

Table 2. Bond distances (Å), bond angles (°) and geometry of the hydrogen bonds (Å, °)

N(1)—C(8)	1.453 (5)	N(1)—C(12)	1.337 (6)
O(1)—C(1)	1.378 (5)	O(2)—C(9)	1.197 (5)
O(3)—C(9)	1.314 (5)	O(3)—C(10)	1.464 (5)
O(4)—C(12)	1.226 (5)	C(1)—C(2)	1.376 (6)
C(1)—C(6)	1.392 (6)	C(2)—C(3)	1.378 (6)
C(3)—C(4)	1.393 (6)	C(4)—C(5)	1.380 (6)
C(4)—C(7)	1.528 (6)	C(5)—C(6)	1.381 (6)
C(7)—C(8)	1.517 (6)	C(8)—C(9)	1.518 (5)
C(10)—C(11)	1.384 (8)	C(12)—C(13)	1.507 (7)
C(8)—N(1)—C(12)	121.8 (4)	C(9)—O(3)—C(10)	118.0 (3)
O(1)—C(1)—C(2)	123.3 (4)	O(1)—C(1)—C(6)	117.3 (4)
C(2)—C(1)—C(6)	119.4 (4)	C(1)—C(2)—C(3)	119.8 (4)
C(2)—C(3)—C(4)	122.1 (4)	C(3)—C(4)—C(5)	117.1 (4)
C(3)—C(4)—C(7)	121.7 (4)	C(5)—C(4)—C(7)	121.2 (4)
C(4)—C(5)—C(6)	121.8 (4)	C(1)—C(6)—C(5)	119.8 (4)
C(4)—C(7)—C(8)	114.3 (4)	N(1)—C(8)—C(7)	111.5 (3)
N(1)—C(8)—C(9)	110.3 (3)	C(7)—C(8)—C(9)	110.2 (3)
O(2)—C(9)—O(3)	123.6 (4)	O(2)—C(9)—C(8)	125.0 (4)
O(3)—C(9)—C(8)	111.4 (3)	O(3)—C(10)—C(11)	111.4 (4)
N(1)—C(12)—O(4)	122.7 (4)	N(1)—C(12)—C(13)	116.7 (4)
O(4)—C(12)—C(13)	120.7 (4)		
D—H...A	D...A	H...A	D—H...A
O(5)—H(5B)...O(2)	2.985 (5)	2.31 (5)	153 (5)
N(1)—H(1)...O(1)	3.005 (5)	2.09 (5)	166 (4)
O(1)—H(1A)...O(5 ^b)	2.702 (5)	2.00 (6)	171 (6)
O(5)—H(5A)...O(4 ^m)	2.809 (5)	1.93 (6)	173 (5)

Symmetry code: (i) $-x, -0.5 + y, 1.5 - z$; (ii) $x, -1 + y, z$; (iii) $-0.5 + x, 1.5 - y, 2.0 - z$.

= 0.076. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The correct absolute molecular structure has been assigned to be *S* at C(8). All computations were performed on a Nova 4S computer and plots drawn

on a Tektronix plotter with the *SHELXTL* system of programs.

Atomic coordinates are given in Table 1.* A perspective molecular drawing and the atom labelling are displayed in Fig. 1. Bond distances, angles and hydrogen-bond geometry are given in Table 2.

Related literature. The crystal structure for *N*-acetyl-L-tyrosine ethyl ester has been published (Pieret, Durant, Germain & Koch, 1972).

I thank Mr R. A. Toscano for technical assistance.

* 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 55407 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1001]

References

- IUPAC-IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *Biochemistry*, **9**, 3471–3479.
 KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
 PIERET, A. F., DURANT, F., GERMAIN, G. & KOCH, M. (1972). *Cryst. Struct. Commun.* **1**, 75–77.
 SHELDRIK, G. M. (1985). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen, Germany.

Acta Cryst. (1993). **C49**, 97–99

Structure of 1,8-Dimethyl-4-oxo-1,2,2a,3,4,5-hexahydrocyclopenta[de]quinoline

BY K. SEKAR AND S. PARTHASARATHY*

Department of Crystallography and Biophysics,† University of Madras, Guindy Campus, Madras - 600 025, India

AND K. JOSEPH PRABAHAR AND V. T. RAMAKRISHNAN

Department of Organic Chemistry, University of Madras, Guindy Campus, Madras - 600 025, India

(Received 20 December 1991; accepted 13 April 1992)

Abstract. $C_{13}H_{15}NO$, $M_r = 201.3$, triclinic, $P\bar{1}$, $a = 8.929$ (2), $b = 8.990$ (2), $c = 8.094$ (2) Å, $\alpha = 103.79$ (2), $\beta = 116.71$ (2), $\gamma = 67.86$ (2)°, $V = 535.7$ (3) Å³, $Z = 2$, $D_x = 1.25$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 5.83$ cm⁻¹, $F(000) = 216$, $T = 295$ K, $R = 0.049$, $wR = 0.066$, for 1493 unique observed reflections [$I > 1.5\sigma(I)$]. The phenyl ring *B* is planar with a maximum deviation of -0.025 (3) Å, and all

molecular dimensions are normal. Ring *A* forms a somewhat flattened half-chair conformation. Ring *C* has an envelope conformation. Molecules are linked by an N—H...O hydrogen bond [2.877 (2) Å, 176 (3)°].

