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Synthesis and Crystal Structure of New Pyridyl Derivative†

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A pyridyl derivative with four stereo centers has been prepared by an efficient synthetic method based on a solvent-free reaction. The structure was characterized by elemental analyses, IR, ^{1}H NMR, mass spectra and single crystal X-ray diffraction. The crystal structure shows that the cyclohexyl group is a chair conformation and three intramolecular hydrogen bonds generate the trimer.

Keywords: Pyridine, Crystal structure, Chair conformation, Pyridyl derivative, Imidazole.

INTRODUCTION

Nitrogen heterocyclic compounds with good coordination, optical properties and biological activity were used in biology, medicine, environment, material and other fields widely[1-4]. The design and synthesis of photoelectric functional pyridine derivatives have always been the hot spot of the study area due to pyridine with electronic absorption performance, good rigid plane and easy molecular modification as electron acceptor[5-8]. In addition, N atom of pyridine derivatives coordinating with various metal ions easily by self-assembly method can form functional complexes with excellent properties. At present, pyridine derivatives are widely used in luminescence, catalysis, separation, adsorption, biological chemistry, *etc.*[9,10].

The paper reported a new pyridiyl derivative 6-phenyl-imidazolyl-2,4-dihydroxy-2-(pyridine-2'-yl)-4-phenyl(cyclohexanecarbonyl-2')pyridine (**L**). The compound was characterized by Elemental analyses, IR, ^{1}H NMR, EI-mass spectra and single crystal X-ray diffraction.

EXPERIMENTAL

All chemicals used were of analytical grade. The solvents were purified by conventional methods before use. Elemental analyses were performed with an Elmentar Vario EL-III analyzer. IR spectra were recorded with a FT-IR spectrometer (KBr discs) in the 4000-400 cm^{-1} region. The NMR spectra were recorded on a 400 MHz NMR instrument using DMSO-d_6 and CD_3COCD_3 as solvent. Mass spectra were obtained on a Micromass GCT-MS Spectrometer. The X-ray diffraction measurements were performed on a Bruker SMART CCD area detector using graphite monochromated MoK_α radiation (λ = 0.71069 Å) at 298 (2) K. Intensity data were collected in the variable *w*-scan mode. The structures were solved by direct methods and difference Fourier synthesis. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed with the SHELXTL-97 program package[11].

The synthetic compound is shown in **Scheme-I**. 4-Imidazolylbenzaldehyde and intermediate compounds are synthesized according to the method of literature[12,13].

Synthesis and characterization: A methanolic solution (40 mL) of NaOH (4 g, 0.1 mol) was added dropwise to a stirred methanol (20 mL) solution of 4-imidazolylbenzaldehyde (1.72 g, 10 mmol) and acetophenone (1.20 g, 10 mmol) in a round-bottom flask at room temperature. The yellow solid product formed immediately. After filtration, the product **A** was washed by methanol and water, dried in vacuum. Yield: 2.33 g (85 %). Anal. calcd. (%) for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found (%): C, 78.53; H, 5.41; N, 10.46. ^{1}H NMR: (400 MHz, CD_3COCD_3), δ (ppm): 7.15 (s, 1H), 7.57-7.61 (t, *J* = 7.6 Hz, 2H), 7.67-7.71 (t, *J* = 7.6 Hz, 1H), 7.78-7.80 (d, *J* = 8.4 Hz, 2H), 7.82 (s, 1H), 7.88 (s, 1H), 7.98-8.02 (d, *J* = 15.6 Hz, 1H), 8.05-8.07 (d, *J* = 8.4 Hz, 2H), 8.17-8.19 (d, *J* = 7.6 Hz, 2H), 8.40 (s, 1H). IR (KBr, ν_{max}, cm^{-1}): 653 (s),

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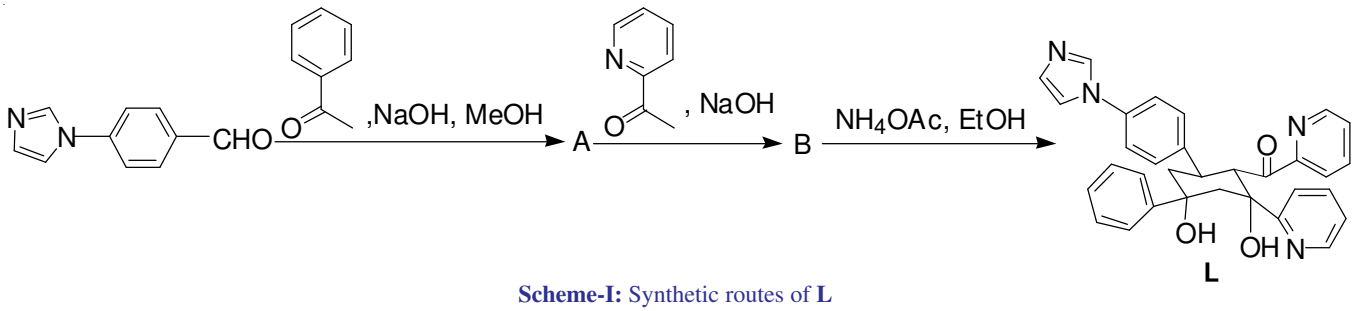

Scheme-I: Synthetic routes of **L**

699 (s), 727 (m), 778 (s), 832 (s), 985 (s), 1019 (m), 1058 (s), 1108 (m), 1185 (m), 1219 (s), 1308 (s), 1336 (s), 1486 (m), 1552 (s), 1574 (s), 1600 (s), 1663 (s), 3093 (s). MS (EI) (*m/z*): Calcd. for $C_{18}H_{14}N_2O$: 274.11 $[M]^+$; found: 274.11 $[M]^+$.

