



## Structure-directed functional properties of symmetrical and unsymmetrical Br-substituted Schiff-bases



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### HIGHLIGHTS

- Very similar low molecular Schiff bases show different solution and solid state optical, electrochemical and thermic properties.
- The presence of a CH<sub>3</sub> group on the aromatic increase the energy gap which hinder the electronic transitions.
- The introduction of a methyl unit as a bulky group induce large intermolecular distances in the crystal packing.

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### ABSTRACT

This study deals with the investigation of two low molecular weight Schiff base compounds with bromine end groups, differing only by the presence or absence of one methyl group, with the aim of better understanding the solution and the solid state optical, electrochemical and thermic properties generated by the small structural features. The compounds were structurally characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and FTIR spectroscopies, single-crystal X-ray diffraction and gas chromatography analysis. Their thermal behavior was evidenced by polarized light microscopy and differential scanning calorimetry. The single crystal structure of the compounds reveals the versatility of bromine substituents which can adopt an attractive or repulsive electron effect, driven by the structural environment. A comparison of the structures shows that the introduction of a methyl unit as a bulky group hinders completely the  $\pi$ - $\pi$  stacking interaction within the structural rows, inducing larger intermolecular distances resulting in quite different functional physical and chemical properties.

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### 1. Introduction

Schiff-bases compounds containing one or more CH=N imine bonds are intensely studied due to their large spectrum of physico-chemical properties: ability to form various coordination complexes, high thermal stability, semiconducting, liquid crystal, optical, therapeutic properties. As a consequence of their well-organized structures, all these features make them useful as thermo resistant materials, pharmaceutical products, or organic substrates in electronic and opto-electronic devices [1–5]. The easily processable imine bonds [6] provide a direct access to complex systems like double helices [7], grids [8], borromean rings [9], dynamic polymers [10], capsules [11], polygons [12], etc. The self-organization of constitutional systems [13] resulting from reversible connectivity (molecular level) [14] and self-assembly (supramolecular level) [15] of subcomponents under the pressure of internal and external

structural factors, is also endowing dynamic features for this type of compounds. Moreover, Schiff bases can give rise to extended conjugated platforms with unique optical, electronic and thermic properties. Depending on their molecular structure and composition, they can exist in various crystalline phases and only slight structural modifications can induce interesting modulation of functional properties.

On the other hand, recent studies reveal the benefit of the halogen bonding in the crystal state which lead to impressive electronic performances that is amplifying triplet generation and activating triplet emission [16]. The Br atom is almost inert from an electronic point of view due to two antagonistic electronic effects: a donor electronic effect due to the lone pair donor 4p orbital and a withdrawing effect due to a vacant 4d orbital acting as a weak electron acceptor [17]. Moreover, the Br moieties can be easily used as anchoring sites for further Suzuki coupling reactions [18,19].

In this context, we present here two examples of Schiff-bases prepared under mild reactional conditions, containing two bromo-phenyl moieties connected via an imine bond, combined with

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the existence of a methyl substituent in one compound rendering unsymmetrical and influencing the planarity of the resulted bis-aromatic conjugated scaffold. It results quite different solid state optical and thermic properties generated by such small structural differences.

## 2. Experimental section

### 2.1. Materials and methods

4-Bromoaniline (97% purity), 4-bromobenzaldehyde (99% purity), 4-bromo-3-methylaniline (99% purity) purchased from Aldrich were used as received. The gas chromatograms were performed using an Agilent Network GC System 6890N instrument.

The infrared (IR) spectra were recorded on a FT-IR Bruker Vertex 70 Spectro-photometer in the transmission mode, by using KBr pellets.

The proton nuclear magnetic resonance ( $^1\text{H}$  NMR) and carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded by a BRUKER Avance DRX 400 MHz spectrometer using  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as internal reference. Chemical shifts are reported in parts per million (ppm).

The elemental analysis was realized on an elemental analyzer CHNS 2400 II Perkin Elmer.

The UV–vis absorption and photoluminescence spectra were recorded on a Carl Zeiss Jena SPECORD M42 spectro-photometer and Perkin Elmer LS 55 spectrophotometer respectively, in very diluted DMF solutions ( $\cong 10^{-5}\%$ ) using 10 mm quartz cells fitted with poly(tetrafluoroethylene) stoppers.

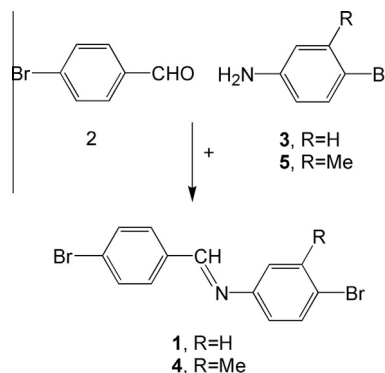
The thermal analysis was performed by using an Olympus BH-2 polarized light microscope equipped with a THMS 600/HSF91 heating stage. The optical observations were performed by using clean untreated glass slides. The differential scanning calorimetry (DSC) measurements were performed with a METTLER Toledo STAR system, under nitrogen atmosphere (nitrogen flow 120 ml/min, sample mass 3–4 mg). The transition temperatures were read at the top of the endothermic and exothermic peaks.

