The molecules in the crystal are stabilized by intra- and intermolecular hydrogen bonds, O(3)—H(O3)···O(2), 2·582 (5) Å; O(3)—H(O3)···O(3) ($-x+2·5$, y, $-z+2$), 2·686 (7) and O(2)—H(O4)···O(4) ($x+0·5$, $-y$, z), 2·825 Å.

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Structure of *N*-(2-Amino-6-purinyl)pyridinium Chloride Dihydrate

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Abstract. $C_{10}H_9N_6^+.Cl^-.2H_2O$, $M_r = 284·7$, monoclinic, $P2_1/c$, $a = 7·3671$ (5), $b = 20·938$ (2), $c = 9·219$ (2) Å, $\beta = 116·09$ (1)°, $V = 1277·1$ (3) Å^3, $Z = 4$, $D_x = 1·481$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 2·62$ mm^{-1}, $F(000) = 592$, $T = 289$ K, $R = 0·045$ for 1485 observed reflexions. The dimensions of the pyrimidine ring are different from those in other purines; the N(1)—C(6)—C(5) angle is very wide [121·9 (2)°]. There is no conjugation between the pyrimidine and pyridinium rings [C(6)—N$^+$(pyridinium) 1·454 (3) Å]. The three rings composing the cation are coplanar. An intramolecular C—H···N hydrogen bond [2·974 (5) Å] cooperates in determining coplanarity between the pyridinium and purine systems. Intermolecular H bonds are arranged in two-dimensional layers perpendicular to **a** with a single C—H···O link between the layers. The main acceptor center is Cl$^-$ (fivefold) and the donors are the NH and OH (water) groups.

Introduction. We recently reported on the formation (Adamiak, Biała & Skalski, 1985*b*; Adamiak, Biała, Gdaniec, Mielewczyk & Skalski, 1986*a*,*b*) and reactivity (Skalski, Adamiak & Paszyc, 1984; Adamiak, Biała & Skalski, 1985*a*,*b*; Adamiak, Biała, Gdaniec, Mielewczyk & Skalski, 1986*a*,*b*) of nucleobase-derived pyridinium salts as new fluorescent ionic side-products in oligonucleotide synthesis by the phosphotriester method and as synthetic intermediates in nucleoside chemistry. Among various salts of hypoxanthine, guanine, uracil and thymine bases and their ribosides only one, namely *N*-(2-amino-6-purinyl)pyridinium chloride, has, up to the present, formed crystals of sufficient stability. The title compound was prepared by

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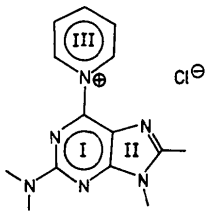
treatment of guanine with 4-chlorophenylphosphorodichloridate in pyridine and isolated as its 9-methylhypoxanthine analogue (Adamiak, Biała & Skalski, 1985*b*).



