



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Solvatochromism of symmetrical 2,6-distyrylpyridines. An experimental and theoretical study



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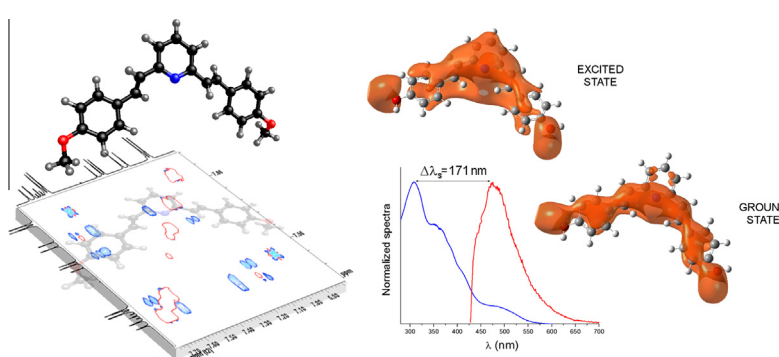
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HIGHLIGHTS

- Synthesis and spectroscopic properties of symmetrical 2,6-distyrylpyridine derivatives are described.
- Population of conformers in solution was estimated by NAMFIS analysis, from NMR data.
- Solvent effects on the UV–Vis spectra are evaluated by the Kamlet–Taft and Catalán LSER models.
- The decomposition of the emission spectra is performed using MCR analysis.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 May 2014

Received in revised form 11 July 2014

Accepted 15 July 2014

Available online 24 July 2014

Keywords:

UV–Vis spectroscopy

Fluorescence spectroscopy

Conformational preferences

ABSTRACT

Seven symmetrical 2,6-distyrylpyridines, phenyl-substituted with hydrogen-bond donors, hydrogen-bond acceptors, halogens and hydrophobic moieties were synthesized and their spectroscopic characterization was done. Solvent effects on the absorption and fluorescence spectra were analyzed and quantified using the Kamlet–Taft and Catalán approach. The obtained results were rationalized by comparison of electrostatic potentials of the molecules in the ground and in excited state and by comparison of the frontier molecular orbitals (HOMO and LUMO), derived from quantum-mechanical calculations (HF, DFT, MP2). Analysis of the results revealed an important influence of non-specific (dispersive) interactions on the solvatochromic behavior of the compounds. 1D and 2D NMR data, *in silico* obtained conformational assembly of the compound, and the NMR analysis of molecular flexibility in solution (NAMFIS), were used to estimate population of conformers and to deconvolute the UV–Vis spectrum of representative derivative; inferring that the conformational assembly is more complex than was assumed in so far published literature data for this class of compounds. Along with this, the emission spectra of the representative compounds were decomposed by the Multivariate Curve Resolution analysis.

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Introduction

Molecules containing the styryl (arylvinylyl) moiety represent one of the most important groups of functional dyes, with a number of favorable properties. These dyes are fluorescent, have higher

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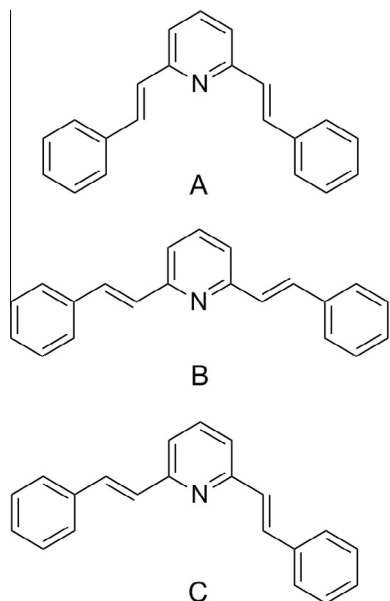


Fig. 1. Schematic representation of preferential conformations of 2,6-distyrylpyridine: *s-cis/s-cis* (A); *s-trans/s-trans* (B); *s-trans/s-cis* (C).

photostability, when compared to classical cyanine dyes, and they can cover the range of the electromagnetic spectrum from the UV to the near infrared region [1]. Styryl dyes are widely used as non-linear optical materials (NLO), optical sensitizers, information recording materials, laser dyes, sensors, two-photon absorption materials, for artificial photosynthesis or photocatalysis [2–6].

