geometry with atomic numbering is shown in Fig. 1. The bond lengths, angles and relevant torsion angles are listed in Table 2. Atom C(12) is substituted by an acetoxy moiety which assumes an α-axial position as is evidenced by the torsion angle C(14)–C(13)–C(12)– O(26) = −67·0 (7)°. The long side chain, *i.e.* the 1′-methyl-3′-methoxycarbonyl-*n*-propyl moiety at C(17), is in a β-equatorial position relative to the C(13)–C(17) bond [C(20)–C(17)–C(13)–C(14) = −167·4 (10)°]. Its zigzag structure can be characterized by the sequence of rotations about the bonds C(13)–C(17), C(17)–C(20), C(20)–C(21), C(21)– C(22), C(22)–C(23) and C(23)–C(24), which is −*ap*, *ap*, −*ap*, −*ap*, −*ap* and −*ap* (*ap*=antiperiplanar). The lowest torsion angle value of −167·4 (10)°, *i.e.* the greatest deviation (12·6°) from 180°, is found about C(22)–C(23) and C(13)–C(17). The position of the side chain relative to the five-membered ring is presumably influenced by the repulsion between the neighbouring C(18) and C(20′) methyl groups which assume an anticlinal position as shown by the non-bonded torsion angle C(20′)–C(20)⋯C(13)– C(18) = −94·7 (5)°. Otherwise, the vicinal C(18) and

O(26) atoms are in *trans* positions. The β-axial C(18) methyl group is almost perfectly eclipsed with the C(19) methyl moiety; C(18)–O(13)⋯C(10)–C(19) is 3·8 (6)°. As a result of the *cis* junction |C(5)–C(10)| between rings *A* and *B*, C(19) is β-equatorial relative to ring *A*. The second acetoxy group linked to C(3) of ring *A* assumes an α-equatorial position.

Rings *A*, *B* and *C* condensed with *cis* (*A*:*B*) and *trans* (*B*:*C*) junctions are invariably in an almost perfect chair conformation. The five-membered ring *D* exhibits a transition form between the envelope and half-chair conformations; the puckering parmeters (Cremer & Pople, 1975) are $Q = 0.462$ (6) Å, $\varphi = 187.6$ (8)°.

References

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Enraf–Nonius (1981). *Structure Determination Package.* Enraf– Nonius, Delft, The Netherlands.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Structure of 4-Dimethylaminopyridine *N*-Oxide Dihydrate

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Abstract. $C_7H_{10}N_2O.2H_2O$, $M_r = 174.2$, monoclinic, $P2_1/c$, $a = 8.391$ (6), $b = 16.320$ (4), $c = 6.847$ (6) Å, $\beta = 103.10$ (7)°, $V = 913.0$ (10) Å^3, $Z = 4$, $D_x = 1.267$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0.71069$ Å, $\mu(\text{Mo }K\alpha) = 0.11$ mm^{-1}, $F(000) = 376$, $T = 295$ K, $R = 0.052$ for 1898 observed reflections $[F_o > \sigma(F_o)]$. The dimethyl-amino group is planar, and the C–N bond length is shorter than that in 4-dimethylaminopyridine. These findings indicate the presence of strong conjugation between the dimethylamino group and the pyridine ring. The two water molecules interact with the O atom in the N–O bond through hydrogen bonds, by which the N–O bond is lengthened to 1·344 (1) Å.

Introduction. Chao & Schempp (1977) have studied the crystal structures of six-membered *N*-heteroaromatics which contain an amino group by X-ray analysis, and found that the planarity of the amino groups was linearly correlated with the bond lengths of C(*ipso*)– N(amino). The bond lengths are a measure of the degree

of conjugation between the amino group and the aromatic ring. Therefore, the planarity also indicates the degree of conjugation. X-ray crystal analyses of 4-dimethylaminopyridine (Ohms & Guth, 1984) and its hydrochloride dihydrate (Chao, Schempp & Rosenstein, 1977) reflect this situation; the conformation of the dimethylamino group is slightly pyramidal in the former but planar in the latter, and the bond length between the dimethylamino nitrogen and the *ipso* carbon is 0·027 Å longer in the former than in the latter.

