

The mean distances within the trimethoxyphenyl moieties are C—C = 1.389 [1.384] Å and the average values within the three methoxy groups are C—O = 1.374 [1.372] Å and O—CH<sub>3</sub> = 1.429 [1.446] Å, respectively.

**Crystal packing.** The packing scheme of the crystal structure is shown in Fig. 3, viewed along the crystallographic *c* axis. The piperazine and trimethoxyphenyl rings are mainly oriented parallel to the coordinate planes of the unit cell. The predominant stabilizing forces between adjacent molecules are likely to be of van der Waals character, but from the molecular packing a conceivable weak  $\pi$ -electron overlap between adjacent trimethoxyphenyl moieties is also expected. A detailed scheme involving distances less than 3.5 Å is found in Table 2. Only a few possible weak hydrogen bonds are found, involving three C atoms of the piperazine ring loosely bonded to three O atoms of a neighbouring trimethoxyphenyl moiety attached to N(1). No hydrogen bonding or short interaction is found which includes the O atoms of the other pseudo-related trimethoxyphenyl moiety. The side chain is stabilized by a short interaction between C(21) and the carbonyl O(41) in an adjacent molecule.

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## Structure of Methyl 1,3-Dihydro-4-methyl-3-oxofuro[3,4-*b*]pyridin-1-ylacetate

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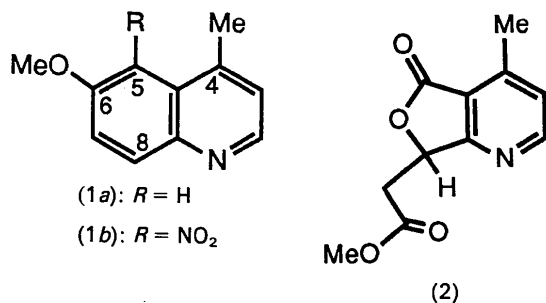
**Abstract.** C<sub>11</sub>H<sub>11</sub>NO<sub>4</sub>, *M<sub>r</sub>* = 221, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 10.28 (1), *b* = 15.45 (3), *c* = 6.752 (2) Å,  $\beta$  = 95.88 (6)°, *V* = 1066 (4) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.378 g cm<sup>-3</sup>,  $\lambda$ (Cu *K* $\alpha$ ) = 1.54178 Å,  $\mu$  =

8.52 cm<sup>-1</sup>, *F*(000) = 464, *T* = 298 K, *R* = 0.056 for 1008 observed reflexions. The bicyclic ring system of the title lactone (2) is essentially flat, the nine atoms of the ring system, together with substituent methyl C and carbonyl O atoms, lying within 0.047 Å of their least-squares best plane. The C and O atoms of

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the acetic ester substituent comprise a second plane forming a dihedral angle of 100.5° to the bicyclic ring. The structure of this bicyclic lactone (2) (an azaphthalide) shows that treatment of 6-methoxy-4-methyl-5-nitroquinoline with fuming nitric acid at 298 K effects a novel oxidative cleavage of a benzene ring.

**Introduction.** In acid solution quinolines typically undergo electrophilic substitution *via* the quinolinium cation (Austin & Ridd, 1963; Moodie, Schofield & Williamson, 1963); nitration of quinoline itself occurs at C5 and C8 in a ratio of 52:48 (Dewar & Maitlis, 1957). With 6-methoxy-4-methylquinoline (Campbell & Schaffner, 1945) (1a) as starting material and requiring from it an intermediate with a nitrogen substituent at C5, we predicted that the intrinsic quinoline 5 = 8 positional electrophilic substitution tendency would be modified, in the desired sense, by the presence of the 6-methoxy group, though it would be expected that the *peri* methyl group at C4 would work against the synthetic goal. In the event, nitration at 233 K did indeed lead cleanly to the desired 5-nitro derivative (1b). In the process of evolving these suitable conditions, the nitroquinoline (1b) was treated with fuming nitric acid at 298 K for 3 days. From this experiment there was isolated a product having three additional O atoms, crystallographic analysis of which showed it to be the azaphthalide (2).



**Experimental.** Reaction of 6-methoxy-4-methylquinoline (1a) with fuming nitric acid at 233 K for 75 min gave a mononitro derivative (91%), m.p. 387–389 K, which was proved to be the 5-monosubstitution product (1b), by the presence of *ortho*-coupled signals for the 7 and 8 protons in its <sup>1</sup>H NMR spectrum. Exposure of this quinoline (1b) to fuming nitric acid at 298 K for 72 h led to the isolation (20%) of lactone (2).

