Crystal Structure of 2-Chloro-4-tolyl-6-phenylpyridine-3-carbonitrile

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In the molecular structure, the central pyridine ring adopts a flat boat conformation. In the solid state, the symmetry-related molecules are linked by weak π - π stacking interactions in addition to the intramolecular C-H...N interaction.

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With respect to biological and medicinal importance, 2-pyridine derivatives represent a significant group of heterocyclic compounds. 2-Pyridine compounds show antituberculosis, anticonvulsant and anti-inflammatory activities. The molecular structure of the title compound, 2-chloro-4-tolyl-6-phenylpyridine-3-carbonitrile is in a continuation of our structural studies of the 2-pyridine group of compounds. We previously reported the structure of 2-substituted ethoxy¹ and

2,3-isopropylidene-dioxypropyloxy pyridine derivatives.² A schematic diagram of the molecule is shown in Fig. 1.

Thin transparent needle-shaped crystals of the compound were grown from a chlorobenzene solution by slow evaporation. An ORTEP diagram of the molecule with the numbering scheme is shown in Fig. 2. The crystal and experimental details are given in Table 1. The structure was solved by direct methods and refined by full-matrix least squares. All of the non-hydrogen atoms were refined anisotropically and all the H atoms were geometrically fixed and allowed to ride on the parent atom in the model with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for terminal methyl and $1.2U_{\text{eq}}(\text{C})$ for all other pyridine and phenyl H-atoms. The

Fig. 1 Schematic diagram of the molecule.

Fig. 2 ORTEP diagram of the molecule at the 50% probability level.

Table 1 Crystal and experimental data

Empirical formula	C ₁₉ H ₁₃ N ₂ Cl
Formula weight	304.76
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit Cell dimensions	$a = 14.992(5)\text{\AA}$ $b = 7.439(5)\text{\AA}$ $c = 15.318(5)\text{\AA}$ $\beta = 113.894(5)^\circ$
Z	4
V	$1561.9(13)\text{\AA}^3$
T	293(2)K
D_x	1.296 Mg/m^3
μ	0.242 mm^{-1}
Radiation(Mo K α)	$\lambda = 0.71069\text{ \AA}$
$F(0\ 0\ 0)$	632
θ range for data collection	2.97 to 25.0°
Reflections used for refinement	2423
Number of parameters	199
Goodness of fit	1.112
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0711$, $wR2 = 0.158$
R indices all data	$R1 = 0.0927$, $wR2 = 0.1722$
$(\Delta/\sigma)_{\text{max}}$	0.000
$(\Delta\rho)_{\text{max}}$	$0.445\text{ e\AA}^{-3}$
$(\Delta\rho)_{\text{min}}$	$-0.202\text{ e\AA}^{-3}$
Measurement	Bruker SMART CCD
Program system	SMART
Structure determination	SIR-97 ⁵
Refinement	SHELXL-97
Graphics	ORTEP III, PLATON
CCDC No.	298036

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Table 2 Atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms

Atom	x	y	z	U_{eq}
C11	0.2695(1)	0.1596(2)	0.4261(1)	0.063(1)
N1	0.2390(2)	0.0317(4)	0.5698(2)	0.045(1)
N2	0.5303(2)	0.2263(4)	0.5430(2)	0.056(1)
C1	0.3075(2)	0.0852(4)	0.5444(2)	0.041(1)
C2	0.4074(2)	0.0915(4)	0.6027(2)	0.036(1)
C3	0.4358(2)	0.0310(4)	0.6974(2)	0.033(1)
C4	0.3615(2)	-0.0239(4)	0.7246(2)	0.038(1)
C5	0.2649(2)	-0.0224(4)	0.6600(2)	0.038(1)
C6	0.5393(2)	0.0241(4)	0.7665(2)	0.035(1)
C7	0.6120(2)	-0.0371(4)	0.7393(2)	0.042(1)
C8	0.7071(2)	-0.0452(5)	0.8035(3)	0.050(1)
C9	0.7338(2)	0.0133(5)	0.8968(3)	0.053(1)
C10	0.6615(3)	0.0762(4)	0.9244(2)	0.049(1)
C11	0.5655(2)	0.0795(4)	0.8604(2)	0.039(1)
C12	0.1838(2)	-0.0805(4)	0.6869(2)	0.044(1)
C13	0.1993(3)	-0.1674(6)	0.7710(3)	0.071(1)
C14	0.1236(3)	-0.2210(8)	0.7931(4)	0.091(2)
C15	0.0287(3)	-0.1894(6)	0.7307(4)	0.078(1)
C16	0.0113(3)	-0.1041(6)	0.6471(4)	0.073(1)
C17	0.0886(3)	-0.0464(6)	0.6257(3)	0.066(1)
C18	0.4754(2)	0.1657(4)	0.5687(2)	0.040(1)
C19	0.8318(3)	0.0127(6)	0.9644(3)	0.075(1)

