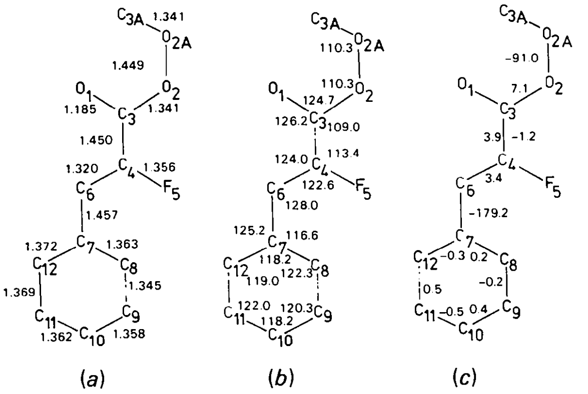

Fig. 3. (*a*) Bond lengths (Å), (*b*) bond angles (°), and (*c*) torsion angles (°) for (1). Torsion angles not shown are: 1—3—4—5, −176·6; 2—3—4—6, 179·3; 2*A*—2—3—4, −168·3; 3—4—6—7, −177·1; 4—6—7—12, 1·3; 6—7—8—9, −179·4; 6—7—12—11, 179·2°. E.s.d.'s are 0·011 Å for bond lengths, 0·7° for bond angles and somewhat larger for torsion angles (excluding H).

In all respects the molecular geometry is closely similar to that reported for *trans*-cinnamoyl peroxide (Bethell, Chadwick, Harding & Maling, 1984). Thus the two α-fluorocinnamoyl groups adopt the *s-cis* conformation and lie in orthogonal planes (torsion angle about the O—O bond, 91·0°) connected through a peroxide bond of length 1·449 (7) Å, somewhat longer than for *trans*-cinnamoyl peroxide, but close to the average of values from diacyl peroxide structures (almost all substituted dibenzoyl peroxides) in the Cambridge Crystallographic Data Base ($R \leq 0{\cdot}14$). The carbonyl bond length of 1·185 (11) Å is again shorter than in unconjugated acyloxy groups, but almost identical with the average in published diacyl peroxide structures, confirming the view that the carbonyl group is affected most by being attached to the peroxide bond, and little by its coplanarity with the conjugated styryl moiety. The presence of the F atom has little discernible effect on the C=C bond length and the C—F bond is almost identical in length to corresponding bonds in two aryl-substituted perfluoro-olefins (Yurchenko, Antipin, Struchkov & Yagupolski, 1978).

The title compound and *trans*-cinnamoyl peroxide show closely similar kinetic behaviour (thermolysis rates and of activation parameters in hexachloroacetone solution); the fluoro-substituted compound reacts some 30% faster than the unsubstituted peroxide at 373·2 K. It seems surprising that the presence of the highly electronegative F atom in the molecule has such a small effect on both the structural and kinetic characteristics. The present structure provides no clue to the origin of 3-fluorocoumarin in the thermolysis products.

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Structure of 4-Oxopyrido[1,2-*a*]pyrimidin-1-ium-2-olate, $C_8H_6N_2O_2$

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Abstract. $M_r = 162{\cdot}15$, monoclinic, $P2_1/c$, $a = 8{\cdot}358$ (2), $b = 5{\cdot}432$ (1), $c = 15{\cdot}153$ (3) Å, $\beta = 94{\cdot}11$ (2)°, $V = 686{\cdot}2$ (6) Å^3, $Z = 4$, $D_m = 1{\cdot}57$ (1), $D_x = 1{\cdot}569$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}109$ mm^{-1}, $T = 295$ K, $F(000) = 336$, $R = 0{\cdot}040$ for 1991 observed unique reflections. Different tautomeric forms of the title compound (alias malonyl-α-aminopyridine) have been suggested since 1924. In

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the solid state the molecules exist in a tautomeric form with the 'acidic' H atom bonded to N in an $=\overset{+}{N}H-C\overset{-}{O}=$ arrangement. Pairs of hydrogen bonds grouped around centres of symmetry stabilize the crystal structure.

Introduction. The structure determination of the title compound is part of an investigation of structural changes associated with the introduction of the nitro group. This structure determination was thus performed to make a comparison with the structure of 3-nitro-4-oxopyrido[1,2-*a*]pyrimidin-1-ium-2-olate which is presently being studied.