Experimental. Suitable crystals from 2-propanol with small addition of water. Crystal 0·2 × 0·3 × 0·4 mm sealed in a glass capillary, Syntex $P2_1$ diffractometer, graphite monochromator, Cu $K\alpha$ radiation. Cell parameters from least-squares treatment of setting angles of 15 reflexions ($25 < 2\theta < 31°$). θ:2θ profiles measured for 1786 unique $+h+k\pm l$ reflexions with $2\theta \le 115°$ ($0 \le h \le 8$, $0 \le k \le 22$, $-10 \le l \le 9$), profile analysis according to Lehmann & Larsen (1974). No significant intensity variation (< 2%) for two standard reflexions measured every 1·5 h. No absorption correction. 1485 observed reflexions with $I \ge 1{\cdot}96\sigma(I)$. Structure solved by heavy-atom Patterson and Fourier techniques. Full-matrix least-squares refinement on F, $w = [\sigma^2(F) + 0{\cdot}0001F^2]^{-1}$; final refinement: anisotropic non-H atoms, isotropic H atoms, empirical isotropic extinction parameter x used to correct F_c according to $F_c' = F_c(1-xF_c^2/\sin\theta)$, which converged at $x = 95\,(16) \times 10^{-7}$, $R = 0{\cdot}045$, $wR = 0{\cdot}059$, $S = 3{\cdot}86$, $(\Delta/\sigma)_{max} = 0{\cdot}4$ for non-H atoms and 1·1 for H atoms, largest peak in final ΔF map = 0·30, largest trough = −0·23 e Å^{-3}. Computer programs: *SHELX*76 (Sheldrick, 1976) and local programs (Jaskólski, 1982*a*), 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 cation are given in Table 2 and its thermal-ellipsoid representation is shown in Fig. 1. The dimensions of the imidazole moiety (ring II) of the purine system do not show any significant deviations from the values for neutral guanine reported by Taylor & Kennard (1982*b*). On the other hand, the dimensions of the pyrimidine ring (I) differ significantly from those characterizing both neutral and cationic [N(7)-protonated] guanines. They are also different from those reported for neutral adenine (Taylor & Kennard, 1982*b*). In particular, the N(1)—C(6)—C(5) angle of the present pyrimidine ring is unusually wide [121·9 (2)°] compared with both neutral and N(7)-protonated guanines [111·7 (2) and 110·5 (1)°, respectively]. The corresponding values in adenines are 117·6 (1) (neutral) and 114·3 (3)° [N(1)-protonated]. Analysis of the possible resonance forms of ring I suggests an appreciable degree of resonance within the pyrimidine system. However, the N(1)—C(6) bond is very short [1·310 (4) Å] and must have predominantly double-bond character. The N^+—C distances in the pyridinium ring (III) are 1·345 (4) and 1·349 (4) Å. The C—C distances are somewhat shortened but such a shortening is often observed in pyridinium cations (Newkome, Theriot & Fronczek, 1985). The C(6)—N(11) linkage between rings I and III

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

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cl	0·8923 (1)	0·20034 (4)	0·16504 (9)	0·0680 (5)
N(1)	0·4834 (4)	0·1483 (1)	0·5071 (3)	0·0476 (9)
C(2)	0·5418 (5)	0·1394 (1)	0·6668 (3)	0·050 (2)
N(2)	0·6560 (5)	0·1854 (1)	0·7649 (4)	0·068 (2)
N(3)	0·4903 (4)	0·0890 (1)	0·7328 (3)	0·049 (1)
C(4)	0·3736 (4)	0·0475 (1)	0·6230 (3)	0·044 (2)
C(5)	0·3034 (4)	0·0508 (1)	0·4553 (3)	0·043 (2)
C(6)	0·3682 (4)	0·1054 (1)	0·4046 (3)	0·044 (2)
N(7)	0·1893 (4)	−0·0027 (1)	0·3814 (3)	0·0497 (9)
C(8)	0·1903 (5)	−0·0359 (1)	0·5019 (4)	0·052 (2)
N(9)	0·2998 (4)	−0·0087 (1)	0·6505 (3)	0·052 (2)
N(11)	0·3168 (3)	0·1183 (1)	0·2360 (3)	0·0436 (9)
C(12)	0·2038 (6)	0·0770 (2)	0·1196 (4)	0·066 (2)
C(13)	0·1501 (6)	0·0904 (2)	−0·0388 (4)	0·071 (2)
C(14)	0·2130 (5)	0·1458 (2)	−0·0805 (4)	0·064 (2)
C(15)	0·3276 (6)	0·1876 (2)	0·0379 (4)	0·067 (2)
O(16)	0·3795 (5)	0·1733 (2)	0·1966 (4)	0·060 (2)
O(1)	0·0317 (5)	0·3247 (1)	0·0356 (4)	0·091 (2)
O(2)	0·2959 (5)	−0·0634 (1)	0·9205 (3)	0·083 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *in the cation*

N(1)—C(2)	1·353 (4)	C(8)—N(7)	1·308 (4)
C(2)—N(2)	1·336 (4)	N(7)—C(5)	1·387 (4)
C(2)—N(3)	1·353 (4)	C(6)—N(11)	1·454 (3)
N(3)—C(4)	1·323 (4)	N(11)—C(12)	1·345 (4)
C(4)—C(5)	1·400 (4)	C(12)—C(13)	1·364 (5)
C(5)—C(6)	1·395 (4)	C(13)—C(14)	1·366 (5)
C(6)—N(1)	1·310 (4)	C(14)—C(15)	1·363 (5)
C(4)—N(9)	1·367 (4)	C(15)—C(16)	1·372 (4)
N(9)—C(8)	1·370 (4)	C(16)—N(11)	1·349 (4)