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

Fig. 3 Crystal packing view down the *a*-axis.

atomic coordinates of non-hydrogen atoms along with equivalent isotropic displacement parameters are presented in Table 2.

In the molecular structure, the central pyridine ring has similar geometries as observed in the crystal structure of other *ortho* substituted pyridine derivatives. The shortening of the C-N distances (1.298(4) Å and 1.337(4) Å) and an opening up of the N1-C1-C2 angle (126.2(3)°) may be attributed to the chlorine substituent at the C1 atom, correlating well with the values observed in *ortho*-substituted derivatives 2-ethoxy-4,6-diphenylpyridine-3-carbonitrile¹ and 2-(2,3-isopropylidenedioxypropyloxy)-4,6-diphenylpyridine-3-carbonitrile.²

A lengthening of the C2-C3 and C3-C4 bonds, and a contraction of the C2-C3-C4 angle may be attributed to the size of comparatively heavy substituent at C3 (a toluene ring). A flat boat conformation of the pyridine ring of molecule is reported in the literature for other compounds incorporating this moiety.^{3,4} Both of the phenyl rings as well as the pyridine rings

are planar within themselves with a maximum deviation of 0.013(4) Å for the C17 atom. The phenyl ring at an orthoposition is almost coplanar, and makes a dihedral angle of 10.81(19)° with the least-squares pyridine ring plane. The orientation of the phenyl rings in other analogous structures is different from the dihedral angles with respect to the pyridine ring plane, ranging from 22.3(1) to 24.6(1)°. This may be attributed due to the involvement of phenyl carbon atom in the intramolecular C-H...N interaction with the pyridine N atom. The steric hindrance rotates the phenyl ring at the para position out of pyridine ring plane by 42.61(15)°. A similar orientation of the phenyl ring is also observed in other analogous structures. The carbonitrile atoms, C18 and N2, of the molecule are deviated by 0.114(3) Å and 0.213(3) Å respectively, from the pyridine ring plane, whereas the deviation of chlorine atom situated at C1 position of the pyridine ring is small (0.024(1) Å). The linear torsional angle, C11-C1-C2-C18 = 3.6(4)°, represents the *cis* conformation of the chlorine atom about the C1-C2 bond with the C18 atom of the carbonitrile moiety.

There is an intramolecular C-H...N interaction involving pyridine N1 and the phenyl carbon C17 atom, where C17-H17...N1 = 2.779(5) Å, H17...N1 = 2.45 Å and C17-H17...N1 = 101°. This intramolecular interaction in the structure is supported by weak π - π stacking interactions. In one of the interactions, there is a π - π stacking between the pyridine ring and the symmetry related to the C6-C11 phenyl ring (1-x, -1/2+y, 3/2-z) with their centroids separated by 3.858(3) Å. In another interaction, pyridine ring exhibits π - π stacking with a symmetry related C6-C11 phenyl ring at 1-x, 1/2+y, 3/2-z with their centroids separated at a distance of 3.656(3) Å. The molecules are stacked in layers parallel to (010) (Fig. 3) within which these two significant intermolecular contacts are observed.

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