We were interested in the effect on the molecular structure of coordination of the O atom to the N atom in pyridine. As crystals of the anhydride of 4-dimethylaminopyridine *N*-oxide could not be obtained, the structure of its dihydrate was determined by X-ray crystal analysis.

Experimental. Prismatic colorless crystals grown from acetonitrile solution. Crystal of dimensions 0·5 ×

0·6 × 0·7 mm used, Rigaku AFC-5 diffractometer, graphite-monochromatized Mo $K\alpha$. Cell dimensions from 2θ angles for 25 reflections $(20 < 2\theta < 22°)$. Intensities measured up to $2\theta = 55°$ in $h - 10/10$, $k\,0/21$ and $l - 8/0$. Three standard reflections monitored every 100 measurements ($\pm1\%$ variation). 2095 unique reflections measured, 1898 intensities observed $[|F_o| > \sigma(F_o)]$, no absorption corrections. Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located on a difference density map. Positional parameters of all atoms and anisotropic thermal parameters of non-H atoms refined by block-diagonal least squares. Temperature factor of each H atom equal to B_{eq} of the bonded atom. $\sum(w|\varDelta F|^2)$ minimized, $w = [\sigma^2(F_o) + 0\cdot00150|F_o|^2]^{-1}$ for $w^{1/2}|F_c| \geq 1$ and $w^{1/2}|\varDelta F| < 3$, $w = 0$ otherwise (155 reflections). Final $R = 0\cdot052$, $wR = 0\cdot055$, $S = 1\cdot2081$. No significant peaks in final difference map, highest peak $0\cdot3$ e Å^{-3}. Max. $\varDelta/\sigma$ in final cycle $0\cdot3$. Atomic scattering factors calculated by $\sum[a_i\exp(-b_i\lambda^{-2}\sin^2\theta)] + c$ $(i = 1,...,4)$ (*International Tables for X-ray Crystallography*, 1974). Calculations performed on FACOM M 340R computer at Shionogi Research Laboratories.

Discussion. Atomic coordinates and equivalent isotropic temperature factors of non-H atoms are listed in Table 1. Bond lengths and angles are given in Table 2.* A perspective view of the molecule with the atom-labeling system and a stereoview of the crystal packing drawn using the program *PLUTO* (Motherwell & Clegg, 1978) are presented in Figs. 1 and 2, respectively.

The pyridine ring is completely planar, and the O atom in the *N*-oxide group is just on the plane. Displacements of atoms in the dimethylamino group from the plane are $0\cdot010$ (2) for N(7), $0\cdot036$ (2) for C(8) and $-0\cdot010$ (2) Å for C(9). Torsion angles C(3)–C(4)–N(7)–C(9) $= -1\cdot3$ (3) and C(5)–C(4)–N(7)–C(8) $= -0\cdot7$ (3)° show about 1° rotation of the dimethylamino group around the bond C(4)–N(7). The planarity of the dimethylamino group is conveniently defined with φ presented by Christen, Norbury, Lister & Palmieri (1975), where φ is the angle between the bisector of the angle C(8)–N(7)–C(9) and the extension of the bond C(4)–N(7). The value of φ is $0\cdot3°$; the conformation of the dimethylamino group is completely planar. The bond length of C(4)–N(7) is $0\cdot016$ Å shorter than that of $1\cdot367$ Å in 4-dimethylaminopyridine with a φ value of $5\cdot5°$. Therefore, the degree of conjugation between the dimethylamino group and the