Experimental. Crystals of the title compound were provided by Professor V. T. Ramakrishnan and K. Joseph Prabahar of the Department of Organic Chemistry, University of Madras. Data were collected for a colourless transparent crystal (0.25 ×

* Author to whom correspondence should be addressed.

† Contribution No. 794.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for non-H atoms

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq}
N1	13039 (2)	1030 (2)	8033 (2)	53 (1)
C2	13894 (3)	-196 (2)	7129 (3)	52 (1)
C3	12982 (3)	-420 (2)	5024 (3)	54 (1)
C3a	11893 (3)	1194 (2)	4179 (2)	48 (1)
C4	10490 (3)	1194 (2)	2194 (2)	54 (1)
C5	9012 (3)	2827 (2)	2144 (3)	55 (1)
C5a	9168 (2)	3140 (2)	4152 (2)	46 (1)
C6	8041 (2)	4190 (2)	4986 (3)	49 (1)
C7	8650 (3)	4166 (2)	6905 (3)	54 (1)
C8	10271 (3)	3155 (2)	7985 (2)	52 (1)
C8a	11372 (2)	2130 (2)	7115 (2)	44 (1)
C8b	10802 (2)	2196 (2)	5238 (2)	44 (1)
O9	15336 (2)	-1148 (2)	7980 (2)	70 (1)
C10	7244 (3)	2762 (3)	619 (3)	76 (1)
C11	6270 (3)	5316 (3)	3902 (4)	68 (1)

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

N1—C2	1.348 (3)	C5—C10	1.517 (3)
C2—C3	1.523 (3)	C5a—C6	1.397 (3)
C2—O9	1.232 (2)	C5a—C8b	1.375 (2)
C3—C3a	1.527 (2)	C6—C11	1.505 (3)
C3a—C8b	1.489 (3)	C6—C7	1.399 (3)
C3a—C4	1.530 (2)	C7—C8	1.391 (2)
C4—C5	1.555 (3)	C8—C8a	1.393 (3)
C5—C5a	1.532 (3)	C8a—C8b	1.377 (2)
N1—C8a	1.411 (2)		
N1—C2—C9	121.2 (2)	C8b—C5a—C6	119.4 (2)
N1—C2—C3	117.9 (2)	C5a—C6—C11	122.4 (2)
O9—C2—C3	120.8 (2)	C5a—C6—C7	116.6 (2)
C2—C3—C3a	111.6 (2)	C7—C6—C11	121.0 (2)
C3—C3a—C4	118.1 (2)	C7—C8—C8a	118.2 (2)
C3—C3a—C8b	108.8 (2)	C8—C8a—N1	124.3 (2)
C8b—C3a—C4	101.6 (2)	C8—C8a—C8b	118.0 (2)
C3a—C4—C5	104.9 (1)	N1—C8a—C8b	117.7 (2)
C4—C5—C10	111.7 (2)	C8a—C8b—C5a	123.9 (2)
C4—C5—C5a	102.1 (1)	C8a—C8b—C3a	122.5 (2)
C5a—C5—C10	117.6 (2)	C3a—C8b—C5a	113.6 (1)
C5—C5a—C8b	108.0 (2)	C6—C7—C8	123.8 (2)
C5—C5a—C6	132.6 (2)	C2—N1—C8a	123.0 (2)
Ring A		C3a—C8b—C8a—N1	-1.8 (3)
N1—C2—C3—C3a	34.9 (3)	C8b—C8a—N1—C2	-16.2 (3)
C2—C3—C3a—C8b	-47.7 (3)	C8a—N1—C2—C3	-1.8 (3)
C3—C3a—C8b—C8a	33.6 (3)		
Ring B		C8—C8a—C8b—C5a	-4.2 (3)
C5a—C6—C7—C8	-1.0 (3)	C8a—C8b—C5a—C6	4.7 (3)
C6—C7—C8—C8a	1.5 (4)	C8b—C5a—C6—C7	-2.0 (3)
C7—C8—C8a—C8b	1.0 (3)		
Ring C		C5a—C8b—C3a—C4	-19.2 (2)
C3a—C4—C5—C5a	-29.8 (2)	C8b—C3a—C4—C5	29.6 (2)
C4—C5—C5a—C8b	18.6 (2)		
C5—C5a—C8b—C3a	0.2 (2)		

