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2-(2-Isopropylanilino)pyridine-3-carboxylic acid

Sihui Long,[a] Maxime Siegler[b] and Tonglei Li[a]*

[a]Department of Pharmaceutical Sciences, University of Kentucky, Lexington, KY 40506-0082, USA, and [b]Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA

Correspondence e-mail: tonglei@uky.edu

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The asymmetric unit of the title compound, $C_{15}H_{16}N_2O_2$, contains two molecules and in each of the molecules, the two aromatic rings, lying in two different planes, are bridged by a secondary amino group. This might be due to steric hindrance caused by the isopropyl group. Intra- and intermolecular N—H···O hydrogen bonds link the molecules, forming an infinite one-dimensional tape structure; they may be effective in the stabilization of the crystal structure.

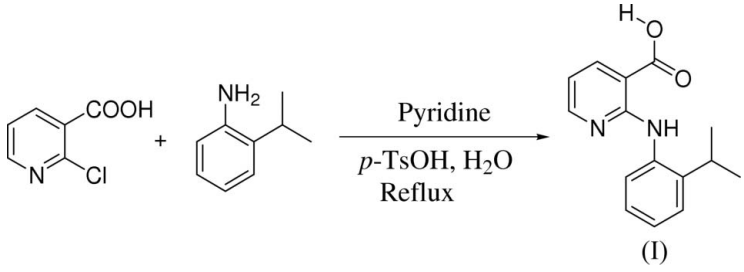
Key indicators

Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.002 Å
R factor = 0.051
wR factor = 0.141
Data-to-parameter ratio = 18.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), was first prepared in 1975 in a search for analgesic, anti-inflammatory, and antipyretic drugs. To study the effect of additives on the polymorphs as well as morphologies of 2-(3-chloro-2-methylanilino)nicotinic acid, we synthesized (I) through a procedure modified from Ting *et al.* (1990).



(I)

The asymmetric unit of (I) (Fig. 1) contains two molecules and the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). Each molecule contains two aromatic rings linked by a secondary amino group. Ideally, the two aromatic

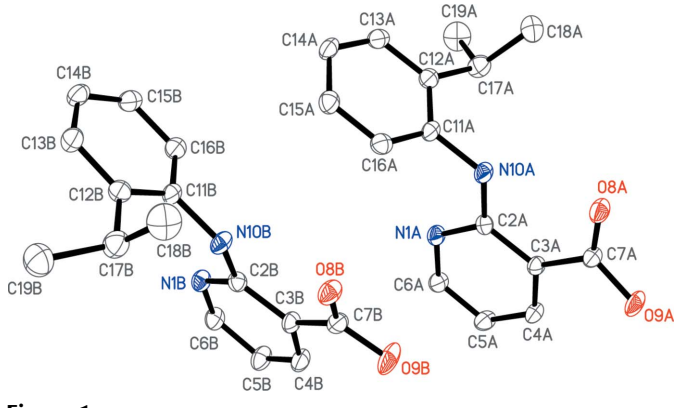


Figure 1
The asymmetric unit of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted.

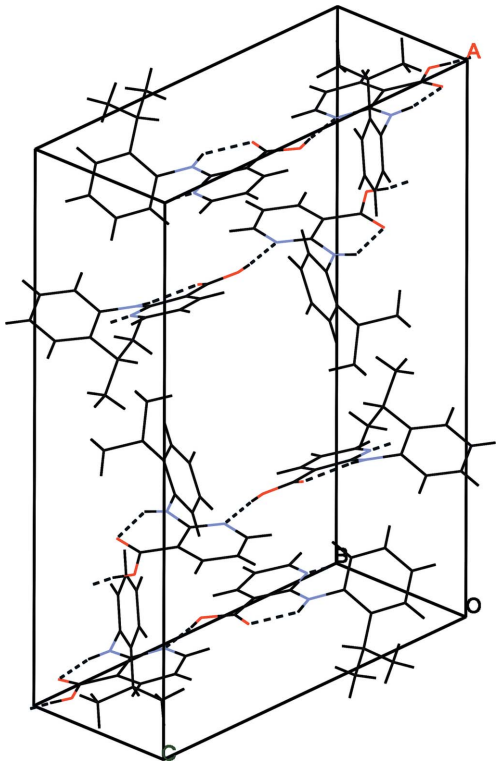


Figure 2
A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

rings would prefer to lie in the same plane, forming a conjugated π system throughout the whole molecule *via* the lone pair orbital of the amino group. In reality, the carboxyl group, N10, C11 and pyridine are almost coplanar, while the *ortho*-subtituted benzene ring is twisted about the N10—C11 bond. The dihedral angles between the planes of rings *A* (N1*A*/C2*A*–C6*A*), *B* (C11*A*–C16*A*) and *A*′ (N1*B*/C2*B*–C6*B*), *B*′ (C11*B*–C16*B*) are *A*/*B* = 88.08 (5)° and *A*′/*B*′ = 61.78 (5)°. This observation is similar to that of the four polymorphs of 2-(3-chloro-2-methylanilino)nicotinic acid (Takasuka *et al.*, 1982).

As can be seen from the packing diagram (Fig. 2), intra- and intermolecular N—H···O hydrogen bonds (Table 1) link the molecules, forming an infinite one-dimensional tape structure; they may be effective in the stabilization of the crystal structure. Dipole–dipole and van der Waals interactions are also effective in the molecular packing.

Experimental

2-Chloronicotinic acid (11.1 g, 0.07 mol) and 2-isopropylaniline (10.3 g, 76 mmol) were dissolved in pyridine (6 ml, 76 mmol) and *p*-TsOH (1.5 g, 9 mmol) in water (40 ml) was added to the mixture. The resulting mixture was refluxed overnight. Solvents were removed under reduced pressure, then water (25 ml) and EtOAc (25 ml) were added. After separation, the organic layer was dried with anhydrous sodium sulfate. After filtration and solvent removal under vacuum, a colorless product was obtained (yield 80%, m.p. 441–443 K). A supersaturated solution was made by dissolving the compound in acetone by heating; the solution was yellow although the compound was colorless. The solution was allowed to evaporate slowly, and crystals were obtained as colorless rods the next day.

Crystal data

$C_{15}H_{16}N_2O_2$
M_r = 256.30
Monoclinic, $P2_1/c$
a = 22.242 (3) Å
b = 8.921 (1) Å
c = 14.367 (2) Å
β = 104.07 (1)°
V = 2765.2 (6) Å^3
Z = 8
D_x = 1.231 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 90.0 (2) K
Rod, colorless
0.40 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.968, T_{max} = 0.988
12239 measured reflections
6330 independent reflections
3912 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.142
S = 1.01
6330 reflections
349 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N10*A*—H10*A*···O8*A*	0.88	1.98	2.6694 (18)	134
N10*B*—H10*B*···O8*B*	0.88	1.98	2.6788 (18)	135
O9*A*—H9*A*···N1*A*^{i}	0.84	1.84	2.6723 (18)	173
O9*B*—H9*B*···N1*B*^{i}	0.84	1.83	2.6614 (18)	169

Symmetry code: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

H atoms were positioned geometrically, with O—H = 0.84 Å (for OH), N—H = 0.88 Å (for NH) and C—H = 0.95, 1.00 and 0.98 Å for aromatic, methine and methyl H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C,N,O), where x = 1.5 for OH and methyl, and x = 1.2 for all other H atoms.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO*–SMN (Otwinowski & Minor, 1997); data reduction: *DENZO*–SMN; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97* and local procedures.

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