

5-acetoxy-6-methoxy-8-nitroquinoline (Sax & Desiderato, 1967) and 6-methoxy-8-nitro-5(1*H*)-quinolone (Sax, Desiderato & Dakin, 1969).

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Structure of Ethyl 5-Formyl-4-hydroxy-6-phenylpyridine-2-carboxylate

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Abstract. C₁₅H₁₃NO₄, $M_r = 271.3$, monoclinic, $P2_1/c$, $a = 8.320$ (3), $b = 7.597$ (3), $c = 20.96$ (2) Å, $\beta = 93.69$ (4)°, $V = 1322$ (1) Å³, $Z = 4$, $D_x = 1.36$ Mg m⁻³, Mo $K\alpha$ radiation (graphite-crystal monochromator), $\lambda = 0.71073$ Å, $\mu = 0.93$ cm⁻¹, $F(000) = 568$, $T = 293$ K, final conventional $R = 0.056$ for 931 'observed' reflections and 152 variables. The structure determination showed a planar central nucleus for the molecule with an intramolecular hydrogen bond between the hydroxy and formyl groups. The angle between the least-squares planes through the pyridine and phenyl rings is 133.0 (1)° while the angle between the pyridine ring and ethoxycarbonyl group is 169.5 (2)°.

Experimental. A deoxygenated solution of 1-cyclohexyl-8a-ethoxy-4-phenyl-8,8a-dihydrofuro[2,3-*b*][1,4]diazepin-7-one (Barluenga, Tomás, Ballesteros, Kong, García-Granda & Pérez-Carreño, 1991) (176 mg, 0.5 mmol) in toluene (5 ml) was heated in a sealed tube at 393 K for 8 h. After cooling to room temperature, toluene was removed at reduced pressure and the resulting crude mixture chromatographed on silica gel, using hexane–ethyl acetate (2/1) to furnish 3-(*N*-cyclohexyl)aminocarbonyl-6-ethoxycarbonyl-4-hydroxy-2-phenylpyridine. Then a solution of this compound in THF (20 ml) was stirred with 1M HCl (2 ml) at room temperature for 3 h; then H₂O (10 ml) was added and the resulting mixture extracted with CH₂Cl₂ (3 × 15 ml) and dried (Na₂SO₄). Removal of the solvents at reduced pressure gave the title compound (115 mg; overall yield from first reaction: 85%); recrystallization from hexane–diethyl ether gave light yellow crystals (m.p. 392–394 K). A crystal of size 0.26 × 0.20 × 0.07 mm was selected for X-ray diffraction, using Mo $K\alpha$ radiation, a graphite-crystal monochromator and an Enraf–Nonius CAD-4 diffractometer. Unit-cell dimensions were determined from the angular settings of 25 reflections with $6 < \theta < 13^\circ$. The space group was determined to be $P2_1/c$ from systematic absences. 2677 reflections were measured over hkl range 0, 0, -24 to 9, 9, 24, and for $0 < \theta < 25^\circ$, using ω - 2θ scans with a variable scan rate and a maximum scan time of 60 s per reflection. Intensity was checked by monitoring three standard reflections every 60 min. Final drift correction factors were between 0.98 and 1.00. Profile analysis was per-

graphed on silica gel, using hexane–ethyl acetate (2/1) to furnish 3-(*N*-cyclohexyl)aminocarbonyl-6-ethoxycarbonyl-4-hydroxy-2-phenylpyridine. Then a solution of this compound in THF (20 ml) was stirred with 1M HCl (2 ml) at room temperature for 3 h; then H₂O (10 ml) was added and the resulting mixture extracted with CH₂Cl₂ (3 × 15 ml) and dried (Na₂SO₄). Removal of the solvents at reduced pressure gave the title compound (115 mg; overall yield from first reaction: 85%); recrystallization from hexane–diethyl ether gave light yellow crystals (m.p. 392–394 K). A crystal of size 0.26 × 0.20 × 0.07 mm was selected for X-ray diffraction, using Mo $K\alpha$ radiation, a graphite-crystal monochromator and an Enraf–Nonius CAD-4 diffractometer. Unit-cell dimensions were determined from the angular settings of 25 reflections with $6 < \theta < 13^\circ$. The space group was determined to be $P2_1/c$ from systematic absences. 2677 reflections were measured over hkl range 0, 0, -24 to 9, 9, 24, and for $0 < \theta < 25^\circ$, using ω - 2θ scans with a variable scan rate and a maximum scan time of 60 s per reflection. Intensity was checked by monitoring three standard reflections every 60 min. Final drift correction factors were between 0.98 and 1.00. Profile analysis was per-

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formed on all reflections (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction was applied using ψ scans (North, Phillips & Mathews, 1968), $\mu(\text{Mo } K\alpha) = 0.93 \text{ cm}^{-1}$ (correction factors in the range 0.98–1.00). Some doubly measured reflections were averaged, $R_{\text{int}} = \sum(I - \langle I \rangle) / \sum I = 0.037$. 2302 reflections were unique of which 931 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and data reduced to $|F_o|$ values.