Experimental. Title compound prepared as described by Tschitschibabin (1924). Yellow-brown plate-shaped crystals elongated in the **b** direction were obtained from the slow cooling of a solution in boiling water. Crystal 0·3 x 0·3 x 0·2 mm. Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$. Lattice parameters from a Guinier–Hägg photograph with Cu $K\alpha_1$ ($\lambda = 1{\cdot}54051$ Å) and Si as an internal standard. 1991 unique reflections $+h$, $+k$, $\pm l$, with $2{\cdot}0 < \theta < 30{\cdot}0°$, 1568 with $I > 2{\cdot}5\sigma(I)$; mixed $\omega/2\theta$ scan technique, scan angle = 1·00° + 0·35° tanθ. Standard reflections $1\bar{1}6$ and 125 used for orientation control every 100 reflections, and $21\bar{6}$ for intensity check every 10800 s of exposure time: standard intensity variations <1·7% from mean value. Systematic absences $h0l$ with l odd and $0k0$ with k odd. Lp correction. Absorption ignored. Direct methods. Anisotropic full-matrix least-squares refinement of non-H atoms. Positional H parameters from a difference density map (remaining peak heights less than half those associated with H atoms); refinements of H(x,y,z) with $\sin\theta/\lambda < 0{\cdot}40$ Å^{-1}; fixed isotropic H temperature factor. $\sum w(\Delta|F|)^2$ minimized; final $R = 0{\cdot}040$ and $wR = 0{\cdot}061$;* weights $w = 1/\{1+[(F_o-6{\cdot}0)/12{\cdot}0]^2\}$ gave average $w\Delta(|F|)^2$ almost independent of $|F_o|$; $S = 2{\cdot}73$. $(\Delta/\sigma)_{\max}$ 1·98 for anisotropic thermal parameters and 0·93 for position parameters. No correction for secondary extinction. Scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs from *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. The positional and thermal parameters are given in Table 1. Dvortsák, Resofszki, Huhn, Zalántai & Kiss (1976) have given the formulae of five tautomeric forms which have been suggested for the title compound (Fig. 1). They conclude from IR, NMR and UV spectroscopy that the compound exists as form (IV) in the solid state and in solution with a pH value below 7·5. The present investigation fully confirms formula (IV) for the solid state. The bonds N(1)—C(10)

Table 1. *Fractional coordinates* (×10^4) *and equivalent isotropic thermal parameters of non*-H *atoms with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}(Å^2)
O(2)	9410 (1)	4174 (2)	1045·5 (7)	2·80 (7)
O(4)	5858 (2)	−2564 (2)	721·5 (7)	3·03 (8)
N(1)	8762 (1)	2436 (2)	9708·7 (7)	2·12 (7)
N(5)	7078 (1)	−979 (2)	9523·5 (7)	1·91 (7)
C(2)	8632 (2)	2540 (3)	620·6 (8)	2·05 (8)
C(3)	7643 (2)	779 (3)	978·0 (9)	2·34 (8)
C(4)	6797 (2)	−1002 (3)	482·1 (9)	2·12 (8)
C(6)	6300 (2)	−2721 (3)	8993 (1)	2·38 (9)
C(7)	6460 (2)	−2738 (3)	8107 (1)	2·8 (1)
C(8)	7437 (2)	−971 (3)	7731·0 (9)	2·8 (1)
C(9)	8215 (2)	749 (3)	8258·3 (9)	2·46 (9)
C(10)	8019 (2)	749 (2)	9175·1 (8)	1·88 (7)

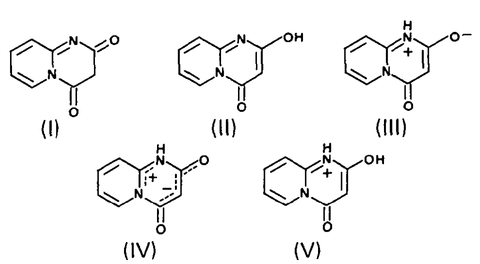

Fig. 1. Tautomeric forms suggested for the title compound, given in a review by Dvortsák, Resofszki, Huhn, Zalántai & Kiss (1976): (I) Tschitschibabin (1924); (II) Snyder & Robinson (1952); (III) and (IV) Katritzky & Waring (1962); (IV) Dvortsák *et al.* (1976); (V) (strongly acidic solution) Urban, Grosjean & Arnold (1970) and Dvortsák *et al.* (1976).

