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Spectral and structural characterization of 2-(fluorophenylamino)- and 2-(nitrophenylamino)-1,4-naphthoquinone derivatives

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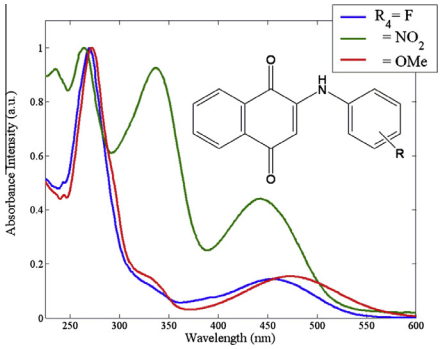
HIGHLIGHTS

- Novel 2-(nitrophenylamino)-1,4-naphthoquinones derivatives were synthesized and characterized.
- Solvent impact on absorbance and emission napthoquinone derivatives is assessed.
- The charge transfer transition is most sensitive to solvent and substituents.
- Quantum calculations confirm the spectral assignments and substituent effects.

GRAPHICAL ABSTRACT

A series of novel 2-(nitrophenylamino)-1,4-naphthoquinones derivatives was synthesized, and their photophysical properties examined using computational and spectroscopic methods.



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ABSTRACT

Naphthoquinone amino derivatives exhibit interesting physicochemical properties and are of interest for potential medicinal purposes. The preparation of novel 2-(nitrophenylamino)-1,4-naphthoquinones derivatives was achieved by reaction of nitroanilines with 1,4-naphthoquinone with a catalytic amount of $FeCl_3$ or by direct nitration of 2-(phenylamino)-1,4-naphthoquinone (PAN). Structural and photophysical properties of a series of NO_2PANs and FPANs derivatives are examined using computational and spectroscopic methods. Absorbance and emission spectra are measured in a range of solvent environments to examine the impact of solvent–solute interactions. Additionally quantum calculations are used to evaluate the electronic nature of the spectral transitions and compare structures of the different PAN derivatives. The lowest energy electronic transitions have charge transfer character, and show the most sensitivity to solvent and substituents. Higher energy π–π^* transitions are relatively insensitive to both factors. Computational predictions are in good agreement with the experimental spectra, and provide molecular-level insight variations amongst the different aniline-substituents.

Introduction

Naphthoquinones are a class of molecules that are naturally occurring chromatic pigments in plants, fungi and some animals, and exhibit potentially useful medicinal properties [1]. They have

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a wide range of biological properties such as significant antimicrobial activity [2]; for example, several plant-derived derivatives have antibacterial effects on some species of aerobic and anaerobic organisms [1]. Antiparasitic [3] and antifungal properties, particularly against species of *Candida*, of naphthoquinones have also been reported [4–7]. Of great potential interest for this type of compounds is their use as anticancer agents with applications in chemotherapy [8].

The biological activity of quinones has been related to their redox properties [9–11] and their capacity to accept one or two electrons to form the corresponding radical-anion ($Q^{\cdot}$) and hydroquinone radical dianion (Q^{2-}). This capacity and several physicochemical properties of a given quinone can be modified by the addition of a substituted aniline to the quinone system [12]. The electron donating or withdrawing properties of the substituents on the aniline modify their redox properties, thereby modifying the ability of the system to exhibit a charge transfer from the substituent to the quinone upon photo-excitation [13].

Several studies of these molecular systems have been reported, and the nature of the electronic spectrum of 1,4-naphthoquinone has been widely investigated [14]. UV–Vis electronic absorption spectra of PAN derivatives show the π–π^* electron transitions bands associated with benzene and naphthoquinone in the regions around 203–211 nm and 265–273 nm. A weak n–π^* transition band is observed at 310–330 nm. A broad, low energy band can be observed in the visible region centered between 438 and 480 nm for some naphthoquinone derivatives [15]. This latter absorption is quite common for amino-substituted quinones and has been previously assigned to have character corresponding to a charge-transfer (CT) transition and weak n–π^* electron transitions of the carbonyl group in the quinone [16].

The impact of solvent environment upon spectral transitions can be used to gain a better understanding about the nature of the electronic states, and types of interactions between solvent and solute. Furthermore, it is interesting to examine the effect of a wide range of solvents varying in properties such as solvent polarity and hydrogen-bonding ability, where the solvent can be proton donor or acceptor [17–19]. Comparison of the solvatochromic behavior of a series of naphthoquinone derivatives provides insight into the specific interactions of different substituents with the solvent and the impact the substituent has upon photo-physical properties of the system. Along with absorbance spectroscopy, fluorescence has proven to be a versatile tool for studying molecular interactions, and can be used to provide a greater understanding about the excited state properties [20].

