O9	0.42552 (9)	0.7240 (4)	0.3740 (2)	0.046 (1)
N4	0.2831 (1)	0.6113 (6)	0.4218 (2)	0.043 (1)
N7	0.3582 (1)	0.3720 (5)	0.2954 (2)	0.041 (1)
C1	0.3811 (1)	0.7164 (6)	0.3964 (2)	0.036 (1)
C2	0.3726 (2)	0.8654 (7)	0.4570 (2)	0.039 (1)
C3	0.3210 (2)	0.8184 (7)	0.4719 (3)	0.041 (1)
C5	0.2877 (2)	0.4414 (7)	0.3581 (2)	0.040 (2)
C6	0.3418 (2)	0.5008 (6)	0.3473 (2)	0.034 (1)
C8	0.4123 (2)	0.5021 (7)	0.3049 (2)	0.042 (1)
C10	0.4693 (2)	0.3342 (9)	0.3556 (4)	0.057 (2)
C11	0.3960 (2)	0.610 (1)	0.2045 (3)	0.065 (2)

Table 2. *Selected geometric parameters* (Å, °)

F2—C2	1.349 (3)	N7—C8	1.459 (4)
O3—C3	1.220 (3)	C1—C2	1.326 (4)
O5 C5	1.193 (4)	C1—C6	1.429 (4)
O9—C1	1.337 (3)	C2—C3	1.456 (4)
O9—C8	1.497 (3)	C5—C6	1.491 (4)
N4—C3	1.382 (4)	C8—C10	1.504 (5)
N4—C5	1.382 (4)	C8—C11	1.501 (5)
N7—C6	1.277 (3)		
C1—O9—C8	105.3 (2)	O5—C5—N4	122.8 (3)
C3—N4—C5	128.1 (3)	O5—C5—C6	125.2 (3)
C6—N7—C8	106.6 (3)	N4—C5—C6	111.9 (3)
O9—C1—C2	129.8 (3)	N7—C6—C1	113.1 (3)
O9—C1—C6	108.8 (3)	N7—C6—C5	125.5 (3)
C2—C1—C6	121.4 (3)	C1—C6—C5	121.4 (3)
F2—C2—C1	124.2 (3)	O9—C8—N7	106.2 (2)
F2—C2—C3	115.4 (3)	O9—C8—C10	106.9 (3)
C1—C2—C3	120.4 (3)	O9—C8—C11	106.8 (3)
O3—C3—N4	121.0 (3)	N7—C8—C10	111.1 (3)
O3—C3—C2	122.2 (3)	N7—C8—C11	110.2 (3)
N4—C3—C2	116.8 (3)	C10—C8—C11	115.1 (3)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*. Literature survey: *CSSR* (1984).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: LI1122). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 517–519

2-Chloro-6-dimethylamino-3,5-pyridinedicarbaldehyde

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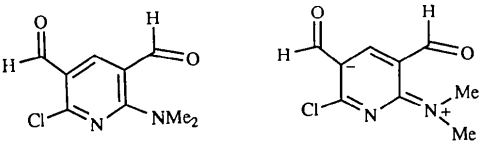
Abstract

The title compound, $C_9H_9ClN_2O_2$, contains a rather distorted pyridine ring (planar to within ±0.07 Å) with four substituents. The O atoms of the formyl groups at C4 and C2 are displaced from the plane of the pyridine ring by *ca* 1.1 and 0.3 Å, respectively. The dimethylamino group at C5, which is planar to within 0.04 Å, forms a dihedral angle of 23.8 (1)° with the plane of the pyridine ring. The C4—C5 bond in the pyridine ring [1.444 (2) Å] is much longer than normal in pyridines [1.379 Å], while N1—C1 [1.304 (2) Å] is shorter and N1—C5 [1.357 (2) Å] is longer than normal [1.337 Å; Allen, Kennard, Watson, Brammer, Orpen & Taylor (1989). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19]. The C5—N(dimethylamino) bond [1.332 (2) Å] is shorter than expected.

Comment

Since we are quite interested in the conformation of highly substituted pyridine derivatives, the determination of the structure of the title compound, which has unsymmetrical substituents, was carried out in order to see how steric and electronic effects in an unsymmetrically substituted pyridine skeleton would be reflected in the bonding geometry, and to compare the structural parameters of the title compound with those of 2,6-bis(dimethylamino)-3,5-pyridinedicarbaldehyde (Lai, Liu, Shiao & Wen, 1994).

The pattern of bond lengths in the title compound indicate that the lone pair of electrons on the N atom of the dimethylamino group is delocalized into the π system of the pyridine ring, as shown by the resonance forms in the scheme below.



