

## Synthesis and X-ray structure Analysis of Schiff base compound;(1E,1E')-N,N'-(naphthalene-1;5-diyl)bis-(1-phenylmethanimine)

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**ABSTRACT:** (1E,1E')-N,N'-(naphthalene-1;5-diyl)bis-(1-phenylmethanimine)(1-EPI) crystallizes in the monoclinic  $P2_{1/c}$  space group with unit cell parameters,  $a = 8.7095(5) \text{ \AA}$ ,  $b = 13.3084(7) \text{ \AA}$ ,  $c = 8.1167(5) \text{ \AA}$  and  $z=2$ . The crystal structural data were collected using a CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018). The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares procedures to the final  $R1$  of 0.0453, using SHELXL programs. The 3D-crystalline network of this compound is stabilized essentially by weak CH/ $\pi$  type hydrogen bonds

**Keywords:** Schiff base; X-ray structure; CH/ $\pi$  hydrogen bonds

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### I. INTRODUCTION

Schiff bases synthesized from the reaction between any primary amine and an aldehyde or a ketone [1], are shown to have significant importance and a wide range of applications. Schiff bases are recognized by the presence of an imine or azomethine group (C=N), formed by the condensation reaction between an amine and a carbonyl compound. Azomethine or imine groups are present in various natural derived or artificial compounds [2, 3] and such compounds are shown to have significant biological effects [4, 5]. In reality, Schiff bases are known to exhibit a broad range of biological activities including anti-inflammatory, anti-pyretic, anti-malarial, anti-fungal, anti-viral and anti-bacterial properties [6-9]. The synthesis and analysis of the solid state structure of our compound will be presented in the case of the extension of our study on the structural characterization of diamine schiff-based compounds.

### II. EXPERIMENTAL

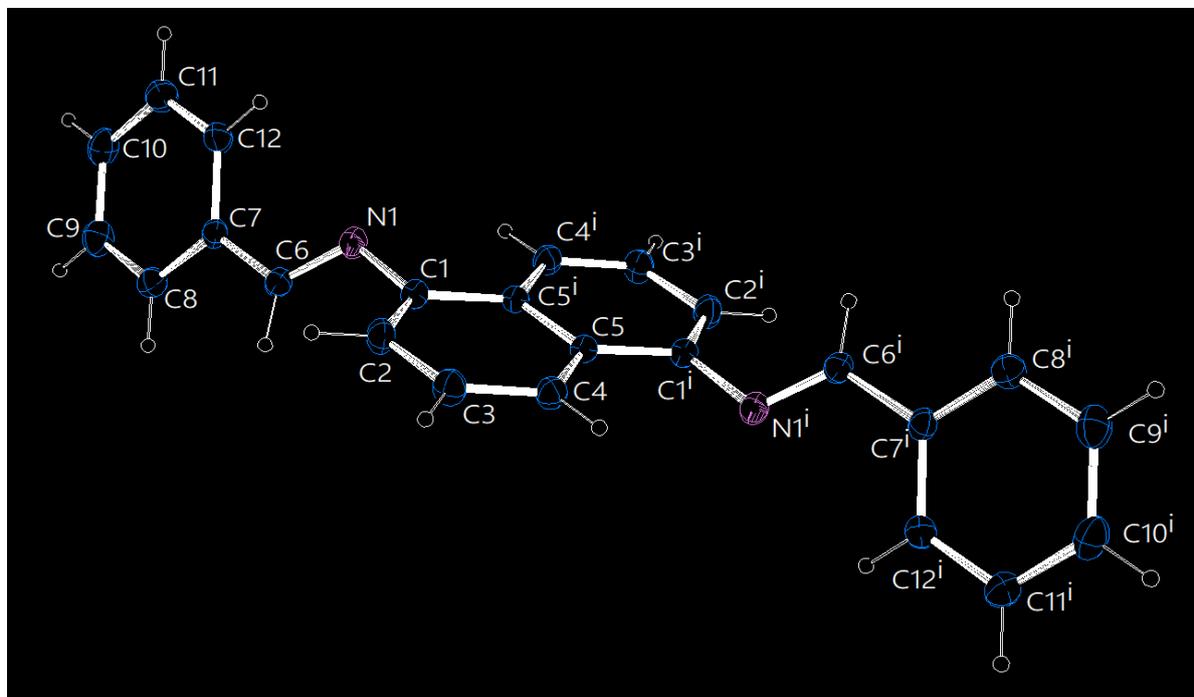
#### 2.1. General

The <sup>13</sup>C NMR and <sup>1</sup>H NMR analyzes were all carried out at Montreal Canada Methodology and Synthesis Laboratory for Natural Products on a Bruker-Avance apparatus 200 MHz. Mass spectroscopy was performed at Laboratoire de Pharmacognosie de la Faculté de Pharmacie of Châtenay-Malabry (France). Mass spectra in ESI were recorded on one device: TOF LCT Premier (WATERS) coupled with HPLC Alliance 2695 (Waters). The software used for data analysis is the Masslynx. The single-crystal X-ray diffraction study method were carried out at the Institut de Chimie des Substances Naturelles (Gif sur Yvette, France) using a CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018).

