

HETEROCYCLES, Vol. 83, No. 12, 2011, pp. 2769 - 2772. © 2011 The Japan Institute of Heterocyclic Chemistry
Received, 3rd August, 2011, Accepted, 30th September, 2011, Published online, 7th October, 2011
DOI: 10.3987/COM-11-12324

INTRINSIC FLUORESCENCE OF 1,3-BENZOXAZINEPHANES

Rodolfo Quevedo* and Cesar A. Sierra

Chemistry Department, Science Faculty, Universidad Nacional de Colombia, Cra.
30 N° 45-03, Bogotá, Colombia. e-mail address: arquevedop@unal.edu.co

Abstract – A new 1,3-benzoxazine nuclei-based fluorescent system is presented. The photophysical aspects are briefly discussed. The results suggested that the presence of oxazinic methylenes is necessary for fluorescence to be present.

The cyclophanes are macrocyclic compounds containing two or more aromatic rings bounded at their *meta* or *para* positions by means of short spacers.¹ Due to the aromatic rings' high electron density, these macrocycles have interesting properties and great potential as hosts due to their ability to trap guest molecules, mainly through non-covalent interactions such as Van der Waals, π - π , π -cation, ion-dipole, dipole-dipole interactions and hydrogen bonds.^{2,3} In addition to their interesting electron characteristics and molecular topology, the size of the cavity and solubility can be modulated by varying the spacer length and the functionalization of the outside of the cavity on either the aromatic rings or the spacers.^{4,5}

The azacyclophanes (cyclophanes having one or more nitrogen atoms in their structure) represent an interesting group of synthetic receptors combining electron-donor and acid-based properties of nitrogenated heterocycles with the π -interaction capacity of cyclophanes. Combining these properties with their conformational rigidity makes this type of macromolecule potentially interesting in host-guest processes by means of specific interactions.⁶

On the other hand, 1,3-benzoxazines are heterocyclic compounds which are useful in obtaining phenolic resins and exhibit a broad range of pharmacological activities. Such heterocyclic compounds are usually synthesized by Mannich condensation of phenols, amines and formaldehyde.^{7,8}

Our research group has recently developed a simple and efficient method for synthesizing a new family of pentacyclic azacyclophanes formed by two units of 3,4-dihydro-2*H*-1,3-benzoxazine joined by two ethylene bridges (benzoxazinephanes).⁹ Continuing our search for molecules which could be useful for developing fluorescent chemical sensors, this article presents benzoxazinephanes as an attractive fluorophore because of their visible emission from a locally-excited (LE) state. The benzoxazinephanes studied here are compounds having two benzoxazine units located face-to-face in their structure (Figure

1).¹⁰ They were obtained by means of macrocyclization by Mannich condensation of the appropriate 4-hydroxyphenylethylamine and formaldehyde.⁹

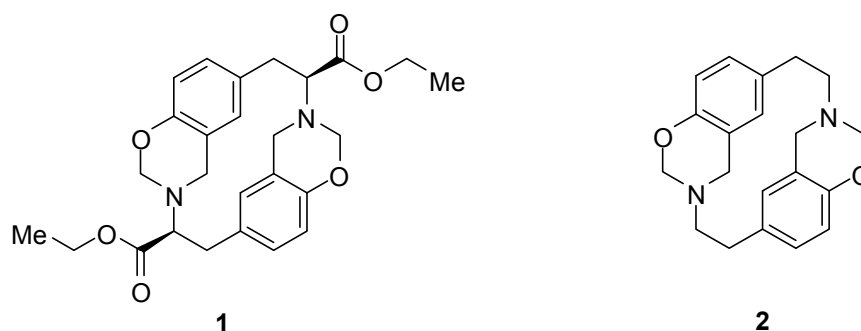


Figure 1. Benzoxazinephanes **1** and **2**

When **1** and **2** were exposed to ultraviolet light at 254 nm in solid state, fluorescence emission was observed by naked human eye (several attempts to make a powder fluorescence spectrum using a solid holder failed due to very low reproducibility of the film and spectrum. An integrating sphere will solve this problem). Such optoelectronic behavior is characteristic of highly conjugated systems but is unexpected in molecules which only have isolated aromatic rings in their structure. Therefore, UV-Vis absorption spectra in solution were taken to explore the photophysical properties of these benzoxazinephanes (Figure 2); these spectra showed similar behavior for **1** and **2** with maximum absorption around 282 nm, but with some differences in intensity due to the presence of ethoxycarbonyl groups in cyclophane **1**. This absorption band is associated with π - π^* intramolecular charge-transfer transitions taking place between the aromatic ring and the substituents, these transitions being expected for substituted aromatic rings in the molecule.