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* Lists of structure factors, anisotropic temperature factors of the non-H atoms and atomic coordinates of the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44542 (16 pp.). Copies may be obtained through The Executive Secretary, Internationl Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	B_{eq}
N(1)	0·8480 (1)	0·3397 (1)	0·1093 (1)	3·07 (2)
C(2)	1·0059 (1)	0·3627 (1)	0·1583 (1)	3·18 (2)
C(3)	1·1305 (1)	0·3069 (1)	0·1949 (1)	3·10 (2)
C(4)	1·0969 (1)	0·2221 (1)	0·1836 (1)	2·90 (2)
C(5)	0·9293 (1)	0·2005 (1)	0·1320 (1)	3·22 (2)
C(6)	0·8113 (1)	0·2593 (1)	0·0962 (1)	3·38 (2)
N(7)	1·2163 (1)	0·1649 (1)	0·2205 (1)	4·35 (2)
C(8)	1·1776 (2)	0·0788 (1)	0·2110 (2)	6·06 (4)
C(9)	1·3875 (2)	0·1869 (1)	0·2704 (3)	6·57 (4)
O(10)	0·7278 (1)	0·3959 (1)	0·0735 (1)	4·51 (2)
O(11)	0·7086 (1)	0·4794 (1)	−0·2783 (1)	4·94 (2)
O(12)	0·5425 (1)	0·3987 (1)	0·3539 (1)	4·89 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

N(1)–C(2)	1·344 (2)	C(4)–C(5)	1·415 (2)
N(1)–C(6)	1·346 (2)	C(4)–N(7)	1·351 (2)
N(1)–O(10)	1·344 (1)	C(5)–C(6)	1·361 (2)
C(2)–C(3)	1·366 (2)	N(7)–C(8)	1·440 (2)
C(3)–C(4)	1·411 (2)	N(7)–C(9)	1·445 (3)

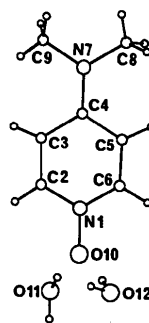| C(2)–N(1)–C(6)	119·1 (1)	C(5)–C(4)–N(7)	121·9 (2)
C(2)–N(1)–O(10)	120·8 (1)	C(4)–C(5)–C(6)	120·7 (2)
C(6)–N(1)–O(10)	120·1 (1)	N(1)–C(6)–C(5)	122·0 (1)
N(1)–C(2)–C(3)	122·0 (1)	C(4)–N(7)–C(8)	121·0 (2)
C(2)–C(3)–C(4)	120·6 (2)	C(4)–N(7)–C(9)	121·9 (2)
C(3)–C(4)–C(5)	115·7 (1)	C(8)–N(7)–C(9)	117·1 (2)
C(3)–C(4)–N(7)	122·5 (2)		

Fig. 1. Perspective view with the atom-labeling system for 4-dimethylaminopyridine *N*-oxide dihydrate.
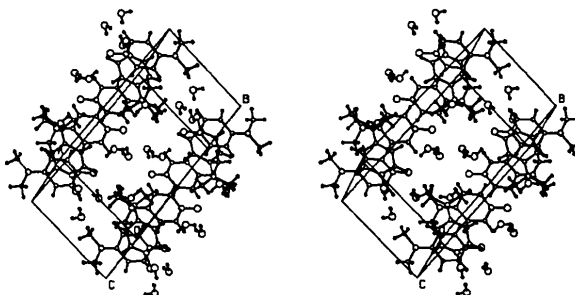

Fig. 2. A stereoview of the unit-cell packing.

pyridine ring is higher than in 4-dimethylamino-pyridine. This suggests that the higher conjugation arises from introduction of the N-oxide group.

The N—O bond distance is considerably longer than the mean of 1·293 Å in free N-oxide groups and is nearly equal to 1·35 Å in strongly hydrogen-bonded N-oxide groups (Eichhorn, 1987). Thus, the long N—O bond length arises from hydrogen bonds with two water molecules which are placed above and below the molecular plane, respectively.

The crystal structure is composed of networks of hydrogen bonds. The hexagonal ring, O(10)—O(11)—O(12′)—O(10′)—O(11′)—O(12)—O(10), in which the primed atoms are related to the corresponding un-primed ones by the operation $(1 - x, 1 - y, -z)$, is formed by hydrogen bonds. The interatomic distances are O(10)···H(O11) = 1·89 (2) [O···O 2·740 (2)], O(10)···H(O12) = 1·89 (2) [2·731 (2)] and O(12)···H′(O11′) = 2·06 (2) Å [2·858 (2) Å]. Each hexagonal ring is linked to adjacent ones along the c axis by the hydrogen bonds between the water molecules, O(11)···H′(O12) $(x,y,z-1) = 2·19$ (2) Å [O···O 2·903 (2) Å].