#### 2.2. Synthesis of (1E, 1E')-N,N'-(naphthalene-1;5-diyl)bis-(1-phenylmethanimine)(1-EPI)

Benzaldehyde (19.6 mmol) and 1,5-diaminonaphthalène (9.79 mmol) were dissolved in ether (30 mL) and the mixture was continuously stirred at room temperature for six days to give a resulting pale yellow precipitate. The precipitate was filtered, washed several times in acetone and air dried to obtain pure colourless

(1E,1E')-N,N'-(naphthalene-1;5-diyl)bis-(1-phenylmethanimine) product (Rf: 0.83 in hexane/acétate d'éthyl (50; 50), showed in Fig. 1. A significant amount of the colorless single crystals product was obtained by the slow evaporation of chloroform solvent after 7 days. <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) ppm 160, 149.1, 137.1, 132.3, 129.8, 125, 122, 113. The <sup>1</sup>H NMR spectra exhibit signals at 8.52 ppm attributed to iminic proton CH=N. The multi-signals within the 8.30-7.20 ppm range are assigned to the aromatic protons. Mass (ESI) m/z (relative intensity): 335 [M+H]<sup>+</sup>.



**Figure 1:** Molecular structure of 1-EPI with atomic numbering scheme. (Displacement ellipsoids are drawn at 20% probability level).

### 2.3. X-ray crystal determination

X-ray diffraction studies of single crystals schiff base compound (1-EPI) were realized . Three dimensional intensity data of the solid-state structure were collected with the help of a CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018). The structure was resolved by direct methods and refined on F<sup>2</sup> by full-matrix least-squares procedures using the SHELXL programs [10]. All the non-hydrogen atoms were refined using isotropic and later anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined and the images were created with ORTEP [11]. In Table 1 are presented the X-ray Crystallographic data.

**Table 1:** Crystal data collection and structure refinement parameters.

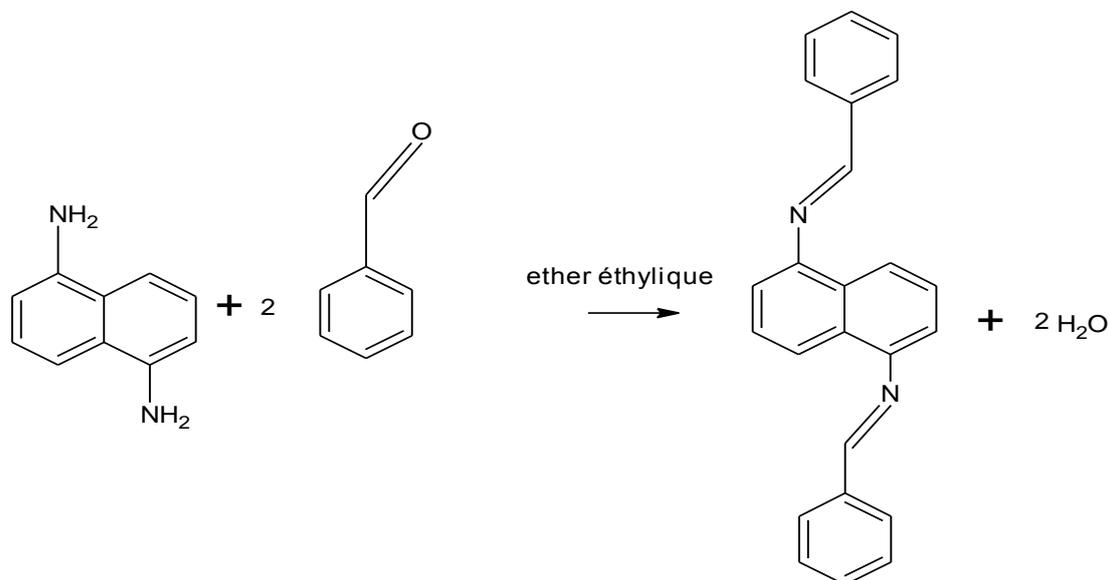
Crystal data	Parameters
Empirical formula: C <sub>24</sub> H <sub>18</sub> N <sub>2</sub>	18530 observed reflexions
Formula weight: 334.40	2456 independante reflexions
Temperature : 293(2)K	119 parameters, F(0 0 0) : 352
X-ray: MoK $\alpha$ ; $\lambda$ = 0.71073Å	Index ranges (h, k, l) -12~11 ; -18~18 ; -11~11
Crystal system: monoclinic	Theta range for data collection: 4.280° ≤ $\theta$ ≤ 30.135°
Space group : P 2 <sub>1</sub> /c	Absorption coefficient ( $\mu$ ) : 0.073 (mm-1)
a = 8.7095 (5)Å	Goodness of fit : 1.089
b = 13.3084 (7)Å	Refinement on F <sup>2</sup>
c = 8.1167 (5)Å	Final R indices [I > 2 $\sigma$ (I)]: R1 = 0.0453 wR2 = 0.131
$\alpha = \gamma = 90^\circ$ ; $\beta = 108.652(6)$	R indices ( all data ) : R1 = 0.1247 wR2 = 0.0561
V = 891.39(9)Å <sup>3</sup>	Maximum; minimum $\Delta\rho$ (eÅ-3) : 0.14 ; -0.20
D <sub>calc</sub> = 1.246Mg m <sup>-3</sup>	CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018)
Z = 2	Structure determination: SHELXS-2018

