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Synthesis, NMR and Single Crystal analysis of Novel 2,9-dimethyl-4,7-diphenyl[1,10]phenanthrolinediium

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Abstract
2,9-dimethyl-4,7-diphenyl[1,10]phenanthrolinediium was made available by acidifying of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline in ethanol solvent using conc. HCl as acid. The bi-protonation of pyridine in phenanthroline was monitored by ^{1}H NMR and confirmed by X-ray single crystal, XRD structure of desired product was found to be a Monoclinic crystal system with C2/c1 space group and Z = 6.

Keywords: Phenanthrolinediium, phenanthroline ligand, NMR, XRD.

1. Introduction
The design and synthesis of functional 1,10-phenanthroline derivatives having more delocalized bi -systems *via* the ring-extension reactions are fascinating areas of research owing to their important and promising applications in chemistry, physics, material and biological sciences [1,2]. However, most of the reported investigations concern the symmetric 1,10-phenanthroline-based compounds prepared from the halogen substituent at different positions [3-5]. Moreover, Phenanthroline and its derivatives considered to be among the most frequently bi-dentate chelating ligands [6-13]. Metals complexes of phenanthroline ligands are of interest to a variety of researchers because of their use in molecular scaffolding in supramolecular assemblies, DNA cleaving, structural studies, building blocks for synthesis of metallo-dendrimers, thin films with luminescent properties, control of redox properties, analytical chemistry, and catalysis [14-17]. M–phen complexes are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA [17–25]. The metals and the ligands in these complexes can be readily varied to facilitate individual applications, thus enabling easy understanding of the details of DNA-binding and cleavage [19–24].

As a part of our ongoing studies on the synthesis of novel ligands and their coordination transition metal complexes for structural, medicinal, and catalytic applications [26–31], 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ligand was bi-protonated in acidic medium to prepare 2,9-dimethyl-4,7-diphenyl[1,10] phenanthrolinediium, the structure was characterized in the base of H-NMR and XRD.

2. Experimental
2.1 Materials
All reactions were carried out in an inert atmosphere (argon) by using standard high vacuum, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ligand was purchased from Across and used as it is.

2.2. Instrumentation
High-resolution ^{1}H-NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. Frequencies are as follows: ^{1}H NMR 250.12 MHz. Chemical shifts in the ^{1}H-NMR spectra were measured relative to partially deuterated solvent peaks which are reported relative to TMS.

2.3 X-ray structural analysis of the 2,9-dimethyl-4,7-diphenyl[1,10]phenanthrolinediium

Crystallographic details obtained from determination of the structure of the complex are summarized in Table 1. The X-ray data for the crystal of the 2,9-dimethyl-4,7-diphenyl[1,10]phenanthrolinediium, colorless, were collected on an Xcalibur E goniometer with enhanced X-ray source and Eos CCD detector, graphite monochromated Mo Ka radiation (k = 0.71073 A°). Five x-scans with a total of 350 frames were acquired at 293 K. Data collection, evaluation of cell parameters, data reduction, and absorption were performed by use of CrysAlisPro version 1.171.35.11 (release 16-05-2011 CrysAlis171.NET; Agilent Technologies). Structure was determined by use of SHELXL software [32]. The structure was solved by direct methods and refined by full-matri least-squares with anisotropic temperature factor, for the non-hydrogen atoms. The hydrogen atoms were positioned constrained with isotropic thermal parameters 1.2 times those of the riding atoms.

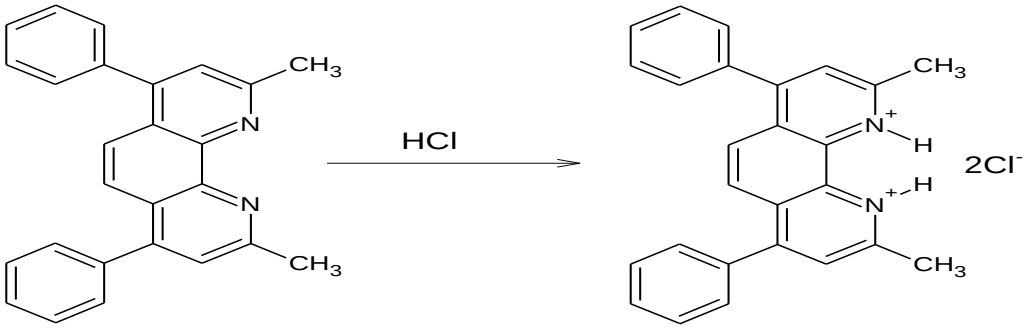
Table 1 Crystal data and structure refinement for the 2,9-dimethyl- 4,7-diphenyl[1,10]phenanthrolinediium

