



# The influence of bonding topology on the electronic properties of new Schiff bases containing phenothiazine building blocks



Emese Gal, Luiza Găină, Castelia Cristea\*, Vera Munteanu\*, Luminița Silaghi-Dumitrescu

*\*Babes-Bolyai\* University, Faculty of Chemistry and Chemical Engineering, RO-400028 Cluj-Napoca, Romania*

## ARTICLE INFO

### Article history:

Received 9 October 2015

Received in revised form 19 February 2016

Accepted 15 March 2016

Available online 16 March 2016

### Keywords:

Phenothiazine

Regioisomers

Schiff bases

Microwave assisted organic synthesis (MAOS)

Cyclic voltammetry

Solvatochromism

## ABSTRACT

Series of new heterocyclic Schiff bases enclosing a systematic variation of the azomethine linker position on the phenothiazine building block were advantageously obtained by the microwave assisted condensation of constitutional isomers of 10-methyl-10Hphenothiazine-carbaldehyde with primary aryl-amines (2-aminonaphthalene, 2-aminofluorene, 2- and 3-amino-10-methyl-phenothiazine respectively). Their electronic properties were emphasized by means of UV–Vis absorption/emission spectroscopy and cyclic voltammetry. The phenothiazine chromophore unit appeared responsible for large Stokes shifts of the UV absorption maxima towards emission maxima situated in the visible range (471–597 nm) largely influenced by the variation of the solvent polarity. Cyclic voltammetry experiments emphasized reversible redox processes suggesting the formation of phenothiazinium radical cation species in consecutive steps correlated to the number of phenothiazine units embedded in the molecular structure. The experimental outcomes and computational data simulating the molecular orbitals of the synthesized phenothiazine derivatives were corroborated for a rational understanding of the similarity in the properties of congeners.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

In current research, phenothiazine derivatives appear as documented compounds with manifold facets of biological activity [1–3] and moreover as stimulating candidates with electro-optic properties suitable for applications in the field of materials science, mainly based on their redox-active character and chromophore system finely modulated by multiple substitution patterns of the heterocyclic core. Among other attractive small molecules presenting the advantage of a precise control on functional properties of the materials, several functional dyes containing electron rich phenothiazine units embedded in extended  $\pi$ -electron conjugate systems were synthesized and their structure–property relationships were emphasized in terms of UV–Vis absorption/emission spectroscopy and cyclic voltammetry records. Thus, bridged or directly linked phenothiazine dyads and triads [4,5], oligophenothiazines [6,7], (hetero)aryl ethynylsubstituted-phenothiazines [8], (oligo) phenothiazinyl carbamates [9] and oligomeric ferrocene–phenothiazine systems [10], thienylphenothiazine decorated carbazoles [11] were proved to be highly fluorescent and electroactive compounds. Numerous donor– $\pi$  bridge-acceptor (D– $\pi$ -A) architectures containing phenothiazine as electron donor were designed in the pursuit for suitable properties such as enhanced fluorescence emission and photovoltaic performance

required in dyes sensitized solar cell applications ([12] and references therein).

Schiff bases are versatile compounds easily accessible by the condensation between amines and carbonyl derivatives, a fact that explains the presence of this structural motif in various biologically active compounds, intermediates in organic synthesis, ligands, catalysts, dyes, etc. [13]. Schiff bases containing phenothiazine units were formerly obtained by starting either with aminophenothiazines and aldehydes [14,15], or with phenothiazine-carbaldehydes and various amines or diamines [16–22]. Among the constitutional isomers, phenothiazine-3-carbaldehyde was the mainly employed reactant due to its availability by means of regioselective formylation procedures implying an electrophilic aromatic substitution reaction mechanism governed by the *para* directing effect of the heterocyclic nitrogen atom (e.g. Vilsmeier–Haak formylation [23,24]); a rather tedious access to the other three position isomers of phenothiazine-carbaldehyde [25] made them less appealing as material precursors.

In this work, our research interest concerning synthetic and structural studies on Schiff bases containing phenothiazine units [16,17,19] was continued with new series of Schiff bases prepared by microwave-assisted condensation of constitutional isomers of phenothiazine-carbaldehyde with aromatic primary amines. The effects of a systematic variation of bonding topology on the electronic properties displayed by the phenothiazine core were highlighted for the first time in this study. For a rational understanding of the similarity and dissimilarities in the properties of congeners, the structural and electronic correlations derived from UV–Vis

\* Corresponding authors.

E-mail addresses: [castelia@chem.ubbcluj.ro](mailto:castelia@chem.ubbcluj.ro) (C. Cristea), [vmunteanu@chem.ubbcluj.ro](mailto:vmunteanu@chem.ubbcluj.ro) (V. Munteanu).

absorption/emission spectroscopy and cyclic voltammetry experimental outcomes were corroborated with computational data.