The structure was solved by direct methods using the program *SHELXS86* (Sheldrick, 1985). Isotropic least-squares refinement, using a locally modified version of *SHELX76* (Sheldrick, 1976; Van der Maelen Uria, 1991), converged to $R = 0.11$. Further empirical absorption correction (Walker & Stuart, 1983) was applied. Maximum and minimum absorption correction factors were 1.20 and 0.74, respectively. Anisotropic refinements followed by a difference Fourier synthesis allowed the location of most of the H atoms.

Positional parameters and anisotropic thermal parameters of the non-H atoms were refined. All the H atoms were isotropically refined, with a common thermal parameter; H41 was fixed; H131, H132, H133 and H31 were left riding, with constrained distances, on their parent atoms; H121, H122 and H2 were left free and the whole phenyl group was fixed to the idealized one to optimize the reflections/parameters ratio. The final conventional agreement factors were $R = 0.056$ and $wR = 0.061$ for the 931 'observed' reflections and 152 variables. The function minimized was $\sum w(F_o - F_c)^2$, where $w = 1/[\sigma^2(F_o) + 0.00060F_o^2]$ in which $\sigma(F_o)$ was obtained from counting statistics. Maximum shift to e.s.d. ratio in the last full-matrix least-squares cycle was less than 0.004. The final difference Fourier map showed no peaks higher than $0.38 \text{ e } \text{\AA}^{-3}$ nor deeper than $-0.17 \text{ e } \text{\AA}^{-3}$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final positional and thermal parameters are given in Table 1.* Molecular geometry data are collected in Table 2. Fig. 1, showing the atomic numbering scheme, was made with the *PLUTO* program (Motherwell & Clegg, 1976). Geometrical calculations were made with *PARST* (Nardelli, 1983). All calculations were performed on a MicroVAX 3400 computer at the Scientific Computer Centre of the University of Oviedo.

Table 1. Fractional positional parameters and isotropic or equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^2$)

Isotropic thermal parameters, U_{iso} , are given for the phenyl C atoms C51–C56. Remaining anisotropically refined atoms have $U_{\text{eq}} = (1/3)\sum_j \sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
N1	1.1444 (5)	0.0144 (5)	0.2136 (2)	4.5 (2)
C1	1.1995 (6)	0.0041 (7)	0.1545 (3)	4.6 (2)
C11	1.3669 (6)	-0.0691 (7)	0.1544 (3)	5.2 (2)
O11	1.4554 (4)	-0.0946 (6)	0.2012 (2)	7.7 (2)
O12	1.4074 (4)	-0.1068 (5)	0.0948 (2)	6.3 (2)
C12	1.5621 (7)	-0.194 (1)	0.0903 (3)	7.4 (3)
C13	1.5723 (8)	-0.254 (1)	0.0242 (3)	9.9 (3)
C2	1.1127 (6)	0.0499 (7)	0.0986 (3)	5.0 (2)
C3	0.9596 (6)	0.1206 (7)	0.1045 (2)	4.8 (2)
O31	0.8743 (4)	0.1728 (6)	0.0505 (2)	6.9 (2)
C4	0.8979 (5)	0.1385 (6)	0.1649 (2)	4.3 (2)
C41	0.7456 (6)	0.2307 (7)	0.1714 (3)	5.6 (2)
O41	0.6582 (4)	0.2777 (5)	0.1243 (2)	7.1 (2)
C5	0.9943 (4)	0.0761 (5)	0.2181 (1)	4.5 (2)
C51	0.9368 (4)	0.0650 (5)	0.2843 (1)	4.6 (1)
C52	1.0387 (4)	0.1216 (5)	0.3357 (1)	5.1 (1)
C53	0.9901 (4)	0.1074 (5)	0.3980 (1)	6.4 (2)
C54	0.8396 (4)	0.0365 (5)	0.4088 (1)	6.9 (2)
C55	0.7378 (4)	-0.0201 (5)	0.3575 (1)	6.6 (2)
C56	0.7864 (4)	-0.0059 (5)	0.2952 (1)	5.5 (1)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