($C_{26}H_{22}N$)	2,9-dimethyl-4,7-diphenyl[1,10]phenanthrolinediium
M_r = 543.39	D_x = 1.413 Mg m^{-3}
Monoclinic, *C*2/*c*	Melting point: 397 K
Hall symbol: ?	Mo *K*α radiation, λ = 0.7107 Å
a = 16.489 (2) Å	Cell parameters from 945 reflections
b = 10.7116 (10) Å	θ = 3.2–29.1°
c = 11.4845 (12) Å	μ = 0.72 mm^{-1}
β = 109.181 (13)°	*T* = 293 K
V = 1915.8 (4) Å^3	$R[F^2 > 2\sigma(F^2)]$ = 0.071
Z = 6	$wR(F^2)$ = 0.216
$(\Delta/\sigma)_{max}$ = 0.002	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}	Least-squares matrix: full
$\Delta\rho_{min}$ = −0.39 e Å^{-3}	Refinement on F^2
($C_{26}H_{22}N$)	2,9-dimethyl-4,7-diphenyl[1,10]phenanthrolinediium
M_r = 543.39	D_x = 1.413 Mg m^{-3}

3. Results and Discussion

3.1 Synthesis of 2,9-dimethyl- 4,7-diphenyl[1,10]phenanthrolinediium

The desired product was isolated in good yield by gentle stirring of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ligand in acidic (conc. HCl) ethanol in the open atmosphere at RT (Scheme 1). The colorless powder product is soluble in water, ROH and insoluble in chlorinated solvents ethers and n-hexane. The structure of the isolated product was deduced from NMR and X-ray single-crystal structure measurements.



Scheme 1. Synthesis of the. 2,9-dimethyl-4,7-diphenyl[1,10]phenanthrolinediium from 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline

3.2 NMR investigation

The ^{1}H-NMR spectra of the desired product together with starting material have been recorded in CD_3OD solution individually. The chemical shifts with integration of the ^{1}H resonances confirm the desired product formation, as in Fig. 1.