## 2. Experimental part

### 2.1. Materials and methods

#### 2.1.1. Synthesis

Microwave-assisted syntheses were performed in a CEM Discover microwave reactor (300 W maximum power, mono-mode irradiation, pressurized reaction vessel, software control) using 20 mL sealed reaction vessels. All chemicals used were of reagent grade. Flash chromatography was performed on silica gel 60 (particle size 0.032–0.063 mm). Thin layer chromatography was performed on Merck DC Alufolien, silica gel 60 F<sub>254</sub> and components were visualized by UV VL-4LC. The melting points were determined in capillaries with an Electrothermal 9100 instrument.

#### 2.1.2. Spectral measurements

EI-MS spectra were recorded on a GC–MS QP 2010 Shimadzu mass spectrometer and HRMS spectra on Thermo LTQ Orbitrap XL.

NMR spectra were recorded at room temperature on 400 or 600 MHz Bruker Avance instruments. Chemical shifts are expressed in terms of  $\delta$  (ppm) relative to standard tetramethylsilane (TMS).

UV–Vis absorption spectra were recorded in solution with a Perkin Elmer Lambda 35 spectrophotometer. Fluorescence emission spectra were recorded in solution using a Perkin Elmer PL 55 spectrophotometer. Solvents Hexane (Hex), Toluene (Tol), Dichloromethane (DCM), N,N-Dimethylformamide (DMF) and Dimethyl sulfoxide (DMSO) were ACS grade.

The crystallographic data were collected on a Super Nova, (Dual source) Agilent Technologies, Cu at zero, Eos using Cu-K $\alpha$  radiation (2.314 mm<sup>-1</sup>). Using Olex2 [26] the structure was solved with the ShelXS [27] structure solution program using Direct Methods and refined with the olex2.refine [28] refinement package using Gauss-Newton minimization. Crystallographic data (excluding structure factors) for the structure **8** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 1029729 CCDC. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

#### 2.1.3. Electrochemical measurements

Tetrabutylammonium hexafluorophosphate, (TBAPF<sub>6</sub>,  $\geq 99\%$ , Fluka), ferrocene (Fc, 98%, Sigma-Aldrich), silver nitrate (AgNO<sub>3</sub>, 99%, Sigma-Aldrich) were used as received, without further purification. Acetonitrile (CH<sub>3</sub>CN  $\geq 99.9\%$ , water  $\leq 30$  ppm VWR BDH Prolabo Chemicals) was dried over molecular sieves 3 Å (1–2 mm beads, Alfa Aesar). Argon (ultra-high purity, 99.999) was purchased from Linde Gas Group.

Cyclic voltammetry (CV) measurements were performed with a computer controlled Metrohm-Autolab PGSTAT302N potentiostat in a conventional three electrode cell with 2 mm platinum disk working electrode, coiled platinum wire auxiliary electrode and Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub> and 0.1 M TBAPF<sub>6</sub> in acetonitrile) reference electrode. Cyclic voltammograms (CVs) were recorded under argon gas atmosphere in dry acetonitrile solutions containing 0.1 M TBAPF<sub>6</sub> as electrolyte and 0.1 mM substrate. Before each experiment, the Pt disk electrode was polished with 1, 0.3, 0.05  $\mu$ m alumina slurry on a polishing pad, washed thoroughly with distilled water, sonicated in a mixture of ethanol and double-distilled water (1:1) for 3 min and rinsed with acetonitrile.

All redox potentials (half-wave potential, E<sub>1/2</sub>, estimated as the average of anodic and cathodic peak potentials and onset oxidation potential, E<sub>ox,onset</sub> determined from the intersection of the tangents drawn at the faradaic current rise and background current of the CV) were reported vs. Ag/Ag<sup>+</sup> within  $\pm 0.003$  V. Ferrocenium/ferrocene (Fc<sup>+0</sup>)

redox couple was used as an external standard for the calibration of the reference electrode, assessment of the electrochemical reversibility of the studied compounds and for the estimation of HOMO energy levels, assuming Fc<sup>+0</sup> energy level at 4.8 eV under vacuum. In good agreement with literature data, the half-wave potential and the peak potential separation values of Fc<sup>+0</sup> couple were 0.086 V [29,30] vs. Ag/Ag<sup>+</sup> and 0.080 V [31] respectively.

### 2.2. Synthesis

The preparation of the starting regioisomers of 10-methyl-10H-phenothiazine-carbaldehyde was based on previously optimized protocols [25]. Three different series of regioisomeric Schiff bases were obtained by microwave-assisted condensation of phenothiazine-carbaldehydes with naphthalen-2-amine (series **5a–d**), 9H-fluoren-2-amine (series **6a–d**) and phenothiazin-3-amine (series **7a–d**) respectively (Scheme 1).

Scheme 2 presented the preparation of Schiff bases starting from amino-phenothiazines and different aromatic carbaldehydes: phenothiazine-3-carbaldehyde (**8**), *p*-hydroxy-benzaldehyde (**9**) and *p*-methoxy-benzaldehyde (**10**) respectively.

#### 2.2.1.1. General procedure for the microwave assisted synthesis of Schiff bases 5–10

(Hetero)aryl-carbaldehyde (1 mmol) and aromatic primary amine (1 mmol) were solved in acetonitrile (8 mL). The reaction mixture was introduced in a quartz reaction vessel, which was sealed and subjected to microwave irradiation for 30 min at 80 °C. The solvent was evaporated to dryness and the crude product was further purified by recrystallization from ethanol.