The effect of substituents on the conformation of this type of compound is important as aminopyridine derivatives form strong hydrogen bonds with carboxylic acids

(Garcia-Tellado, Goswami, Chang, Geib & Hamilton, 1992). The title compound is also a useful intermediate in the formation of various aromatic heterocycles which function as DNA intercalators (Mitcher & Rao, 1984).

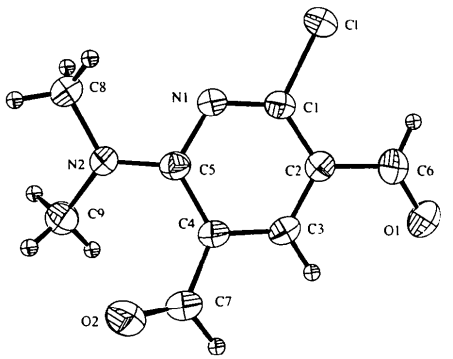


Fig. 1. View of the title compound showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary size.

Experimental

The title compound was obtained by reaction of 2,6-dimethoxypyridine with Vilsmeier's reagent following a literature procedure (Shiao, Shyu & Tarng, 1990). Suitable crystals for this study were obtained from dichloromethane–hexane (1:2); m.p. 415–416 K.

Crystal data

$C_9H_9ClN_2O_2$
$M_r = 212.63$
Triclinic
$P\bar{1}$
$a = 7.162$ (1) Å
$b = 7.417$ (1) Å
$c = 9.469$ (2) Å
$\alpha = 69.27$ (2)°
$\beta = 93.79$ (2)°
$\gamma = 92.41$ (2)°
$V = 469.3$ (2) Å^3
$Z = 2$
$D_x = 1.505$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 24 reflections
$\theta = 8.48$–17.115°
$\mu = 0.38$ mm^{-1}
$T = 298$ K
Rod
0.47 × 0.38 × 0.25 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.961$, $T_{max} = 0.998$
1789 measured reflections
1646 independent reflections
1375 observed reflections [$I > 2.5\sigma(I)$]
$R_{int} = 0.010$
$\theta_{max} = 25.0$°
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 8$
$l = -9 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.028$
$wR = 0.037$
$S = 1.95$
1646 reflections
163 parameters
All H-atom parameters refined
$1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.200$ e Å^{-3}
$\Delta\rho_{min} = -0.160$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: 0.48 (16)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cl	0.2225 (1)	0.7384 (1)	0.3173 (1)	0.046 (1)
N1	0.2787 (2)	0.4585 (2)	0.5698 (2)	0.033 (1)
N2	0.3085 (2)	0.2418 (2)	0.8111 (2)	0.035 (1)
O1	0.0411 (2)	0.2826 (2)	0.1539 (2)	0.061 (1)
O2	0.4528 (2)	−0.1270 (2)	0.7790 (2)	0.054 (1)
C1	0.2245 (2)	0.4940 (2)	0.4285 (2)	0.032 (1)
C2	0.1689 (3)	0.3583 (3)	0.3624 (2)	0.035 (1)
C3	0.1962 (3)	0.1677 (3)	0.4561 (2)	0.037 (1)
C4	0.2619 (3)	0.1182 (2)	0.6034 (2)	0.034 (1)
C5	0.2845 (2)	0.2717 (2)	0.6639 (2)	0.031 (1)
C6	0.0992 (3)	0.4035 (3)	0.2056 (2)	0.046 (1)
C7	0.3377 (3)	−0.0762 (3)	0.6751 (2)	0.046 (1)
C8	0.3720 (4)	0.3990 (3)	0.8632 (3)	0.044 (1)
C9	0.2442 (4)	0.0669 (3)	0.9278 (2)	0.044 (1)

Table 2. *Selected geometric parameters* (Å, °)

Cl—C1	1.745 (2)	O2—C7	1.202 (3)
N1—C1	1.304 (2)	C1—C2	1.394 (3)
N1—C5	1.357 (2)	C2—C3	1.391 (3)
N2—C5	1.332 (2)	C2—C6	1.460 (3)
N2—C8	1.464 (2)	C3—C4	1.367 (3)
N2—C9	1.456 (3)	C4—C5	1.444 (2)
O1—C6	1.212 (3)	C4—C7	1.470 (3)
C1—N1—C5	118.02 (15)	C2—C3—C4	122.45 (17)
C5—N2—C8	120.60 (15)	C3—C4—C5	116.90 (16)
C5—N2—C9	123.03 (15)	C3—C4—C7	116.53 (16)
C8—N2—C9	115.52 (16)	C5—C4—C7	125.38 (17)
Cl—C1—N1	114.33 (13)	N1—C5—N2	116.27 (15)
Cl—C1—C2	119.16 (13)	N1—C5—C4	120.18 (15)
N1—C1—C2	126.51 (16)	N2—C5—C4	123.54 (15)
C1—C2—C3	114.47 (16)	O1—C6—C2	123.53 (20)
C1—C2—C6	125.10 (17)	O2—C7—C4	126.54 (19)
C3—C2—C6	120.30 (17)		

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Intensity data were corrected for Lorentz, polarization and absorption effects. Data reduction and structure refinement were performed using the *NRCVAX* package (Gabe, Lee & Le Page, 1985). The structure was solved by direct methods and refined using full-matrix least squares. All non-H atoms were refined with anisotropic displacement parameters. Molecular graphics were produced using *ORTEP*II (Johnson, 1976).