2,6-Distyrylpyridine and its derivatives (Fig. 1) have attracted significant attention over the last decade. The physico-chemical properties of these compounds are determined by the existence of the dynamic equilibrium between conformational isomers, which occurs due to the lack of the free rotation of the arylvinyl moieties around the quasi-single bonds with the central pyridine [7]. The preferred conformation of 2,6-distyrylpyridine in solid state is governed by the weak steric interactions between the vinyl hydrogens and the nearby hydrogens of the phenyl or pyridyl rings [8]. *Ab initio* calculations have revealed that among three conformations, conformation A (Fig. 1) is the most stable one, in agreement with the reported crystallographic data. Conformation C is somewhat less stable and conformation B is the least stable [9]. A spectral and photochemical study of 2,6-distyrylpyridine has shown that the relative abundance of different rotamers depends on the solvent used [10]. Its UV–Vis spectra are complex, and reveal the presence of two or three not well-separated electronic transitions. The shape of spectra probably depends on the number and the abundance of rotamers. It is assumed that formation of intramolecular hydrogen bonds stabilizes the sterically favoured, longer lived, rotamer [10].

Pyridinium salts of 2,6-distyrylpyridines exhibit significantly different photophysical properties in comparison with the corresponding neutral forms. Wang et al. have reported that absorption and emission maxima of 2,6-bis(4-dimethylaminostyryl)pyridine are dramatically red shifted upon methylation [11]. They have pointed out that alkylation of the pyridine nitrogen converts this atom to a member of a cyanine array. Increasing the electron-donating ability, number of electron-donating substituents, and the coplanarity of polysubstituted pyridinium molecules is favorable for NLO absorption, especially for saturated absorption at the picosecond pulse [12].

Solvatochromism has been established as an efficient tool to study bulk and local polarity in macrosystems [13–15]. The

solvatochromic comparison methods of Kamlet and Taft [16] and Catalán [17] have been commonly applied to separate effects of non-specific solvent–solute interactions (electrostatic effects) from specific interactions (hydrogen bonding). Recently, it has been demonstrated that a clear and univocal influence of solvent on the position of absorption and fluorescence maxima cannot be obtained using simplified solvation models. A detailed analysis of the static and dynamic aspects of solvation should be taken into account [18].

In this study, we report the set of seven symmetrical 2,6-distyrylpyridines (Fig. 2) substituted with the hydrogen-bond donors and acceptors, bulky hydrophobic moiety and bearing permanently charged fragment. Molecules are able to form hydrogen bonds with the solvent, as well as intramolecular hydrogen bonds, hydrophobic interactions and ion–dipole interactions. Compound 7 is a bent-core mesogen and its liquid crystalline behavior has already been reported [19]. The absorption and emission spectra of the investigated compounds in various solvents have been investigated. Their solvatochromic properties are also described. It is demonstrated that the interpretation of solvent effects on the position of the absorption maxima using both Kamlet–Taft and Catalán models should be taken into consideration cautiously. This is further explained using electrostatic potential of molecules. It is shown that the solvatochromic properties of the investigated molecules originate in greater extent from non-specific solvent–solute interactions (electrostatic effects) than from hydrogen bonding. Furthermore, an analysis of the frontier orbitals and charge distribution, obtained from calculations performed on MP2, DFT and HF level of theory, is described in details.

Experimental part

Synthesis

Compounds 1–7 were obtained following the synthetic protocol shown in Scheme 1. Condensation of 2,6-lutidine with the excess of 4-methoxybenzaldehyde in acetic anhydride at the reflux temperature afforded compound 1. Compounds 2–5 were prepared according to the procedure described by Bergmann and Pinchas [20]. Analogously, condensation of 2,6-lutidine with the excess of substituted 4-hydroxybenzaldehydes in acetic anhydride at the reflux temperature gave rise to 2,6-bis[2-(substituted-4-acetoxyphenyl)ethenyl]pyridine. Subsequent base catalyzed hydrolysis led to compounds 2–5. Compound 6 was synthesized in a reaction between *N*-Me-2,6-lutidinium iodide and 4-hydroxybenzaldehyde in the presence of catalytic amount of piperidine. Compound 7 was obtained by acylation of compound 2 with the corresponding 4-*n*-heptyloxybenzoyl chloride. A detailed description of the experimental procedures and the characterization of reported compounds are given in the Supplementary Material.

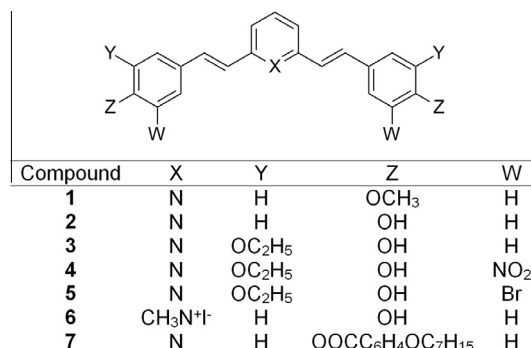


Fig. 2. Schematic depictions of the structure of compounds 1–7.

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