C(6)—N(1)—C(2)	119·1 (2)	N(7)—C(5)—C(4)	110·6 (2)
N(1)—C(2)—N(3)	125·4 (3)	N(7)—C(5)—C(6)	136·0 (3)
N(1)—C(2)—N(2)	116·2 (3)	C(5)—C(6)—N(11)	123·0 (3)
N(2)—C(2)—N(3)	118·4 (3)	N(1)—C(6)—N(11)	115·1 (2)
C(2)—N(3)—C(4)	112·6 (2)	C(6)—N(11)—C(12)	120·7 (3)
N(3)—C(4)—C(5)	127·7 (3)	C(6)—N(11)—C(16)	119·2 (2)
C(4)—C(5)—C(6)	113·3 (3)	N(11)—C(12)—C(13)	120·5 (3)
C(5)—C(6)—N(1)	121·9 (2)	C(12)—C(13)—C(14)	120·1 (3)
C(5)—C(4)—N(9)	105·3 (3)	C(13)—C(14)—C(15)	119·2 (3)
N(3)—C(4)—N(9)	127·0 (3)	C(14)—C(15)—C(16)	119·9 (3)
C(4)—N(9)—C(8)	106·2 (3)	C(15)—C(16)—N(11)	120·3 (3)
N(9)—C(8)—N(7)	114·2 (3)	C(16)—N(11)—C(12)	120·0 (3)
C(8)—N(7)—C(5)	103·6 (2)		

* 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 43997 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is long [1·454 (3) Å] and clearly indicates no conjugation between these two aromatic systems. The two pyrimidine exocyclic angles at C(6)—N(11) are very different: N(11)—C(6)—C(5) [123·0 (3)°] is 7·9° larger than N(11)—C(6)—N(1) [115·1 (2)°], possibly owing to the steric effect of the imidazole ring. It is interesting to note that a similar difference between these exocyclic angles exists in both neutral and N(7)-protonated guanines in spite of the fact that in guanines the individual angles are *ca* 5·4° larger than in the present case [128·3 (2) and 120·0 (2)° in neutral guanines, 129 (1) and 121 (1)° in N(7)-protonated guanines (Taylor & Kennard, 1982*b*)]. The three rings composing the *N*-(2-amino-6-purinyl)pyridinium cation are planar (χ^2: I 0·92, II 11·3, III 2·11). The *N*-substituents at the pyrimidine ring deviate slightly but significantly from its best plane [N(2) −0·027 (3), N(11) 0·026 (2) Å]. The three rings composing the cation are nearly coplanar, as illustrated by the dihedral angles: I/II 1·2 (4)°, I/III 2·3 (4)°. Of particular interest is the coplanarity between rings I and III since no conjugation can be expected to exist between these rings [see above and compare with the results concerning reactivity of pyridinium salts towards nucleophilic attack at C(6) (Adamiak, Biała, Gdaniec, Mielewczyk & Skalski, 1986*a*,*b*; Adamiak, Biała & Skalski, 1985*a*)]. It is possible that the coplanar arrangement of ring III and the purine system is due to an intramolecular C(12)—H(12)···N(7) hydrogen bond (see below). The exocyclic $-N(2)H_2$ amino group is twisted by 9 (3)° relative to the pyrimidine ring.

There is a complicated network of H bonds in the structure in which all available NH and OH (water) donors are utilized (Table 3, Fig. 2). According to their *ΔHA* parameters* (Jaskólski, 1982*b*), these H bonds can be classified as weak and medium strong. The main acceptor is Cl^- (fivefold) and the remaining acceptor centers are N(3), and N(7) and water O atoms. Interestingly, no H bonds are accepted by N(1). The N(2)—H donors interact exclusively with the Cl^- anion. There is a H bond between C(8)—H(8) and O(1). It is not unusual that C(8) is a H-bond donor since it is adjacent to two N atoms and since such C atoms are particularly likely to form C—H···*A* hydrogen bonds (Taylor & Kennard, 1982*a*). There are two relatively strong (according to their *ΔHA* values) C—H···*A* hydrogen bonds formed by C(12) and C(14) on the pyridinium ring (both atoms bear partial positive charge). One of them [C(12)—H(12)···N(7)] has intramolecular character and possibly contributes to the forces responsible for the coplanar disposition of rings I and III. An interesting feature of the H-bond network is that it is predominantly two-dimensional: all H bonds but one are arranged in two-dimensional arrays perpendicular to **a** and C(14)—H(14)···O(1) is a link between those layers. All H bonds within a layer are arranged in a pattern of circular systems, most of which