References

CHAO, M. & SCHEMPP, E. (1977). Acta Cryst. B33, 1557–1564.
CHAO, M., SCHEMPP, E. & ROSENSTEIN, R. D. (1977). Acta Cryst. B33, 1820–1823.
CHRISTEN, D., NORBURY, D., LISTER, D. G. & PALMIERI, P. (1975). J. Chem. Soc. Faraday Trans. 2, 71, 438–446.
EICHHORN, K. (1987). Acta Cryst. B43, 111–112.
International Tables for X-ray Crystallography. (1974). Vol. IV. Birmingham: Kynoch Press. (Present Distributor D. Reidel, Dordrecht.)
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England. and Louvain, Belgium.
MOTHERWELL, W. D. S. & CLEGG, W. (1978). PLUTO. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
OHMS, U. & GUTH, H. (1984). Z. Kristallogr. 166, 213–217.

Structure of 1-(2-Carbamoylethyl)thymine

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Abstract. $C_8H_{11}N_3O_3$, $M_r = 197·20$, monoclinic, $P2_1/n$, $a = 15·537$ (2), $b = 15·845$ (2), $c = 7·446$ (1) Å, $\beta = 96·50$ (1)°, $V = 1821·3$ (4) Å³, $Z = 8$, $D_m = 1·439$, $D_x = 1·438$ g cm⁻³, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1·21$ cm⁻¹, $F(000) = 832$, $T = 293$ K, $R = 0·064$ for 1389 observed reflexions $(F_o \geq 3\sigma)$. Two independent molecules, A and B, are related by pseudo-centrosymmetry and are linked together by two N(amide)—H···O(2) hydrogen bonds. N(3) of the B molecule is also hydrogen-bonded to O(amide) of the A molecule. The thymine moieties of A related by the crystallographic inversion form a pair through N(3)—H···O(4) hydrogen bonds.

Introduction. As part of serial studies on elementary patterns in protein–nucleic acid interactions, we have been engaged in analysing model crystals that contain the side groups of amino acids and nucleotide bases (e.g. Takenaka & Sasada, 1985). The present paper deals with the interaction between thymine and the carbamoyl group.

Experimental. 1-(2-Carboxyethyl)thymine, synthesized from thymine and β-propiolactone according to Kondo, Sato & Takemoto (1973), was purified by ion-exchange column chromatography (Diaion SA10, CH_3COO^- type). Esterification of 1-(2-carboxyethyl)thymine with HCl-saturated methanol and then ammonolysis with NH_3-saturated methanol gave the carbamoylethyl derivative. The products were purified on an ion-exchange column. Colourless rod-like crystals obtained from methanol solution, space group from Weissenberg photographs; systematic absences $h + l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$. Crystal size 0·25 × 0·1 × 0·1 mm, Rigaku four-circle diffractometer, graphite-monochromated Mo $K\alpha$. Unit-cell dimensions from 52 reflexions with $10 < 2\theta < 37°$. Intensities by ω scan, scan width 1·3° (ω), scan rate 4° min⁻¹. Five reference reflexions monitored every 50 reflexions showed no significant intensity deterioration. Out of 3319 independent reflexions, 1930 with $F_o < 3\sigma$ considered unobserved; $2\theta_{max} = 41°$, h −15→15, k 0→15, l 0→7. Correction for Lorentz and polarization factors but not for absorption effects. $\sigma^2(F_o) = \sigma_p^2(F_o) + qF_o^2$ where σ_p evaluated by counting statistics and q (=0·001) from measurement of monitored reflexions (McCandlish & Stout, 1975). Structure solved by direct methods, refined by block-matrix least squares; all H atoms found on a difference map refined isotropically; $\sum w(|F_o| - |F_c|)^2$