Theoretical studies are very useful for spectral interpretation and to gain a molecular level understanding about the nature of electronic and structural properties [14]. Interactions between solute and solvent like hydrogen bonding, solvent–solute complexation, changes in the electronic charge distribution and excited-state reactions are important to understand when interpreting spectral events [19,21].

We synthesized several novel NO_2PAN derivatives and were interested in comparing their physicochemical properties with the FPAN derivatives previously synthesized [15]. We present a combination of spectroscopic and computational analysis of a series shown in Fig. 1 and Table 1. Spectral properties in a wide range of solvents were examined to understand the nature of molecular excited states and the effect of different solvents on solute–solvent interactions. Both absorbance and emission spectroscopy are presented, in combination with computational studies, to gain a greater understanding of the nature of the spectral transitions. A fundamental understanding about the molecular nature of some physicochemical properties of the naphthoquinone derivatives as a function of solvent and substituent provide a basic knowledge to exploit potentially useful applications of this family of compounds.

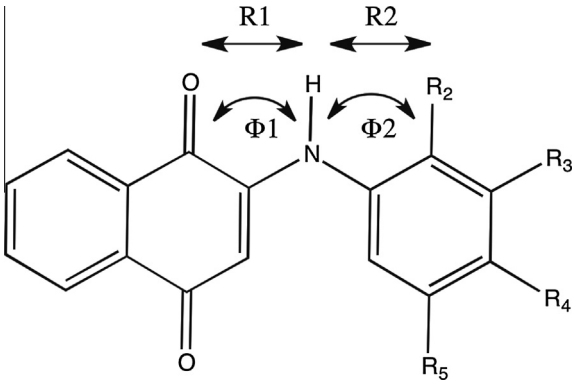

Fig. 1. Structure of PAN derivatives, where R_n are substituents, where the number indicates the position and n = H, F, NO_2, or OCH_3. The dihedral angles and bond distances of interest are labeled.

Table 1
PAN derivatives under investigation.

Compound	R_2	R_3	R_4	R_5	m.p. (°C)
PAN[a]	H	H	H	H	188–189[20]
2FPAN	F	H	H	H	155–156[13]
3FPAN	H	F	H	H	200–201[13]
4FPAN	H	H	F	H	244–245[13]
23FPAN	F	F	H	H	154–155[13]
24FPAN	F	H	F	H	205–206[13]
25FPAN	F	H	H	F	190–191[13]
34FPAN	H	F	F	H	260–261[13]
35FPAN	H	F	F	H	261–262[13]
245FPAN	H	H	F	F	202–203[13]
$2NO_2$PAN[b]	NO_2	H	H	H	205–207
$4NO_2$PAN	H	H	NO_2	H	337–339[21]
$2,4NO_2$PAN[b]	NO_2	H	NO_2	H	264–266
$4F2NO_2$PAN[b]	NO_2	H	F	H	246–248
2OMePAN[a]	Ome	H	H	H	147–148[20]
4OMePAN[a]	H	H	OMe	H	154–155[20]

[a] These compounds were prepared for comparison.
[b] These compounds have not been previously described.

Experimental

Spectral studies

Sample preparation

Solutions (2×10^{-4} M) were made in five solvents: acetonitrile (Pharmco-AAPer, 99.9% pure), dichloromethane (Pharmco-AAPer, 99.5%), hexane (Pharmco-AAPer, 99% pure), methanol (Pharmco-AAper, 100% pure) and 1-propanol (Sigma–Aldrich, 99.9%). Stock solutions were diluted to ensure the maximum absorbance in the UV region was between 0.1 and 1. For fluorescence measurements solutions were diluted such that the absorbance maximum at the lowest energy absorbance band was between 0.1 and 0.2.

UV–Vis absorbance measurements

UV–Vis spectra were obtained at room temperature on a Varian Cary 50 Bio Spectrophotometer. Spectra were corrected for solvent background by calibrating the instrument to the blank solvent. Spectra were taken in the range of 200–600 nm at a scan rate of 600 nm/min using the dual beam mode.

Fluorescence measurements

The emission spectra were obtained using a Varian Cary Eclipse fluorescence spectrophotometer. Samples were excited