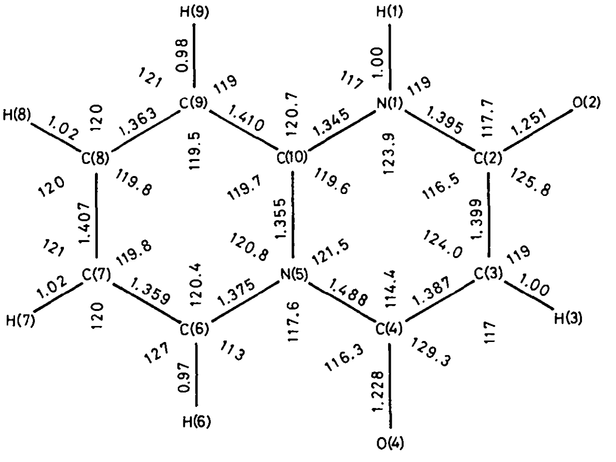

Fig. 2. Bond distances (Å), angles (°), and the atom-numbering scheme. The estimated standard deviations are 0·002 Å and 0·1° when no H atoms are involved, else 0·03 Å and 2°.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39852 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

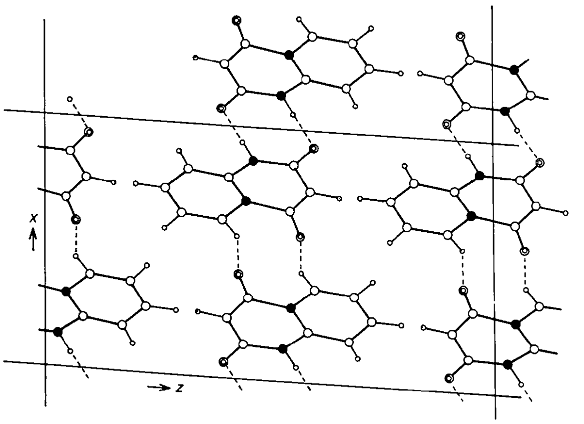

Fig. 3. Projection of the crystal structure down the *b* axis. Black circles: N atoms, double circles: O atoms. The dotted lines represent the hydrogen-bonding system.

1·345 (2) and N(5)—C(10) 1·355 (2) Å (Fig. 2) have values characteristic of C—N partial double bonds. *International Tables for X-ray Crystallography* (1962) gives 1·352 (5) Å for such bonds. There is a significant difference between the bonds C(2)—O(2) 1·251 (2) and C(4)—O(4) 1·228 (2) Å; this may be because O(2) and O(4) are involved in a strong and a weak intermolecular hydrogen bond, respectively.

The crystal structure is stabilized by pairs of hydrogen bonds grouped around centres of symmetry (Fig. 3). Two types of hydrogen bonds occur: strong linear N(1)—H(1)···O(2) bonds and weak bent C(6)—H(1)···O(4) bonds; the former agrees well with the observation that strong N—H···O hydrogen bonds prefer a linear or nearly linear arrangement (Taylor, Kennard & Versichel, 1984). The hydrogen-bond dimensions are: N(1)—H(1) 1·00 (3), H(1)···O(2) 1·70 (3), N(1)···O(2) 2·698 (2) Å, N(1)—H(1)···O(2) 179 (3)°; and C(6)—H(6) 0·97 (3), H(6)···O(4) 2·33 (3), C(6)···O(4) 3·180 (2) Å, C(6)—H(6)···O(4) 146 (3)°.

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3-Ethoxy-5,6,7,8-tetrahydro-1-hydroxyisoquinoline-4-carbonitrile, $C_{12}H_{14}N_2O_2$

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Abstract. $M_r = 218{\cdot}25$, monoclinic, $P2_1/n$, $a = 20{\cdot}000\,(2)$, $b = 6{\cdot}219\,(1)$, $c = 8{\cdot}794\,(1)$ Å, $\beta = 94{\cdot}31\,(2)°$, $V = 1090{\cdot}7\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}33$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}86$ cm^{-1}, $F(000) = 464$, $T = 298$ K. Final $R = 0{\cdot}056$ for 1369 observed reflections. The pyridine ring is planar; two