A (2 g, 7.3 mmol), acetylpyridine (0.88 g, 7.3 mmol) and NaOH (1.17 g, 29.2 mmol) were placed in a mortar. The mixture was ground for 0.5 h, thin layer chromatographic analysis showed the reaction was completed. Light yellow solid product **B** without purification, NH_4OAc (5.6 g, 7.3 mmol × 10) and ethanol (100 mL) were added to the 150 mL round bottom flask, stirred 10 h, the reaction was completed according to thin layer chromatography analysis. The mixture was cooled and filtered. The product was recrystallized from anhydrous ethanol and got white solid. Yield: 1.71 g (45.0 %). Anal. calcd. (%) for $C_{32}H_{28}N_4O_3$: C, 74.40; H, 5.46; N, 10.85. Found (%): C, 74.85; H, 5.21; N, 10.42. ^{1}H NMR: (400 MHz, DMSO-d_6), δ (ppm): 1.77-1.79 (d, *J* = 12.0 Hz, 1H), 1.98-2.01 (d, *J* = 8.0 Hz, 1H), 2.72-2.78 (t, *J* = 8.0 Hz, 1H) , 3.31-3.33 (d, *J* = 12.0 Hz, 1H), 4.25-4.30 (t, *J* = 6.0 Hz, 1H), 4.81-4.83 (d, *J* = 12.0 Hz, 1H), 5.75 (s, 1H), 6.89-6.92 (*m*, 1H), 7.02 (s, 1H), 7.07-7.12 (t, *J* = 8.0 Hz, 2H), 7.20-7.32 (*m*, 2H), 7.33-7.45 (q, *J* = 8.0 Hz, 6H), 7.52-7.58 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.73-7.75 (d, *J* = 8.0 Hz, 1H), 7.82-7.84 (t, *J* = 8.0 Hz, 1H), 8.12 (s, 1H), 8.35-8.39 (d, *J* = 8.0 Hz, 1H), 8.56-8.60 (d, *J* = 4.0 Hz, 1H). IR (KBr, ν_{max}, cm^{-1}): 689 (m), 739 (m), 771 (m), 816 (m), 858 (m), 893 (w), 965 (m), 1004 (m), 1063 (s), 1105 (m), 1131 (m), 1255 (s), 1298 (s), 1438 (s), 1518 (s), 1587 (s), 1673 (s), 2914 (m), 3080 (s), 3375 (s). MS (EI) (*m/z*): Calcd. for $C_{32}H_{28}N_4O_3$: 516.22 $[M]^+$; Found: 516.22 $[M]^+$.

RESULTS AND DISCUSSION

Synthesis: According to the literature, the highly useful C-C bond formation through Michael addition of acetylpyridine to α,β-unsaturated ketones always forms the diketone using two equivalents of the acetylpyridine[14]. Compound **L** was obtained when 2-acetylpyridine was used excessively in an attempt to prepare terpyridines. The reaction was carried out in the solventless condition described above. As shown in Fig. 1, the structure of 6-phenylimidazolyl-2,4-dihydroxy-2-(pyridine-2'-yl)-4-phenyl(cyclohexanecarbonyl-2')pyridine has been determined from X-ray diffraction data. Raston *et al.*[14] have shown that, when these solvent-based methods are adopted in an attempt to prepare terpyridines, only the cyclohexyl product is isolated from the complex reaction mixture, rather than the target molecule. However, we obtained the different imidazolyl products compared to reference in the solventless conditions[12,15]. The mechanism is still unclear, but the possible reason may be the change of room temperature. In our future work, we will try to prove our proposal by some other electron-rich groups.

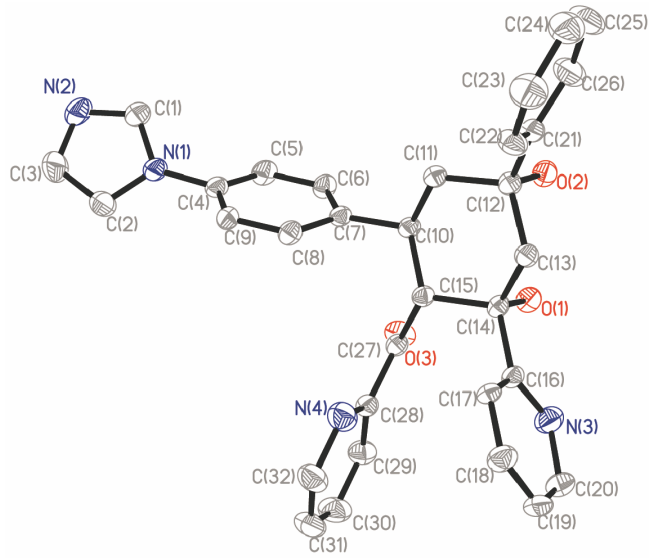

Fig. 1. Molecular structure and atom numbering of **L**. All hydrogen atoms are omitted for clarity

Crystal structure: Hydrogen-bonding geometries of compound are given in Table-1 and details of the crystallographic data are listed in Table-2. The compound is a disubstituted pyridine derivative containing three coordinating sites, which may be a good multidentate ligand.