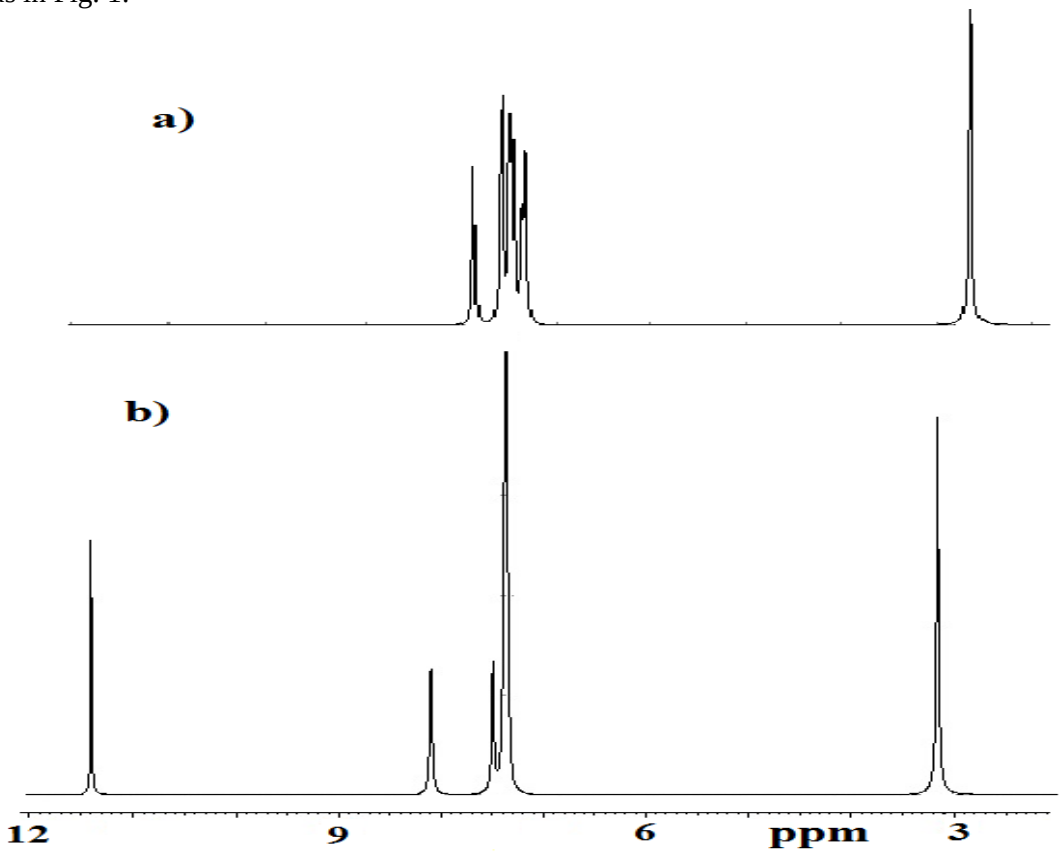


Fig. 1. ^{1}H NMR spectrum of a) 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline free ligand and b) 2,9-dimethyl-4,7-diphenyl[1,10]phenanthrolinediium dissolved in CD_3OD at RT.

The ^{1}H NMR spectrum corroborate the structure of the 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline revealed only two functional group (CH_3 and phenyl) signals at 2.8 and 7-8 ppm respectively, as recorded as in Fig. 1a. By di-hydro of both pyridine in phenanthroline with excess HCl in order to produce 2,9-dimethyl- 4,7-diphenyl[1,10]phenanthrolinediium the chemical shifts of CH_3 (3.3 ppm) and phenyl (7.3-8.2) were shifted toward slightly higher values of chemical shifts due to the protonation, another chemical shift at 11.4 ppm was detected and signed to be for the protonated N atoms in phenanthroline ligand as in Fig. 1b.

3.3 X-ray structural determination of the 2,9-dimethyl- 4,7-diphenyl[1,10]phenanthrolinediium

Solvent-free crystals suitable for X-ray structural analysis were prepared from 2,9-dimethyl- 4,7-diphenyl[1,10]phenanthrolinediium. The molecular structure and packing view are shown in Figs. 2 and 3, respectively, selected bond distances and angles are given in Tables 2 and 3, respectively.

The X-ray single crystal-solved structure of phenanthrolinediium was found to be a Monoclinic crystal system with C 1 2/c 1 space group and Z = 6. The phenanthroline unit is not planar; the dihedral angles between this benzene ring and the other pyridyl rings are 9.62 (4) and 9.31 (4) The crystal packing is stabilized by H-N hydrogen bond, π to π centroid–centroid interactions between two phenanthroline ring systems were not detected. No Cl^- anions were detected in the backbone of the phenanthrolinediium product.

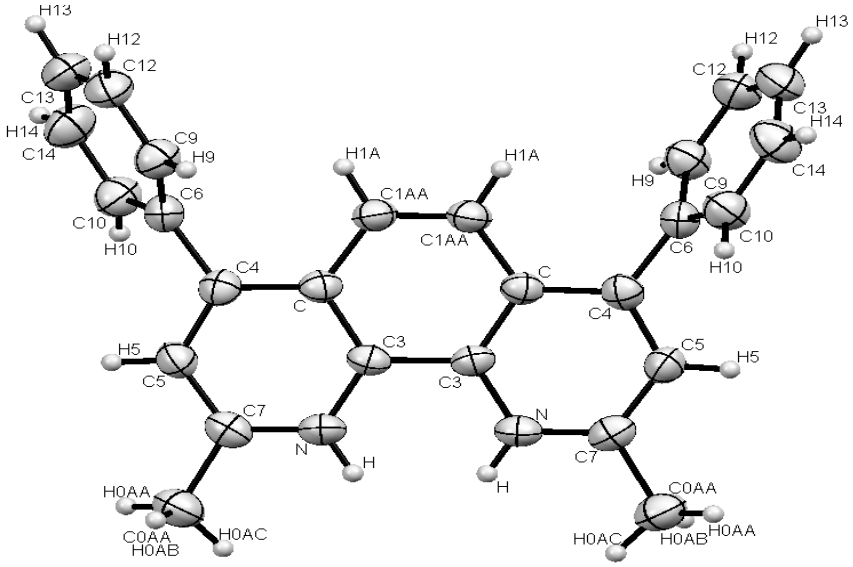


Fig. 2. Molecular structure of the 2,9-dimethyl- 4,7-diphenyl[1,10]phenanthrolinediium, with atom labeling. Thermal ellipsoids are drawn at the 50% probability level

