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# 2-Anilino-4,6-dimethylpyridine-3-carbonitrile, an Intermediate in the Synthesis of 5-Aminobenzo[*b*][1,8]naphthyridines

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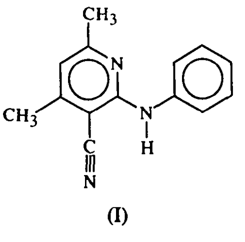
## Abstract

The title compound, $C_{14}H_{13}N_3$, is an intermediate in the synthesis of the corresponding 5-aminobenzo[*b*][1,8]-naphthyridine. Problems of isomerism occur with this series. According to the crystal structure, conformational features do not appear to be involved either in the mechanism of the reaction or in determination of the isomers obtained.

## Comment

Diphenylamine and *N*-phenyl-2-pyridylamine are well known for their anti-inflammatory properties, but they can also act as intermediates in the synthesis of tricyclic derivatives belonging to the acridine and benzonaphthyridine series, respectively. Our interest in these compounds lies in this last point. When the phenyl moiety is substituted, there are two potential sites for the cyclization reaction, leading to two different isomers. According to the nature of the substituents, we can obtain either a pure isomer or a mixture of isomers. We have shown that electronic features could be an explanation (Mefetah, Brouant, Galy, Galy & Barbe, 1995) and in this study we intend to establish whether conformational features could also be involved. The crystal structure of 2-anilino-4,6-dimethylpyridine-3-carbonitrile, (I), has therefore been determined.



(I)

The crystal structures of several diphenylamines and some phenyl 2-pyridylamines are available in the Cambridge Structural Database (Allen *et al.*, 1979). We noticed for those compounds that the torsion angles $\tau1$ (N1—C1—N3—C9) and $\tau2$ (C14—C9—N3—C1), measured around the bonds linking the two aromatic moieties to the N atom, are consistently different from one series to the other; the mean values calculated are $\tau1 = 3\,(4)$ and $\tau2 = 19\,(27)°$ for the *N*-phenyl-2-pyridylamine series, and $\tau1 = 14\,(11)$ and $\tau2 = 49\,(12)°$ for the diphenylamine series. These values show a greater planarity for the first group and the present compound is in agreement with these values, having $\tau1 = 2.7\,(5)$ and $\tau2 = 22.7\,(5)°$ (Fig. 1), as a result of the less demanding steric requirements of the H atom attached to the C14 atom. Consequently, the cyano group lies removed from the atoms of the phenyl ring involved in the cyclization reaction and, thus, the crystal conformation cannot provide any explanation for the reaction mechanism.

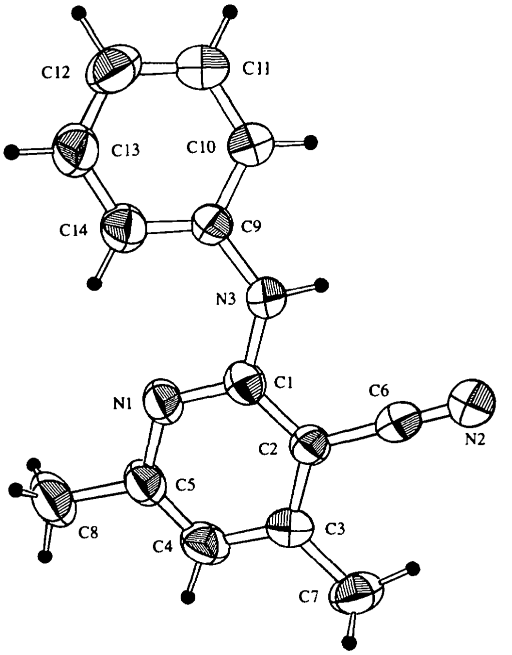


Fig. 1. A perspective *ORTEP*II (Johnson, 1976) view of (I) showing 50% probability displacement ellipsoids. H atoms are shown with a small arbitrary radius.

## Experimental

The synthesis of 2-anilino-4,6-dimethylpyridine-3-carbonitrile was carried out by reaction of 2-chloro-3-cyano-4,6-dimethylpyridine and aniline (molar ratio 1:1) without solvent at 413 K for 3 h. The product was recrystallized from methanol.