A sample of (2), m.p. 404–405 K, suitable for crystallography was obtained by recrystallization from methanol/water as transparent plates. A crystal of approximate size 0.010 × 0.250 × 0.300 mm was mounted on a glass fibre and used for data collection on a Rigaku AFC5R diffractometer with graphite-

Table 1. *Positional and thermal parameters for lactone (2) with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_j$$

	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
O5'	0.4023 (3)	-0.0216 (2)	0.7036 (4)	5.0 (1)
O6	0.6154 (2)	-0.0237 (2)	0.8054 (4)	4.7 (1)
O11	0.8945 (4)	-0.1026 (3)	0.9388 (5)	8.4 (2)
O12	0.9623 (3)	-0.0921 (2)	0.6402 (5)	6.3 (2)
N1'	0.7160 (3)	0.1993 (3)	0.8480 (5)	4.4 (2)
C1	0.8988 (4)	-0.0645 (3)	0.7838 (7)	5.2 (2)
C2	0.8312 (5)	0.0206 (3)	0.7368 (7)	4.9 (2)
C2'	0.6357 (4)	0.2671 (3)	0.8127 (6)	4.4 (2)
C3	1.0285 (7)	-0.1741 (5)	0.673 (1)	7.2 (4)
C3'	0.5030 (4)	0.2605 (3)	0.7561 (5)	4.0 (2)
C4	0.2997 (5)	0.1740 (5)	0.665 (1)	6.1 (3)
C4'	0.4419 (3)	0.1817 (3)	0.7301 (5)	3.6 (2)
C4'A	0.5245 (3)	0.1113 (3)	0.7651 (5)	3.4 (2)
C5'	0.5008 (4)	0.0190 (3)	0.7508 (6)	3.9 (2)
C7'	0.7215 (4)	0.0378 (3)	0.8589 (6)	4.5 (2)
C7'A	0.6558 (3)	0.1238 (3)	0.8242 (5)	3.7 (2)
H2'	0.677 (3)	0.323 (3)	0.839 (5)	3.9 (9)
H3'	0.459 (3)	0.310 (3)	0.740 (5)	3.5 (9)
H7'	0.755 (3)	0.028 (2)	1.008 (5)	3.4 (7)
H21	0.794 (4)	0.023 (3)	0.595 (6)	6 (1)
H22	0.896 (5)	0.073 (3)	0.753 (6)	8 (1)
H31	0.958 (6)	-0.223 (4)	0.693 (8)	11 (2)
H32	1.059 (7)	-0.181 (5)	0.57 (1)	13 (3)
H33	1.095 (5)	-0.161 (3)	0.780 (8)	8 (2)
H41	0.254 (6)	0.235 (4)	0.640 (7)	10 (2)
H42	0.261 (5)	0.145 (3)	0.727 (7)	6 (2)
H43	0.282 (6)	0.130 (4)	0.571 (9)	11 (2)

monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) and a 12 kW rotating-anode generator. Cell constants and an orientation matrix were determined by least-squares refinement using the setting angles of eight carefully centred reflexions in the range 50.44 < 2 $\theta$  < 58.17°. Data were collected at 298 (1) K using the  $\omega/2\theta$  scan technique to a maximum 2 $\theta$  value of 120.1°.  $\omega$  scans of several intense reflexions, made prior to data collection, had an average width at half height of 0.39° with a take-off angle of 6.0°. Scans of (1.52 + 0.30tan $\theta$ )° were made at speed of 8.0° min<sup>-1</sup> (in  $\omega$ ). The weak reflexions [ $I < 10.0\sigma(I)$ ] were rescanned and the counts accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflexion. The ratio of peak counting time to background counting time was 2. The diameter of the incident beam collimator was 0.5 mm and the crystal was 400.0 mm from the detector. Of the 1512 reflexions, 1406 were unique ( $R_{\text{int}} = 0.037$ ). Intensities of three representative reflexions, measured after every 150 reflexions, declined by -1.70%, so a linear correction factor was applied. The maximum absorption correction applied was 9.1%, the minimum 0.0%, with an average of 2.7%. Except for 38 reflections which were measured as - $h$ , - $k$ , - $l$  because of instrumental blind regions, the range of  $hkl$  was:  $h - 11$  to 11,  $k 0$  to 13 and  $l 0$  to 7.