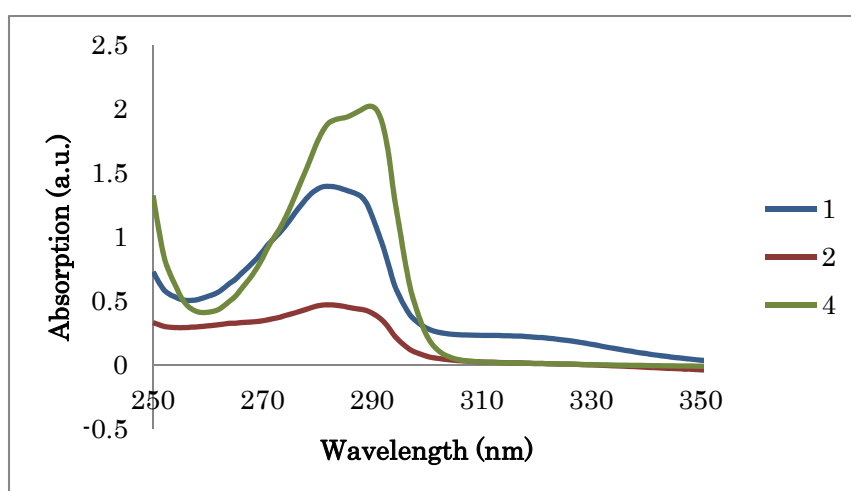


Figure 2. Absorption spectra for **1**, **2** and **4** in chloroform (5×10^{-4} M)

The fluorescence spectra showed dual emission at 310 and 450 nm for compound **1** (quantum yield:

0.0555%) and at 349 and 451 nm for compound **2** (quantum yield: 1.1105%) when it was excited at 282 nm in freshly distilled chloroform as solvent (Figure 3).

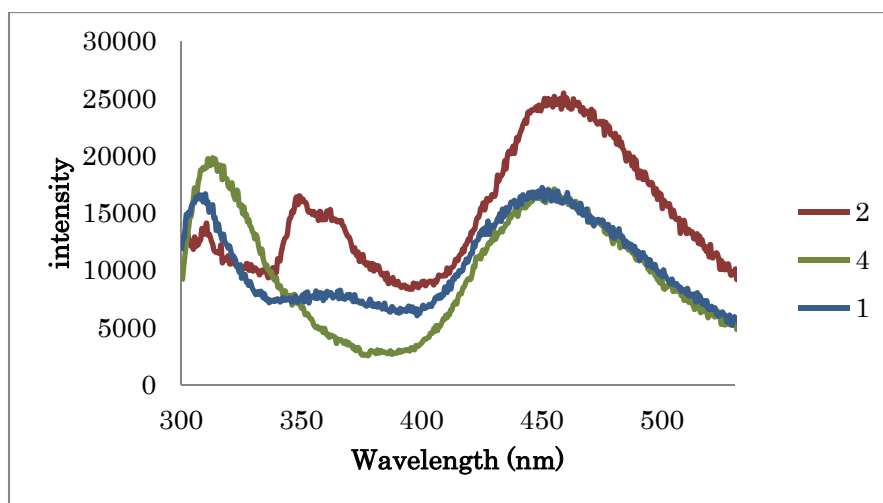


Figure 3. Fluorescence spectra for **1**, **2** and **4** in chloroform (5×10^{-4} M)

Regarding these benzoxazinephanes, it can be proposed that fluorescence comes from intramolecular excimer formation between the singlet excited state of the arene and the heterocyclic ring. To obtain better information about the nature of the excimer formation, the behavior of a tricyclic azacyclophane **3** (Figure 4) formed by two units of *L*-tyrosine joined by two methylene groups was studied. This is an azacyclophane product from removing the oxazinic methylenes and ethyl groups from benzoxazinephane **1**. The UV-Vis absorption spectrum of **3** showed a maximum at 297 nm and as expecting, it did not show fluorescence in solution, thereby indicating that the oxazinic methylene is directly involved in excimer formation and thus, its absence, completely suppressed these azacyclophanes' fluorescent behavior.

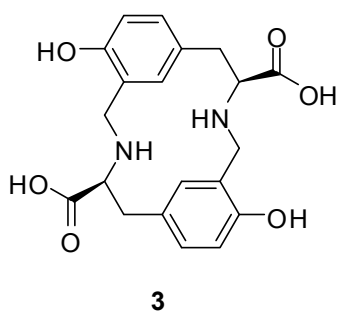


Figure 4. Non-fluorescent tricyclic azacyclophane **3**

To establish whether the benzoxazinephanes' rigid structure is necessary for excimer formation, a lineal compound was synthesized; this has two benzoxazinic nuclei [3,3-ethylene-*bis*-(3,4-dihydro-6-chloro-5,7-dimethyl-2*H*-1,3-benzoxazine)] **4** (Figure 5) in its structure by means of Mannich condensation-based route between ethylenediamine, formaldehyde and 4-chloro-3,5-dimethylphenol.^{7,11} This benzoxazine **4** showed

absorption and emission spectra in solution, similar to that obtained for **1** and **2**, having maximum absorption at 290 nm (Figure 2) and dual emission at 314 and 455 nm (quantum yield: 0.0043 %) (Figure 3), differently from **1** and **2**, in **4** the emission at 314 nm has greater intensity than emission at 455 nm.

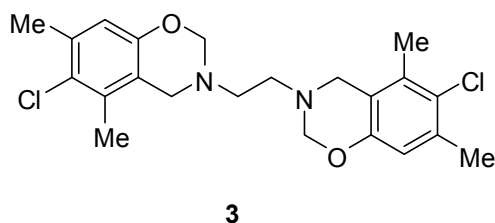


Figure 5. Lineal 1,3-bis-benzoxazine **4**

In summary, this work presents a new 1,3-benzoxazine nuclei-based fluorescent system. The photophysical behavior of compounds **1**, **2**, **3** and **4** suggested that presence of the oxazinic methylenes group is necessary for fluorescence and that the benzoxazinephanes' rigid structure increases emission intensity in the visible region of the spectra.

ACKNOWLEDGEMENTS

The author wish to acknowledge the División de Investigaciones Bogotá (DIB) and the Universidad Nacional de Colombia for providing financial support.

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