We thank the National Science Council and Academia Sinica for the financial support.

Lists of structure factors, anisotropic displacement parameters and complete geometry, and a packing diagram have been deposited with the IUCr (Reference: BK1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 519–521

6-Ethyl-9-fluoro-6,7-dihydro-8-(4-hydroxy-piperidino)-5-methyl-1-oxo-1*H*,5*H*-benzo[*ij*]quinolizine-2-carboxylic Acid

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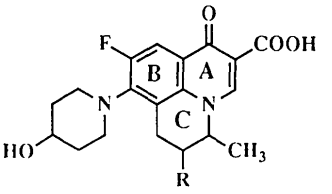
Abstract

The molecular structure of the title compound, $C_{21}H_{25}FN_2O_4$, (1), has been established by X-ray diffraction. The conformation of the methyl and ethyl groups is *gauche*. The methyl group is at a right angle to the 4-quinolone ring, but the ethyl group is equatorial.

Comment

As part of an investigation into structure–activity relationships of quinolone antibacterial drugs, the molecular structure of nadifloxacin, (2), was confirmed by three-dimensional structure analysis (Kido & Hashimoto, 1994). The molecular skeleton of nadifloxacin comprises a system of three six-membered rings, *A*, *B* and *C*. The aromatic rings *A* and *B* of the 4-quinolone moiety are almost coplanar, while the saturated ring *C* is twisted and the methyl group protrudes at a right angle from the 4-quinolone moiety. The same conformation was suggested by molecular-mechanics calculations for an analogous drug, ofloxacin, and this conformation plays an important role in bioactivity (Sato & Matsuhashi, 1991). The determination of the title structure, (1), will contribute to the knowledge of the geometrical effects of various substituents in the position next to the methyl group. An *ORTEP* (Johnson, 1965) drawing of the title compound with the atomic labelling scheme is shown in Fig. 1. Bond distances and angles agree with those of nadifloxacin.



(1) $R = C_2H_5$
(2) $R = H$

The methyl and ethyl groups adopt a *gauche* conformation [C(13)—C(10)—C(11)—C(20) = −66.3 (6)°]. The methyl group protrudes at a right angle from the 4-quinolone moiety but the ethyl group is equatorial. The two C—O bonds of the carboxylic acid group differ in length: C(14)—O(1) and C(14)—O(2) are 1.216 (6) and 1.332 (6) Å, respectively. The intramolecular distance between O(2) and O(3) of 2.543 (6) Å suggests that an intramolecular hydrogen bond exists between the two O atoms.

The piperidine ring adopts a typical chair conformation with N(2) and C(17) deviating −0.687 and 0.660 Å, respectively, from the mean plane through C(15), C(16), C(18) and C(19). Each molecule in the crystal structure is linked to its neighbor by an O(4)—H···O(1) hydrogen bond with a distance of 2.849 (6) Å [O(1) at $\frac{1}{2} - x$, $y - \frac{3}{2}$, $\frac{1}{2} + z$].

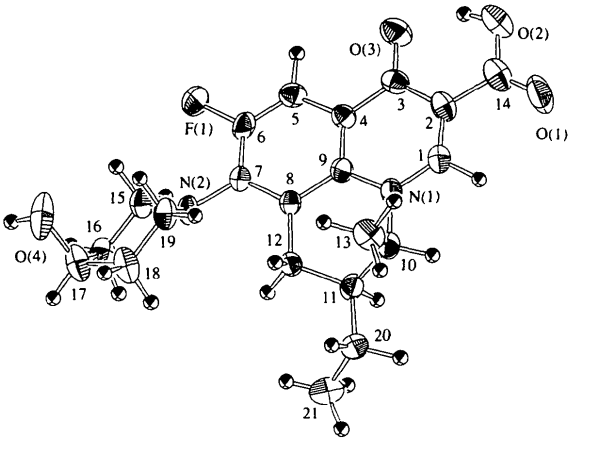


Fig. 1. *ORTEP* (Johnson, 1965) drawing of (1) with the atomic labeling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary size.