All calculations were performed using the TEXSAN crystallographic software package (Molecular Structure Corporation, 1985). The structure

was solved by direct methods (Gilmore, 1984; Beurskens, 1984). Non-H atoms were refined anisotropically. H-atom positions were calculated and then refined. The final cycle of full-matrix least-squares refinement was based on 1008 observed reflexions [ $I > 3.00\sigma(I)$ ] and 189 variable parameters and converged (largest parameter shift was  $< 0.01$  times its e.s.d.) with unweighted and weighted factors of  $R = 0.056$ ,  $wR = 0.068$ .

The standard deviation,  $S$ , of an observation of unit weight was 2.81. The weighting scheme was based on counting statistics. Plots of  $\sum w(|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflexion order in data collection,  $\sin\theta/\lambda$ , and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and  $-0.16 \text{ e } \text{\AA}^{-3}$ , respectively.

Anomalous-dispersion effects were included in  $F_{\text{calc}}$ ; the values of  $\Delta f'$  and  $\Delta f''$  were from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1).

**Discussion.** The atomic parameters for methyl 1,3-dihydro-4-methyl-3-oxofuro[3,4-*b*]pyridin-1-ylacetate (2) are listed in Table 1; \* Fig. 1 shows a *PLUTO*

\* Lists of structure factors, anisotropic thermal parameters, full lists of bond lengths and angles, least-squares-planes data, and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53723 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

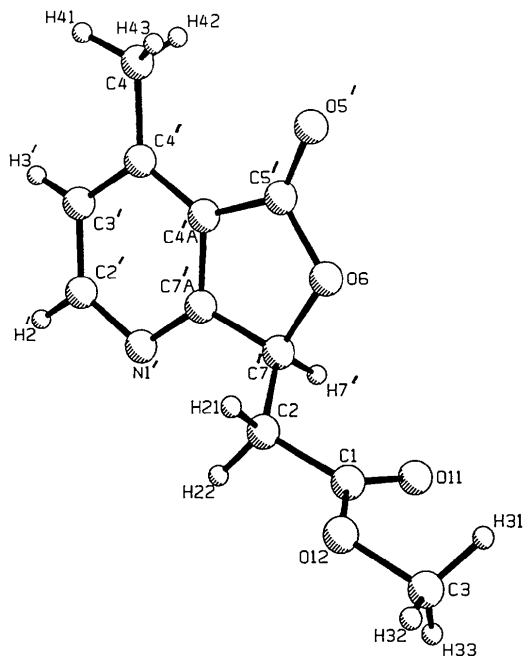
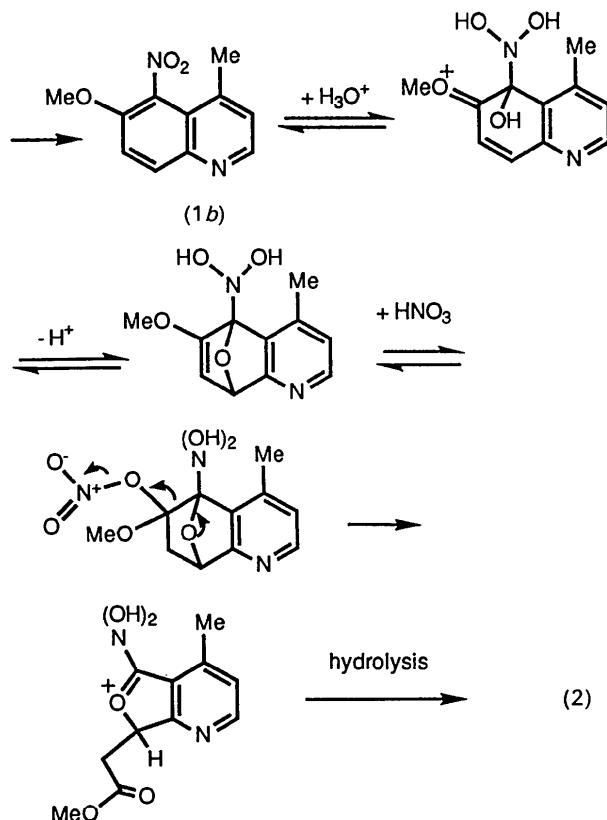


Fig. 1. *PLUTO* drawing of lactone (2), showing the numbering scheme used in Table 1.

(Motherwell & Clegg, 1978) drawing of the molecule and the numbering system used in Table 1. The furo[3,4-*b*]pyridine nucleus is essentially planar, each of the nine ring atoms together with substituent methyl carbon and carbonyl O atoms being within 0.0006–0.05 Å from their least-squares best plane. The C and O atoms of the acetic ester substituent comprise a second plane which forms a dihedral angle of  $100.5^\circ$  to the bicyclic ring.