Where  $w = 1 / [s^2 + (0.0699P)^2 + 0.0720P]$  with  $P = (Fo^2 + 2Fc^2) / 3'$

### III. RESULTS AND DISCUSSION

#### 3.1. Chemistry

Schiff base compound (1E,1E')-N,N'-(naphthalene-1;5-diyl)bis-(1-phenylmethanimine) , was synthesized from the condensation of benzaldehyde and 1,5-diaminonaphthalène in Diethyl ether at room temperature (in scheme 1), followed by slow evaporation of the chloroform solvent after 7 days to obtain colorless single crystals. Mass spectrum (ESI) of 1-EPI compound shows a peak at  $m/z$  335  $[M+H]^+$ , which allow us to propose  $C_{24}H_{18}N_2$  as formula.



**Scheme 1:** Synthesis of (1E, 1E')-N,N'-(naphthalene-1;5-diyl)bis-(1-phenylmethanimine)

The  $^{13}C$  NMR spectra confirmed the presence of the aromatic system by the existence of resonance structure with chemical shifts ranging from 110 - 160 ppm. The signals observed at  $\delta C$  160 ppm correspond to the carbon atoms in the imine group (C6). The  $^1H$  NMR spectra present signals at 8.52 ppm attributed to the imine proton  $CH = N$ . The structure of the schiff base compound (1-EPI) has been fully analyzed using both theoretical calculation data and experimental data, which are in complete agreement. The concordance of the spectral data (MS,  $^{13}C$  NMR,  $^1H$  NMR) and the comparative table, allow us to predict the structure of the 1-EPI to be (1E,1E')-N,N'-(naphthalene-1;5-diyl)bis-(1-phenylmethanimine).

#### 3.2. Crystal Structure of 1-EPI

Bond lengths, valence angles and torsion angles which are some geometric parameters are grouped in Table 2. Since the asymmetric unit of this compound consists of a half-molecule, the Table 3 contains only one half of the values.

**Table 2:** Selected bond lengths and angles ( $\text{\AA}$ ,  $^\circ$ ).

Bond lengths	Angles ( $\text{\AA}$ , $^\circ$ )	Bond lengths	Angles ( $\text{\AA}$ , $^\circ$ )
C1-C2	1.3716(15)	C <sub>6</sub> =N <sub>1</sub> -C <sub>1</sub>	119.29(9)
C2-C3	1.4060(15)	N <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	122.43(9)
C3-C4	1.3652(14)	C <sub>5</sub> -C <sub>1</sub> -C <sub>2</sub>	120.30(9)
C4-C5	1.4144(13)	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	120.65(9)
N1-C1	1.4137(12)	C <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub>	120.58(9)
C5-C5	1.4227(17)	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	120.57(9)
C6-C7	1.4701(13)	C <sub>9</sub> -C <sub>8</sub> -C <sub>7</sub>	120.23(10)
N1=C6	1.2659(13)	C <sub>10</sub> -C <sub>9</sub> -C <sub>8</sub>	120.23(10)
C7-C8	1.3879(15)	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> -C <sub>5</sub>	0.93(16)
C8-C9	1.3861(16)	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	-0.40(16)
N1-C6-C7-C12	-16.26(15)	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	0.09(17)
N1-C6-C7-C8	164.03(10)	C <sub>5</sub> -C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	-0.30(16)

With an average value of about 1.3960 $\text{\AA}$ , the C-C bond lengths of the aromatic ring in 1-EPI (Table 2), are in conformity with the values proposed by Allen et al [12]. The valence angles associated to these aromatic rings do not also undergo major deformations and have values around 120 $^\circ$  characteristic of the benzene ring. Like many Schiff bases [13-16], the two azomethine functions present in our schiff base compound (1- EPI), with

