)—C(43)	1.362 (4)
C(23)—C(24)	1.375 (4)	C(43)—C(44)	1.383 (5)
C(24)—C(25)	1.376 (5)	C(44)—C(45)	1.377 (5)
C(25)—C(26)	1.367 (3)	C(45)—C(46)	1.373 (4)
C(26)—N(21)	1.347 (3)	C(46)—N(41)	1.356 (4)
C(5)—C(51)	1.499 (3)		
N(1)—C(2)—N(3)	128.7 (3)	C(4)—C(5)—C(6)	113.0 (2)
C(2)—N(1)—C(6)	114.2 (3)	C(2)—N(3)—C(4)	114.3 (2)
N(1)—C(6)—C(5)	124.4 (3)	N(3)—C(4)—C(5)	125.2 (2)
N(1)—C(2)—N(21)	115.9 (2)	N(3)—C(4)—N(41)	112.7 (2)
N(3)—C(2)—N(21)	115.3 (2)	C(5)—C(4)—N(41)	122.0 (2)
C(2)—N(21)—C(22)	119.1 (2)	C(4)—N(41)—C(42)	117.8 (2)
C(2)—N(21)—C(26)	119.2 (2)	C(4)—N(41)—C(46)	120.5 (2)
N(21)—C(22)—C(23)	119.3 (3)	N(41)—C(42)—C(43)	119.4 (3)
C(22)—C(23)—C(24)	119.9 (3)	C(42)—C(43)—C(44)	120.1 (3)
C(23)—C(24)—C(25)	119.8 (3)	C(43)—C(44)—C(45)	119.7 (3)
C(24)—C(25)—C(26)	119.4 (3)	C(44)—C(45)—C(46)	119.5 (3)
C(25)—C(26)—N(21)	119.9 (3)	C(45)—C(46)—N(41)	119.6 (3)
C(26)—N(21)—C(22)	121.8 (3)	C(46)—N(41)—C(42)	121.7 (2)
C(4)—C(5)—C(51)	125.7 (3)	C(6)—C(5)—C(51)	121.3 (3)

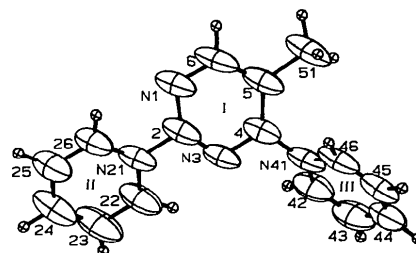


Fig. 1. An *ORTEP* (Johnson, 1976) view of the dication. H atoms are represented as spheres of arbitrary size, all other ellipsoids are at 25% probability level.

in comparison to 1,1'-(2,4-pyrimidinediyl)dipyridinium dichloride monohydrate (Jaskólski, Skalski & Adamiak, 1988), in the present case we should take into consideration the influence of another arrangement of packing forces caused by the additional water molecule. The dihedral angle II/III 134.7 (3)^o illustrates that the pyridinium rings are rotated in the same sense relative to ring I, *i.e.* this situation is opposite to that observed in the 1,1'-(2,4-pyrimidinediyl)dipyridinium dication. We can also describe coplanarity in a polycyclic system using an algorithm similar to that described by Winkler & Dunitz (1971), based on the torsion angles. Applying this one can determine the twist (τ) between two connected triatomic groups as well as nonplanarity (pyramidalization, χ) of the three bonds around each of the connected atoms. In the present case $\tau_{C(2)-N(21)} = -24.8 (4)$, $\chi_{C(2)} = 1.5 (4)$, $\chi_{N(21)} = 0.7 (4)^\circ$ and $\tau_{C(4)-N(41)} = 54.31 (3)$, $\chi_{C(4)} = 1.2 (3)$, $\chi_{N(41)} = 4.0 (3)^\circ$. The τ values confirm the twisting of the two pyridine rings relative to the pyrimidine ring and the $\chi_{N(41)}$ value shows the slight pyramidalization of N(41).

There are short contacts between the pyrimidine N atoms and all suitable C _{α} -H groups on the pyridinium substituent in the 1,1'-(2,4-pyrimidinediyl)dipyridinium dication [H \cdots N distances: C(26)H(26) \cdots N(1) 2.32 (3), C(22)H(22) \cdots N(3) 2.31 (2), C(42)H(42) \cdots N(3) 2.21 (2) Å]. In the present dication the corresponding values are longer [2.36 (2), 2.34 (3), 2.54 (3) Å], particularly C(42)H(42) \cdots N(3). In both cases the C-H \cdots N angles [103 (2), 103 (2), 105 (1)^o and 107 (2), 104 (2), 96 (2)^o, respectively] exclude the possibility of intramolecular hydrogen-bond formation (Jaskólski, 1984). Comparing these structures we can conclude that the presence of these short contacts (C-H \cdots N) is a weak stabilizing factor promoting coplanarity of the rings when compared to the twisting effect of the methyl group.

In contrast to the situation observed in the 1,1'-(2,4-pyrimidinediyl)dipyridinium dication, C _{α} -H groups show very little activity as hydrogen-bond donors. Only the distance C(45)H(45) \cdots Cl(2) [2.58 (4) Å] and corresponding C-H \cdots Cl angle [141 (2)^o] implicate the hydrogen interaction between the dication and the cluster formed from the two water molecules and both Cl⁻ anions. The cluster is built in such a way that Cl(1) is an acceptor of one H atom from W(1) and one from W(2). The Cl(2) is connected in the same way, so, both hydrogen-bond donor functions of W(1) and W(2) are utilized (Table 3, Fig. 2).

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Table 3. *Geometry of the hydrogen bonds* (Å, °)

D-H \cdots A	D-H	H \cdots A	D \cdots A	D-H \cdots A
O(W1)-H(1W1) \cdots Cl(1)	0.94 (3)	2.24 (3)	3.166 (3)	178 (4)
O(W1)-H(2W1) \cdots Cl(2)	0.83 (5)	2.34 (4)	3.164 (4)	171 (4)
O(W2)-H(1W2) \cdots Cl(2)	0.78 (3)	2.40 (3)	3.173 (3)	170 (3)
O(W2)-H(2W2) \cdots Cl(1)	0.94 (7)	2.34 (6)	3.238 (4)	161 (5)
C(45)-H(45) \cdots Cl(2)	1.01 (4)	2.58 (4)	3.426 (4)	141 (2)

Symmetry code: (i) 1 - x, -y, -z.

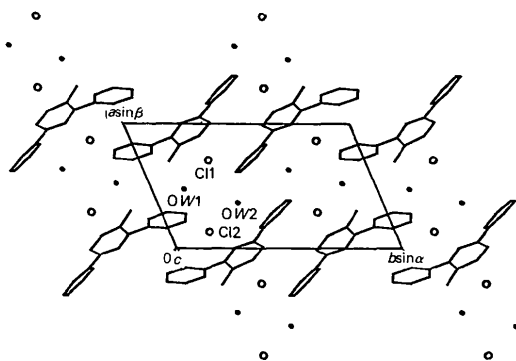


Fig. 2. Projection of the structure down the *c* axis. H atoms are omitted.

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