Table 3. *Parameters characterizing the hydrogen bonds*

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	∠*D*—H···*A* (°)	*ΔHA**
N(2)—H(21)···Cl^{i}	0·84 (4)	2·50 (4)	3·330 (4)	167 (2)	17·1
N(2)—H(22)···Cl^{ii}	0·88 (4)	2·46 (4)	3·319 (3)	167 (3)	17·5
C(8)—H(8)···O(1^{iii})	1·01 (3)	2·28 (3)	3·288 (4)	176 (2)	7·9
N(9)—H(9)···O(2)	0·91 (3)	1·86 (4)	2·751 (5)	166 (2)	27·0
C(12)—H(12)···N(7)	0·91 (5)	2·24 (6)	2·974 (5)	138 (4)	12·0
C(14)—H(14)···O(1^{iv})	0·96 (4)	2·29 (4)	3·245 (5)	171 (2)	9·4
O(1)—H(11*W*)···Cl^{v}	0·85 (6)	2·31 (7)	3·149 (4)	172 (4)	22·2
O(1)—H(12*W*)···Cl^{vi}	0·94 (6)	2·29 (6)	3·216 (3)	172 (4)	19·8
O(2)—H(21*W*)···N(3^{vii})	0·85 (4)	2·10 (5)	2·925 (4)	164 (3)	17·4
O(2)—H(22*W*)···Cl^{viii}	0·85 (6)	2·29 (6)	3·131 (3)	171 (5)	22·8

Symmetry codes: (i) *x*, *y*, 1+*z*; (ii) *x*, 0·5−*y*, 0·5+*z*; (iii) −*x*, *y*−0·5, 0·5−*z*; (iv) *x*, 0·5−*y*, *z*−0·5; (v) *x*−1, 0·5−*y*, *z*−0·5; (vi) *x*−1, *y*, *z*; (vii) 1−*x*, −*y*, 2−*z*; (viii) 1−*x*, −*y*, 1−*z*.

* Jaskólski (1982*b*).

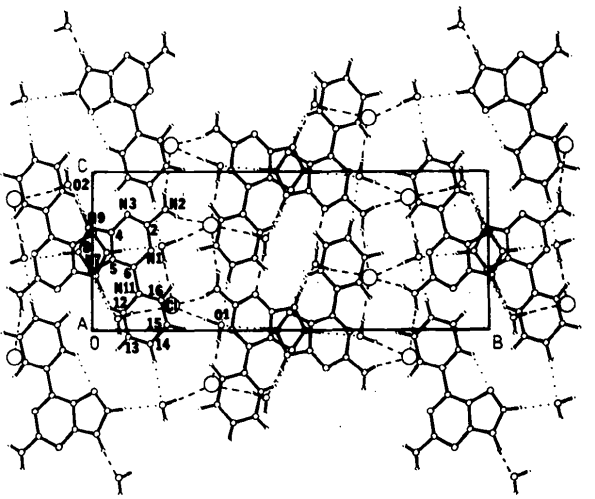


Fig. 2. Projection of the structure down **a**. Broken lines indicate N(O)—H···*A* hydrogen bonds and dotted lines C—H···*A* hydrogen bonds.

* *ΔHA* describes the shortening of the hydrogen···acceptor distance (d_{HA}) with respect to the sum of the corresponding van der Waals radii ($r_H + r_A$). The shortening ($r_H + r_A - d_{HA}$) is expressed as a fraction of ($r_H + r_A$): $\Delta HA = 100(r_H + r_A - d_{HA})/(r_H + r_A)$.