#### 2.2.1.2. N-((10-methyl-10H-phenothiazin-1-yl)methylene)naphthalen-2-amine **5a**

Dark green powder (73 mg, 20%), mp 96–97.5 °C;  $\delta_{\text{H}}$  (600 MHz, CDCl<sub>3</sub>) 3.14 (3H, s, CH<sub>3</sub>), 6.75 (1H, d, *J* = 7.0 Hz, H<sub>9</sub>), 6.91 (1H, s, *J* = 6.9 Hz, H<sub>7</sub>), 7.10–7.06 (2H, m, H<sub>3</sub>, H<sub>8</sub>), 7.15 (1H, d, *J* = 6.9 Hz, H<sub>6</sub>), 7.35 (1H, d, *J* = 7.3 Hz, H<sub>4</sub>), 7.42–7.41 (2H, m, H<sub>naph</sub>), 7.50 (1H, d, *J* = 7.5 Hz, H<sub>naph</sub>), 7.55 (1H, d, *J* = 7.5 Hz, H<sub>naph</sub>), 7.75–7.79 (3H, m, H<sub>naph</sub>), 7.96 (1H, s, H<sub>naph</sub>), 9.40 (1H, s, CH=N).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>) 37.5, 113.2, 114.3, 114.9, 117.5, 122.6, 123.3, 124.0, 125, 125.8, 126.9, 127.0, 127.6, 128, 128.2, 128.4, 128.7, 131.5, 132.8, 134.8, 142.2, 144.9, 145.4, 158.4. m/z (EI, 70 eV): 366 (M<sup>+</sup>), 351; HRMS found 367.1261 C<sub>24</sub>H<sub>18</sub>N<sub>2</sub>S requires 367.1263.

#### 2.2.1.3. N-((10-methyl-10H-phenothiazin-2-yl)methylene)naphthalen-2-amine **5b**

Dark brownish green powder (91.5 mg, 25%), mp 66–68 °C;  $\delta_{\text{H}}$  (600 MHz, CDCl<sub>3</sub>) 3.46 (3H, s, CH<sub>3</sub>), 6.70 (1H, d, *J* = 6.7 Hz, H<sub>9</sub>), 6.90 (1H, t, *J* = 6.9 Hz, H<sub>7</sub>), 7.06–7.03 (2H, m, H<sub>1</sub>, H<sub>8</sub>), 7.15 (1H, d, *J* = 6.9 Hz, H<sub>6</sub>), 7.43–7.37 (5H, m, H<sub>3</sub>, H<sub>4</sub>, 3H<sub>naph</sub>), 7.78–7.71 (3H, m, H<sub>naph</sub>), 7.88 (1H, s, H<sub>naph</sub>), 8.39 (1H, s, CH=N);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 150 MHz) 35.6, 113.6, 114.4, 117.5, 119.9, 121, 122.2, 122.6, 123.1, 123.4, 123.7, 125, 126.9, 127, 127.6, 128, 128.1, 130.2, 134.8, 137.3, 144.4, 144.8, 145.8, 158.3; m/z (EI, 70 eV) 366 (M<sup>+</sup>), 351. HRMS found 367.1260 C<sub>24</sub>H<sub>18</sub>N<sub>2</sub>S requires 367.1263.

#### 2.2.1.4. N-((10-methyl-10H-phenothiazin-3-yl)methylene)naphthalen-2-amine **5c**

Yellow powder (128 mg 35%), mp 126–128 °C;  $\delta_{\text{H}}$  (600 MHz, CDCl<sub>3</sub>) 3.41 (3H, s, CH<sub>3</sub>), 6.86–6.83 (2H, m, H<sub>1</sub>, H<sub>9</sub>), 6.97 (1H, t, *J* = 7.2 Hz, H<sub>7</sub>), 7.15 (1H, d, *J* = 7.2 Hz, H<sub>6</sub>), 7.19 (1H, t, H<sub>8</sub>), 7.43–7.42 (2H, m, H<sub>naph</sub>), 7.45 (1H, t, H<sub>7</sub>), 7.57 (1H, s, H<sub>naph</sub>), 7.69 (1H, d, *J* = 8.2 Hz, H<sub>2</sub>), 7.76 (1H, s, H<sub>4</sub>), 7.86–7.83 (3H, m, H<sub>naph</sub>), 8.44 (1H, s, CH=N);  $\delta_{\text{C}}$  (150 MHz, CDCl<sub>3</sub>)  $\delta$  35.7, 113.9, 114.5, 117.8, 121.3, 123, 123.2, 124.1, 125.3, 126.4, 127.1, 127.3, 127.7, 127.8, 128, 129, 129.1, 131, 132,

Download English Version:

<https://daneshyari.com/en/article/217872>

Download Persian Version:

<https://daneshyari.com/article/217872>

[Daneshyari.com](https://daneshyari.com)