*Crystal data*

$C_{14}H_{13}N_3$
$M_r = 223.28$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Triclinic
$P\bar{1}$
$a = 7.956\ (2)$ Å
$b = 8.193\ (2)$ Å
$c = 9.313\ (2)$ Å
$\alpha = 89.89\ (1)°$
$\beta = 94.79\ (1)°$
$\gamma = 90.95\ (1)°$
$V = 604.8\ (4)$ Å$^3$
$Z = 2$
$D_x = 1.23$ Mg m$^{-3}$
$D_m$ not measured

Cell parameters from 25 reflections
$\theta = 8–14°$
$\mu = 0.070$ mm$^{-1}$
$T = 294$ K
Square prism
0.40 × 0.25 × 0.25 mm
Colorless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2032 measured reflections
1899 independent reflections
924 observed reflections $[I > 3\sigma(I)]$

$R_{\rm int} = 0.025$
$\theta_{\rm max} = 23.97°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = 0 \rightarrow 10$
2 standard reflections
frequency: 60 min
intensity decay: 1.70%

*Refinement*

Refinement on $F$
$R = 0.047$
$wR = 0.054$
$S = 1.613$
924 reflections
158 parameters
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.21$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.21$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| N1 | 0.5116 (3) | 0.2118 (3) | 0.9014 (3) | 0.0488 (8) |
| N2 | 0.0836 (4) | 0.4678 (4) | 1.1465 (3) | 0.074 (1) |
| N3 | 0.2364 (3) | 0.2919 (3) | 0.8390 (3) | 0.0513 (8) |
| C1 | 0.3736 (4) | 0.2829 (4) | 0.9399 (4) | 0.044 (1) |
| C2 | 0.3625 (4) | 0.3470 (4) | 1.0784 (3) | 0.0409 (9) |
| C3 | 0.5009 (4) | 0.3433 (4) | 1.1786 (4) | 0.046 (1) |
| C4 | 0.6444 (4) | 0.2713 (4) | 1.1350 (4) | 0.057 (1) |
| C5 | 0.6451 (4) | 0.2056 (4) | 1.0000 (4) | 0.052 (1) |
| C6 | 0.2084 (4) | 0.4155 (4) | 1.1158 (4) | 0.052 (1) |
| C7 | 0.4955 (5) | 0.4139 (5) | 1.3258 (4) | 0.063 (1) |
| C8 | 0.7969 (4) | 0.1219 (5) | 0.9514 (5) | 0.074 (1) |
| C9 | 0.2153 (4) | 0.2301 (4) | 0.6968 (3) | 0.043 (1) |
| C10 | 0.0907 (4) | 0.3025 (4) | 0.6069 (4) | 0.054 (1) |
| C11 | 0.0581 (5) | 0.2468 (5) | 0.4673 (4) | 0.063 (1) |
| C12 | 0.1469 (5) | 0.1197 (5) | 0.4163 (4) | 0.067 (1) |
| C13 | 0.2695 (4) | 0.0513 (4) | 0.5058 (4) | 0.064 (1) |
| C14 | 0.3051 (4) | 0.1038 (4) | 0.6465 (4) | 0.058 (1) |
| H8 | 0.161 (4) | 0.363 (4) | 0.859 (4) | 0.04 (1) |

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

| | | | |
|---|---|---|---|
| N2—C6 | 1.146 (5) | N3—C9 | 1.414 (4) |
| N3—C1 | 1.383 (4) | N3—H8 | 0.87 (3) |
| C1—N3—C9 | 129.6 (3) | C9—N3—H8 | 115 (2) |
| C1—N3—H8 | 114 (2) | N2—C6—C2 | 178.8 (4) |

All H atoms were introduced at fixed idealized positions and not refined, except for H8 (attached to N3), which was found by difference Fourier synthesis and refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *BEGIN* in *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *SDP-Plus*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# (–)-*cis*-Pinononic Acid: Hydrogen-Bonding Pattern of a δ-Keto Acid

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## Abstract

In the title compound, (–)-*cis*-3-acetyl-2,2-dimethylcyclobutanecarboxylic acid, $C_9H_{14}O_3$, carboxyl-to-ketone chains (catemers) are formed between screw-related molecules spiraling along the $b$ cell axis, with an O—H···O distance of 2.747 (3) Å. The carboxyl C═O