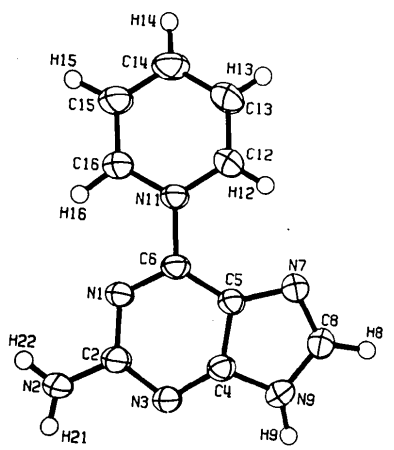


Fig. 1. Thermal-ellipsoid representation of the cation. H-atom spheres have been set to an arbitrary scale.

pass through Cl^- (Fig. 2): $Cl^-\cdots H(11W)-O(1)-H(12W)\cdots Cl^-\cdots H(21)-N(2)-H(22)\cdots Cl^-$ (two such rings at each Cl^- ion), $Cl^-\cdots H(22W)-O(2)-H(21W)\cdots N(3)-C(2)-N(2)-H(21)\cdots Cl^-$, $Cl^-\cdots H(22W)-O(2)\cdots H(9)-N(9)-C(8)-H(8)\cdots O(1)-H(11W)\cdots Cl^-$ and $O(2)-H(21W)\cdots N(3)-C(4)-N(9)-H(9)\cdots O(2)-H(21W)\cdots N(3)-C(4)-N(9)-H(9)\cdots O(2)$.

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Dopaminergic 3-Benzazepines: SKF 87516 (II) and SKF 82526 (III)

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Abstract. (II): (1*R*)-6-Fluoro-2,3,4,5-tetrahydro-1-(*p*-hydroxyphenyl)-1*H*-3-benzazepine-7,8-diol hydrobromide, $C_{16}H_{17}FNO_3^+.Br^-$, $M_r = 370{\cdot}23$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}293\ (2)$, $b = 10{\cdot}309\ (1)$, $c = 16{\cdot}479\ (4)$ Å, $V = 1578{\cdot}7\ (6)$ Å^3, $Z = 4$, D_m (flotation in $CHCl_3/C_2H_4Cl_2$) $= 1{\cdot}54\ (2)$, $D_x = 1{\cdot}558$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) $= 0{\cdot}71073$ Å, $\mu = 2{\cdot}5973$ mm^{-1}, $F(000) = 752$, $T = 293$ K, $R = 0{\cdot}039$, $wR = 0{\cdot}043$ for 1282 observations. (III): (1*R*)-6-Chloro-2,3,4,5-tetrahydro-1-(*p*-hydroxyphenyl)-1*H*-3-benzazepine-7,8-diol hydrobromide, $C_{16}H_{17}ClNO_3^+.Br^-$, $M_r = 386{\cdot}68$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}254\ (1)$, $b = 10{\cdot}011\ (2)$, $c = 17{\cdot}555\ (4)$ Å, $V = 1626{\cdot}3\ (6)$ Å^3, $Z = 4$, D_m not measured, $D_x = 1{\cdot}58$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1{\cdot}54184$ Å, $\mu = 5{\cdot}41$ mm^{-1}, $F(000) = 784$, $T = 296$ K, $R = 0{\cdot}034$, $wR = 0{\cdot}046$ for 1693 observations. (II) and (III), members of a novel class of dopamine receptor agonists, incorporate the phenethylamine skeleton of dopamine in a moderately constrained fashion and differ only in the halogen substituent attached to the catechol ring. Both molecules crystallize with the seven-membered azepine ring adopting a chair conformation; the 1-(*p*-hydroxyphenyl) substituent sits in an equatorial orientation relative to the benzazepine ring with the phenyl ring also perpendicular to the catechol nucleus. Significant differences in catechol C—O bond lengths are observed in both structures with the bond *ortho* to the halogen substituent 0·18 Å shorter. Observed bond-angle distortions about the catechol ring are also consistent with the σ-withdrawing ability of the halo substituents at C(6). Intermolecular hydrogen bonding involves all available donors in both structures. The bromide ions are 'coordinated' in a distorted square-planar fashion by four H-bonding interactions. The possibility of a three-center interaction involving the catechol group adjacent to the halo substituent is also noted.

Introduction. The observations of Goldberg (1972), that low doses of dopamine increased renal blood flow

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