C=N bond lengths of 1.2659(4)Å are significantly shorter than the literature value [17]. In addition, the bond angle; C<sub>1</sub>-N<sub>1</sub>=C<sub>6</sub> [119.29(9)°], (Table 2) are congruent with their SP<sup>2</sup> hybridization characters. The value of the torsional angle N<sub>1</sub>-C<sub>6</sub>-C<sub>7</sub>-C<sub>12</sub> observed, indicates that the mean planes formed by the six carbon atoms C<sub>7</sub> to C<sub>12</sub> of aromatic nucleus on the one hand and the four central atoms C<sub>7</sub>, C<sub>6</sub>, N<sub>1</sub>, C<sub>1</sub> that bridge the two cycles on the other hand, are not coplanar. The various mean planes are defined in Table 3 for the rest of the description of this structure.

**Table 3:** Mean planes

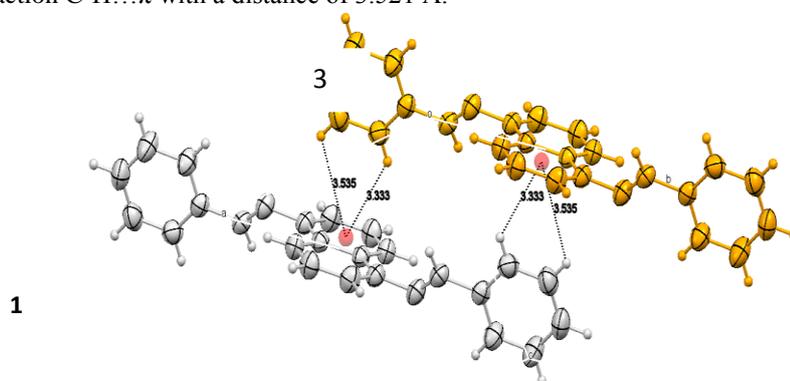
Plane	Atoms defining each plane
I	C <sub>1</sub> , C <sub>2</sub> , C <sub>3</sub> , C <sub>4</sub> , C <sub>5</sub>
II	C <sub>7</sub> , C <sub>8</sub> , C <sub>9</sub> , C <sub>10</sub> , C <sub>11</sub> , C <sub>12</sub>
III	C <sub>1</sub> , N <sub>1</sub> , C <sub>6</sub> , C <sub>7</sub>

**Table 4:** Dihedral angles between mean planes (°)

	I	II	III
I	0	70.79	53.82
II		0	16.08
III			0

The relative orientations of the different mean planes are revealed in Table 4. Analysis of this table shows that the plane II deviates the most from the median plane of the double aromatic nucleus with a deviation angle of 70.79°, while plane III deviate by an angle of 53.82°. Between planes II and III the dihedral angle is about 16.08°. The tow hand of the molecule are in parallel plane. It is the same thing for the four central atoms C<sub>7</sub>, C<sub>6</sub>, N<sub>1</sub>, C<sub>1</sub> that bridge the two cycles on the other hand. This molecule possess a remarkable central symmetric.

In the centrosymmetric dimer consisting of the molecule 1(x,y,z) and 3(-x,-y,-z) showed in Figure 2, the hydrogen atom H8 and H9 of molecule 1 points to the aromatic nucleus of molecule 3 with a length of 3.333Å and 3.535Å respectively and with linearity angle of 134.81°C and 125.34°C as indicate in Table 5. The molecule 1(x, y, z) symmetric of molecule 2(-x, ½+y, 1/2- z) with regard to the screw axis parallel to [0,1,0] direction with screw component (0,1/2,0), establishes C-H...π interaction with hydrogen atom H10 and H11 points to the aromatic nucleus of molecule 2 as indicate in Table 5. This C-H...π (arene) interaction, although weaker in strength is conform to weak hydrogen bond compared to those reported by other authors [18-20], their combine effect contribute significantly to the stability of the 3-D crystal network in this direction. Compare to the N,N'-bis(4-nitrophenylmethylene)cyclohexane-1,2-diamine [21], a high interaction C-H...π has been found with a distance of 2.655 Å. But the N,N'-bis(3-nitrophenylmethylene)cyclohexane-1,2-diamine [22] show less interaction C-H...π with a distance of 3.521 Å.



**Figure 2:** C-H...π(arene) interaction between 1 and 3.

**Table 5:** Intermolecular interaction (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
C8-H8...π(i)	0.93	3.333	4.042	134.81
C9-H9...π(i)	0.93	3.535	4.143	125.34
C10-H10...π(ii)	0.93	3.326	3.967	128.02
C11-H11...π(ii)	0.93	3.315	3.962	128.58

Symmetry code (i) - x,-y,-z; (ii) x, ½+y, 1/2-z



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