0.20 \times 0.25 mm) with an Enraf-Nonius CAD-4 diffractometer using Ni-filtered Cu $K\alpha$ radiation. Unit-cell parameters were derived from a least-squares analysis of 25 reflections with $25 \leq 2\theta \leq 35^\circ$. Intensity data were collected with the ω - 2θ scan technique. 1646 unique reflections ($R_{int} = 0.0075$) were measured ($h -7 \rightarrow 7$, $k -13 \rightarrow 13$, $l 0 \rightarrow 15$; $2\theta_{max} = 120^\circ$), of which 1493 had intensities greater than $1.5\sigma(I)$. Two standard reflections, monitored after every 2 h of X-ray exposure, indicated no decay over the full 20 h of data collection. The intensity data were corrected for Lorentz, polarization and absorp-

tion (ψ -scan method; transmission factor range 0.971–0.992) effects. Using *STATC*, a Fortran program for conducting statistical tests for centrosymmetry, developed in this department (Parthasarathy, Ponnuswamy, Elango & Sekar, 1990), the space group of the crystal was found to be $P\bar{1}$. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990) and refined on F by weighted full-matrix least squares on a MicroVAX II computer with *SHELX76* (Sheldrick, 1976). H atoms were located from a difference Fourier map. All H atoms were allowed to refine with isotropic atomic displacement parameters in the final cycles. Final maximum $\Delta/\sigma = 0.05$ and maximum and minimum heights in the final $\Delta\rho$ maps were 0.16 and -0.19 e \AA^{-3} , respectively. Refinement with weights given by $w = [\sigma^2(F) + 0.005381(F_o^2)]^{-1}$ converged at $R = 0.049$, $wR = 0.066$ and $S = 1.16$ for 196 parameters. Atomic scattering factors were those contained in *SHELX76* taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final positional and displacement parameters are listed in Table 1* and bond lengths and angles obtained using *PARST* (Nardelli, 1983) in Table 2. A *PLUTO* (Motherwell & Clegg, 1978) stereoview of the molecule showing the molecular geometry is presented in Fig. 1.

Related literature. N1—C2 and N1—C8a distances are shorter than the normally expected values. Similar shortening is found to occur in the quinoline ring of other structures, namely, 8-hydroxyquinoline *N*-oxide (Desiderato, Terry & Freeman, 1971), copper 8-hydroxyquinolate (Palenik, 1964a), zinc 8-hydroxyquinolate dihydrate (Palenik, 1964b),

* Lists of structure factors, anisotropic displacement parameters, H-atom parameters, bond distances and angles involving H atoms, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55379 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0271]

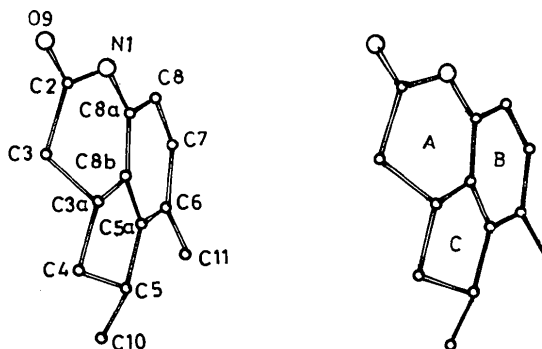


Fig. 1. A stereoview of the molecule with atom numbering.

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

Thanks are due to the Council of Scientific and Industrial Research, India, for the award of a Senior Research Fellowship to KS.

References

DESIDERATO, R., TERRY, J. C. & FREEMAN, G. R. (1971). *Acta Cryst.* **B27**, 2443–2447.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.

PALENIK, G. J. (1964*a*). *Acta Cryst.* **17**, 687–695.

PALENIK, G. J. (1964*b*). *Acta Cryst.* **17**, 696–700.

PARTHASARATHY, S., PONNUSWAMY, M. N., ELANGO, N. & SEKAR, K. (1990). *Acta Cryst.* **A46**, C-37.

SAX, M. & DESIDERATO, R. (1967). *Acta Cryst.* **23**, 319–326.

SAX, M., DESIDERATO, R. & DAKIN, T. W. (1969). *Acta Cryst.* **B25**, 362–368.

SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRIK, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Acta Cryst. (1993). **C49**, 99–101

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

BY S. GARCÍA-GRANDA* AND J. F. VAN DER MAELEN URÍA

Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Julián Clavería s/n, 33006 Oviedo, Spain

AND J. BARLUENGA, M. TOMÁS, A. BALLESTEROS AND JIAN-SHE KONG

Departamento de Química Organometálica, Facultad de Química, Universidad de Oviedo, Julián Clavería s/n, 33006 Oviedo, Spain

(Received 2 August 1991; accepted 29 April 1992)

Abstract. $C_{15}H_{13}NO_4$, $M_r = 271.3$, 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 chromato-

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 1*M* 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-

* To whom correspondence should be addressed.