The oxidative degradation of the benzene ring of quinoline, producing pyridine-2,3-dicarboxylic acid and from this, by decarboxylation, nicotinic acid, is well known (Hoogerwerff & van Dorp, 1880; Cochran & Little, 1961). There is also an isolated report of the isolation of 3-(3-carboxypyridin-2-yl)acrylic acid from an electrolytic oxidation (Yokoyama & Yamamoto, 1943); however, the present report seems to be the first to record a chemical quinoline–benzene ring cleavage with retention of all C atoms. One may rationalize the transformation in a number of reasonable ways, one of which is shown below.



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## Structure of 3,*N*<sup>4</sup>-Ethenocytidinium Dihydrogenphosphate

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**Abstract.** 5-Oxo-6-β-D-ribofuranosyl-1*H*<sup>+</sup>-imidazol[1,2-*c*]pyrimidinium dihydrogenphosphate, C<sub>11</sub>H<sub>14</sub>N<sub>3</sub>O<sub>5</sub><sup>+</sup>·H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, *M<sub>r</sub>* = 365.2, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 6.767 (2), *b* = 13.770 (3), *c* = 16.093 (3) Å, *V* = 1499.7 (6) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.62 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 2.3 cm<sup>-1</sup>, *F*(000) = 760, *T* = 291 K, *R* = 0.052 for 991 observed reflections. The ribose conformation is characterized by *P* = 164.5 (6)° (<sup>2</sup>*E*) and τ<sub>*m*</sub> = 38.2 (4)°. The glycoside torsion angle [O(4')—C(1')—N(1)—C(2)—128.0 (7)°] is in the *anti* region and the side chain has the preferred *gauche*<sup>+</sup> conformation [γ = 55 (1)°]. The H<sub>2</sub>PO<sub>4</sub><sup>-</sup> groups are arranged in a helical pattern in which a single O atom of each anion accepts two strong hydrogen bonds from two different OH donors of the neighboring H<sub>2</sub>PO<sub>4</sub><sup>-</sup> units. The fourth O atom of the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> anion is an acceptor of hydrogen bonds from both the protonation site [N(4)H<sup>+</sup>] and the ribose of the cation. The cations are also linked directly, *via* an O(3')H⋯O(5') hydrogen bond.

**Introduction.** This work continues a series of structural studies of phosphate salts of nucleosides in which the two main components of the nucleotide coexist as separate ions in the crystal. The first report in this series (cytidinium dihydrogenphosphate, CydH<sup>+</sup>·H<sub>2</sub>PO<sub>4</sub><sup>-</sup>; Jaskólski, 1989) revealed a pattern of infinite ⋯phosphate⋯sugar⋯ chains in which the

dihydrogenphosphate anions are hydrogen bonded, *via* their POH donors, to O(3') and O(5') of neighboring nucleosides. One interesting aspect of the hydrogen bonds along these chains is that they mimic the O(3')—P—O(5') ester bonds in the backbone of a real polynucleotide. Secondly, as the chains do not involve the ribose O(2')H function, an identical pattern of nucleoside⋯phosphate association could be maintained in the crystals of 2'-deoxycytidinium dihydrogenphosphate (Jaskólski, 1991). In the present paper, which describes the structure of 3,*N*<sup>4</sup>-ethenocytidinium dihydrogenphosphate, our aim is to verify the conclusion drawn from the previous structures that the driving force determining the packing mode in nucleoside phosphates is the phosphate anion. Additionally, the ethenocytidine system (*ε*Cyd) is an interesting subject for study in itself. This derivative of cytidine was first introduced by Barrio, Sotssangi, Gruber, Damman & Leonard (1976) as a useful fluorescent anchor in the studies of nucleic acids. To date, the structure of *ε*Cyd has been described in the neutral form (Jaskólski, Krzyżosiak, Sierzputowska-Gracz & Wiewiórowski, 1981) and in the *N*<sup>4</sup>-protonated form as *ε*CydH<sup>+</sup>·Cl<sup>-</sup> (Wang, Barrio & Paul, 1976). The effects of etheno bridging and protonation in the Cyd/*ε*Cyd system have been analyzed in detail by Jaskólski *et al.* (1981), Krzyżosiak, Jaskólski, Sierzputowska-Gracz & Wiewiórowski (1982) and Kozerski, Sierzputowska-Gracz, Krzyżosiak, Bratek-Wiewiórowska, Jaskólski & Wiewiórowski (1984).

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