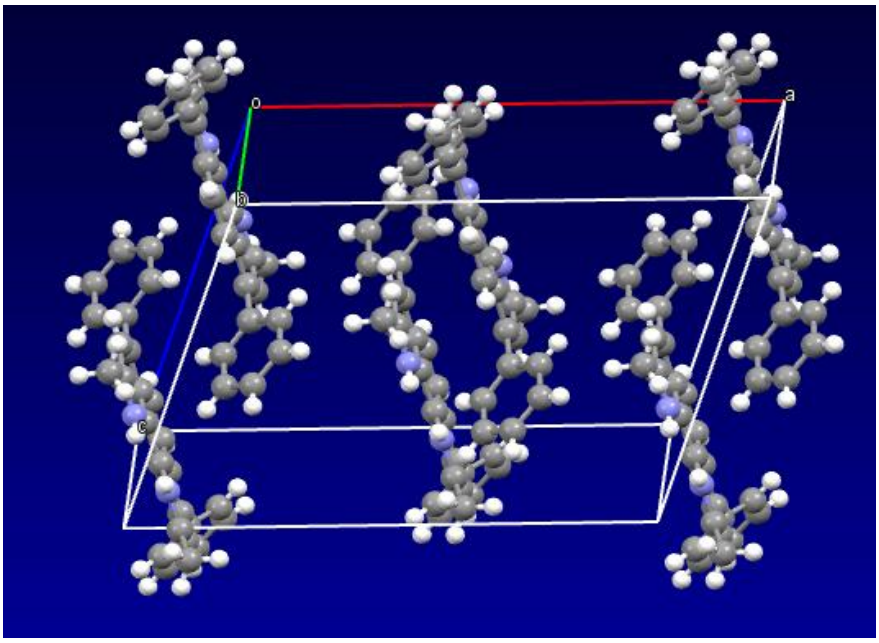


Fig. 3. View of packing the 2,9-dimethyl- 4,7-diphenyl[1,10]phenanthrolinediium chains extending along the a axis.

Table 2 Selected bond distances (A°) of the 2,9-dimethyl- 4,7-diphenyl[1,10]phenanthrolinediium

Bond Type	bond distance	Bond Type	bond distance
N—C3	1.352 (3)	C6—C9	1.392 (4)
N—C7	1.322 (3)	C6—C10	1.390 (4)
C—C3	1.416 (3)	C7—C0AA	1.502 (4)
C—C4	1.424 (3)	C9—C12	1.379 (4)
C—C1AA	1.430 (3)	C10—C14	1.383 (4)
C3—C3^{i}	1.457 (5)	C12—C13	1.380 (4)
C4—C5	1.369 (3)	C13—C14	1.368 (4)
C4—C6	1.489 (3)	C1AA—C1AA^{i}	1.339 (5)
C5—C7	1.396 (4)		

Table 3 Selected angles (°) of the 2,9-dimethyl- 4,7-diphenyl[1,10]phenanthrolinediium

Angle type	Angle value	Angle type	Angle value
C7—N—C3	119.1 (2)	C10—C6—C4	120.1 (2)
C3—C—C4	117.7 (2)	C10—C6—C9	118.3 (2)
C3—C—C1AA	118.9 (2)	N—C7—C5	121.9 (2)
C4—C—C1AA	123.3 (2)	N—C7—C0AA	117.5 (2)
N—C3—C	122.3 (2)	C5—C7—C0AA	120.6 (2)
N—C3—C3^{i}	118.44 (14)	C12—C9—C6	121.0 (3)
C—C3—C3^{i}	119.26 (14)	C14—C10—C6	120.2 (3)
C—C4—C6	121.5 (2)	C9—C12—C13	119.7 (3)
C5—C4—C	117.6 (2)	C14—C13—C12	120.0 (3)
C5—C4—C6	120.9 (2)	C13—C14—C10	120.7 (3)
C4—C5—C7	121.2 (2)	C1AA^{i}—C1AA—C	121.68 (14)
C7—N—C3	119.1 (2)	C10—C6—C4	120.1 (2)
C3—C—C4	117.7 (2)	C10—C6—C9	118.3 (2)

Symmetry code: (i) $-x+1, y, -z+1/2$.

Conclusions

Novel bi-protonation of both pyridine in 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline was carried out in mild acidic condition, the process was monitored by ^{1}H-NMR, the structure of desired 2,9-dimethyl-4,7-diphenyl[1,10]phenanthrolinediium was confirmed by X-ray single crystal.

Supplementary material

Crystallographic data for the structures of **2** have been deposited at the Cambridge Crystallographic Data Center (CCDC 948766). Copies of this information may be obtained from the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Tel.: +44 1223 762910; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or on the web www: http//www.ccdc.cam.ac.uk/deposit.

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