N1—C1	1.349 (6)	N1—C5	1.343 (5)
C1—C11	1.500 (7)	C11—O12	1.345 (6)
C1—C2	1.381 (6)	C11—O11	1.204 (6)
O12—C12	1.457 (7)	C12—C13	1.466 (8)
C2—C3	1.395 (7)	C4—C41	1.462 (6)
C3—O31	1.355 (5)	C3—C4	1.404 (6)
C4—C5	1.412 (5)	C41—O41	1.239 (6)
C5—C51	1.500 (1)	C52—C53	1.395 (1)
C51—C52	1.395 (1)	C51—C56	1.395 (1)
C53—C54	1.395 (1)	C54—C55	1.395 (1)
C55—C56	1.395 (1)		
C5—N1—C1	117.2 (3)	C11—C1—N1	113.2 (5)
O2—C1—N1	125.0 (5)	C2—C1—C11	121.7 (5)
O11—C11—C1	125.2 (5)	O12—C11—C1	111.6 (5)
O12—C11—O11	123.1 (5)	C12—O12—C11	115.6 (4)
C13—C12—O12	107.9 (5)	C3—C2—C1	116.9 (5)
O31—C3—C2	118.1 (5)	C4—C3—C2	120.4 (5)
C4—C3—O31	121.5 (5)	C41—C4—C3	122.0 (4)
C5—C4—C3	117.2 (4)	C5—C4—C41	122.7 (4)
O41—C41—C4	122.1 (5)	C4—C5—N1	123.0 (3)
C51—C5—N1	113.5 (5)	C51—C5—C4	123.4 (2)
C52—C51—C5	118.90 (1)	C56—C51—C5	121.10 (1)
C56—C51—C52	120.00 (1)	C53—C52—C51	120.00 (1)
C54—C53—C52	120.00 (1)	C55—C54—C53	120.00 (1)
C56—C55—C54	120.00 (1)	C55—C56—C51	120.00 (1)

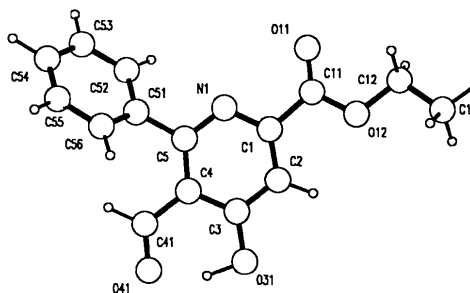


Fig. 1. *PLUTO* (Motherwell & Clegg, 1976) plot of the molecule showing the atomic numbering scheme.

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms, hydrogen-bond distances and angles, least-squares-planes data and principal torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55417 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Related literature. The pyridine nucleus is a structural unit in many natural products having simple or very complex structures, like co-enzymes, alkaloids and others (Yates, 1984). Because of the importance of this ring system and the pharmacological properties of functionalized pyridines, a number of methods of pyridine synthesis have been developed (Jones, 1984; Barluenga, Fustero & Gotor, 1975; Barluenga, Joglar, González, Gotor & Fustero, 1988; Guzmán, Romero, Maddox & Muchowski, 1990).

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4-Methoxyindan-1-one Oxime

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Abstract. $C_{10}H_{11}NO_2$, $M_r = 177.19$, monoclinic, $P2_1/n$, $a = 14.422$ (3), $b = 7.468$ (8), $c = 8.270$ (2) Å, $\beta = 97.47$ (1)°, $V = 883.2$ Å³, $Z = 4$, $D_x = 1.338$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.087$ mm⁻¹, $F(000) = 376$, $T = 291$ K, $R = 0.0385$ for 1770 unique reflections with $F > 6\sigma(F)$. The bond lengths and angles are all close to their expected values and the molecule is essentially planar with the nine atoms of the ring system having an r.m.s. deviation of 0.011 Å and methoxy O and C atoms being 0.002 (1) and 0.094 (2) Å, respectively, away from this plane. The oxime N and O atoms are respectively 0.104 (1) and 0.118 (1) Å above the ring

plane with molecules related by a centre of symmetry forming hydrogen-bonded dimers through the oxime atoms. The crystal is made up of extended sheets of molecules stacked perpendicular to the b axis.

Experimental. The title compound was prepared by oximation of 4-methoxyindan-1-one (Barco, Benetti & Pollini, 1976) with hydroxylamine hydrochloride and pyridine. Recrystallization from methanol gave colourless prisms. A single crystal, $0.8 \times 0.8 \times 0.8$ mm, was mounted on a Stoe Stadi-2 two-circle diffractometer equipped with graphite-monochromated Mo $K\alpha$ X-radiation. Cell parameters were obtained from 12 $h0l$ and four $0k0$ reflections

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