TABLE-1
HYDROGEN-BONDING GEOMETRY OF COMPOUND **L**

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
C9-H9···O3	0.930	2.429	3.079	126.97
C8-H8···O3	0.930	2.638	3.185	118.24
O2-H2···N2	0.821	1.992	2.798	167.20

The crystal structure of compound **L** (Fig. 1) contains a chair conformation cyclohexane, which increased non-planarity of the molecule. There are one pyridyl, one phenyl, two hydroxyls and 2-acetyl pyridyl which are attached to the cyclohexyl group. Trimer structure of containing intermolecular hydrogen bonds is shown in Fig. 2.

Conclusion

In summary, we have presented synthesis, characterization and crystal structure of a novel pyridyl derivative prepared from a solvent-free reaction. The compound containing a chair conformation cyclohexyl group suggests many new avenues of further

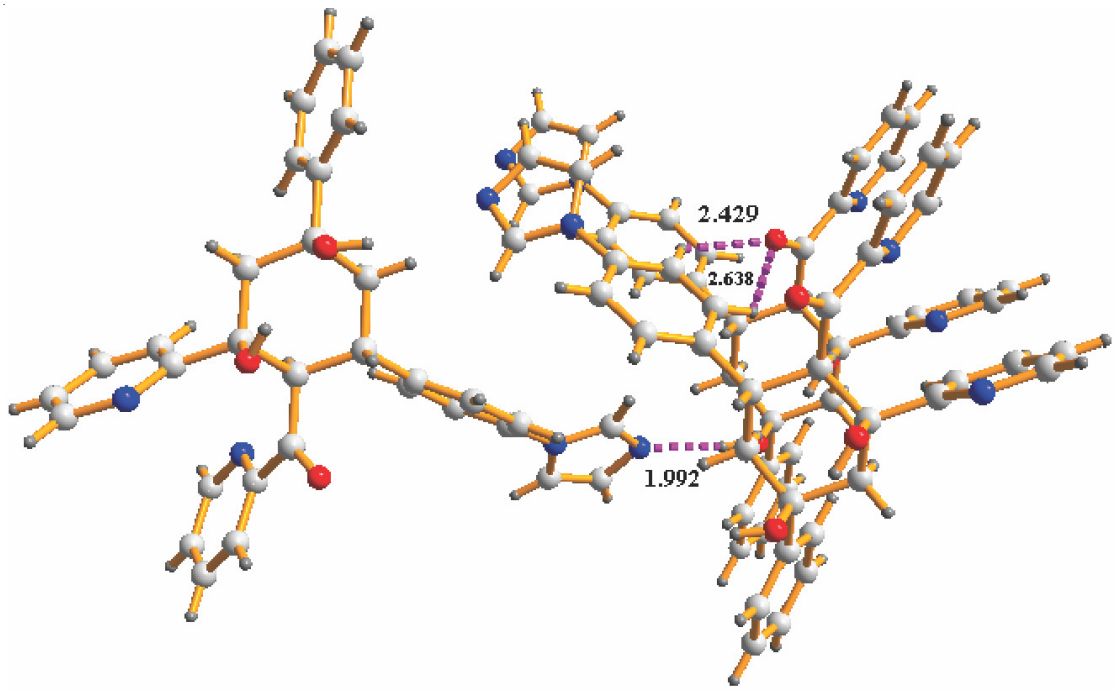

Fig. 2. Trimer structure of **L** containing intermolecular hydrogen bonds (shown as dotted lines)

TABLE-2
CRYSTALLOGRAPHIC DATA FOR **L**

Compound	**L**
Empirical formula	$C_{32}H_{28}N_4O_3$
Formula weight	516.58
Crystal system	Triclinic
Space group	C2
a (Å)	39.642(5)
b (Å)	6.067(5)
c (Å)	11.265(5)
α (°)	90
β (°)	101.277(5)
γ (°)	90
V (Å3)	2657(3)
Z	4
T (K)	298(2)
$D_{calcd.}$ (g cm^{-3})	1.291
μ (mm^{-1})	0.085
θ range (°)	1.44-27.470
Total No. of data	6111
No. unique data	3344
No. params refined	354
R_1	0.0532
wR_2	0.1555
GO_F	1.031

study, which has potential application as a building block in supramolecular chemistry due to two pyridyls as two coordination sites.

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