Wide angle X-ray diffraction measurements (WAXD) were performed on a Bruker D8 Advance diffractometer, using Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.1541$  nm). An MRI-WRTC – temperature chamber (with nitrogen inert atmosphere) and an MRI-TCPU1 – temperature Control and Power Unit were used. The working conditions were 36 kV and 30 mA. The measuring angular range was  $1.5\text{--}60^\circ$  in  $2\theta$ . The samples for X-ray measurements were powders obtained by grinding single crystals formed by recrystallization from ethanol. All diffractograms are reported as observed. The single crystal diffraction intensities were collected at the joint X-ray Scattering Service of the Pôle Balard of the University of Montpellier II, France, at 175 K using an Agilent Technologies and a Gemini-S diffractometer with  $\text{Mo K}\alpha$  radiation. The structures were solved by *ab initio* (charge-flipping) methods using *SUPERFLIP* [20] and refined by least-squares methods on  $F$  using *CRYSTALS* [21] against  $|F|$  on data having  $I > 2\sigma(I)$ ;  $R$ -factors are based on these data. Hydrogen atoms were located from difference Fourier synthesis, except the hydrogen atom in the  $\text{CH}=\text{N}$  linkage of compound **1** which was placed geometrically. Non-hydrogen atoms were refined anisotropically. The single crystal parameters of the compounds **1** and **4** are given in Table 1.

Cyclic voltammetry (CV) was employed to study the electrochemical behavior of **1** and **4** compounds deposited as thin films from  $\text{CHCl}_3$  solution on the glassy carbon (GC) electrode. The cyclic voltammetry (CV) measurements were performed using AUTOLAB PGSTAT302N system from ECO CHEMIE Utrecht, The Netherlands. The electrochemical studies were carried out in a single compartment electrochemical cell of 3 ml 0.1 M tetrabutylammonium

**Table 1**  
Crystal data for the compounds **1** and **4**.

Compound	<b>1</b>	<b>4</b>
Empirical formula	$\text{C}_{13}\text{H}_9\text{Br}_2\text{N}$	$\text{C}_{14}\text{H}_{11}\text{Br}_2\text{N}$
Space group	$P2_1/c$	$Pbcn$
$a$ (Å)	3.97116(11)	14.5003(8)
$b$ (Å)	5.84810(15)	6.1560(3)
$c$ (Å)	24.8821(6)	28.737(2)
$\alpha^\circ$	90	90
$\beta^\circ$	92.426(2)	90
$\gamma^\circ$	90	90
$V$ (Å <sup>3</sup> )	577.34(3)	2565.2(3)
$Z$	2	8
Size	$0.20 \times 0.25 \times 0.30$	$0.04 \times 0.20 \times 0.35$
$\rho_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.950	1.828
Resolution (Å)	0.73	0.73
Total data	24518	11354
Unique data	1369	2456
$R_{\text{int}}$	0.042	0.051
$\langle \sigma(I) \rangle$	0.0765	0.1004
Parameters	71	154
$R$	0.0236	0.0574
$wR^2$	0.0568	0.1189
GOF	0.9163	1.0443



**Scheme 1.** Synthesis of compounds **1** and **4**.

fluoride/acetonitrile, at room temperature under nitrogen atmosphere, using glassy carbon electrodes purchased from BASi – Bio-analytical Systems, Inc., USA as working electrode, an  $\text{Ag}/\text{AgCl}$  electrode and a platinum wire as reference and auxiliary electrodes. All reported potentials have been read versus  $\text{Ag}/\text{AgCl}$ .

### 2.2. Synthetic procedure for imine-compounds **1**, **4**

The synthesis of the (4-bromobenzylidene)-(4-bromo-phenyl)imine (**1**) has been performed by the acid catalyzed condensation reaction of the 4-bromobenzaldehyde (**2**) with 4-bromoaniline (**3**) (Scheme 1): 5 mmol (0.88 g) of **3** and 4 ml ethanol were placed into a round bottom flask fitted with a condenser, a dropwise funnel, a nitrogen inlet and outlet. A solution of 5 mmol (0.93 g) of **2** in 4 ml ethanol was added slowly, under vigorous stirring, as well as few drops of glacial acetic acid as catalyst. The obtained mixture was gently refluxed overnight. The reaction mixture was kept for 24 h until the crystals grew sufficiently. The crystals of **1** were filtered off, washed and recrystallized from ethanol. Finally, the obtained single crystals were dried under vacuum for 24 h. The yield was 87%. The same experimental protocol has been applied for the synthesis of (4-bromo-3-methyl-benzylidene)-(4-bromo-phenyl)imine **4** from 5 mmol (0.94 g) of 4-bromo-3-methylaniline (**5**) and 5 mmol (0.93 g) of 4-bromobenzaldehyde (**2**). The com-

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