Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 189 (2018) 578–585

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Review Article

Spectroscopic study of 2-methylindole and 3-methylindole: Solvents interactions and DFT studies

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ARTICLE INFO

Article history:
Received 21 June 2017
Received in revised form 16 August 2017
Accepted 29 August 2017
Available online 01 September 2017

Keywords:
3-Methylindole
Tryptophan
Interaction
Quenching
Acetonitrile
1,4-Dioxane
Kamlet-Taft equation
Lippert equation
Density functional theory (DFT)

ABSTRACT

The interaction between the 2- and 3-methylindole derivatives has been studied using spectroscopic technique and molecular modeling. Solvent polarity was found to play a great role in the interaction with acetonitrile showing greatest interaction with indole derivatives but less hydrogen bonding contribution. Good agreement was found between the models used for the analysis of experimental data and the theoretical calculations. Moreover, on the part of the quenching, benzonitrile was found to be better quencher over chlorobenzene, with 3-methylindole giving higher dynamic quenching constants.

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1. Introduction

Indole is a chromophore of the amino acid tryptophan that has gained appreciable interest of many researchers to investigate the mechanisms of the various photophysical reactions going on within tryptophan molecule in various environments [1]. The aromatic fluorophore responsible for tryptophan's fluorescence is indole and hence the understanding of photophysics of indole is essential in physical, chemical, biochemical and in biological sciences [1]. Amino acid tryptophan possesses unique spectroscopic properties different from other amino acids owing to its large size. This property, together with

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http://dx.doi.org/10.1016/j.saa.2017.08.062
1386-1425/

the response of its ultraviolet emission spectrum and fluorescence lifetime to its immediate surroundings, makes it an important internal fluorescent probe for protein configuration: an essential parameter in understanding protein functionality as well as solvent accessibility [2,3].

In the recent time, efforts have been centered on the fluorescent behaviour of indolic compounds in non-aqueous environments [4]. It has been found that addition of small amount of alcohols to a non-polar solvent would result to striking changes in the emission spectra of indolic compounds [5,6]. This phenomenon has been attributed to the formation of exciplexes between molecule of indole and that of polar additive [4]. In the same trend, non-polar aromatics like benzene have also been noticed of having striking consequence on the emission pattern of indole and a few of its derivatives as they greatly reduce the fluorescence intensity of indole and thereby causing red shifted. For this behaviour, N—H bond in the indole ring was found to be responsible through the excited state complex formation in benzene solution [7]. Contrarily, quenching experiments on indole in acetonitrile gave different behaviours. The quenching of indole by benzonitrile or chlorobenzene in acetonitrile, occurred at rate constants comparable to that of cyclohexane and this was due to charge transfer property of the exciplex [4].

Spectroscopic study of the 1:1 polar clusters of 3-methylindole has revealed that their structures are hydrogen bonded with the NH group which acts as the proton donor. Likewise, time and frequency-resolved measurements has also confirmed that clustering with these ligands gives rise to enhanced coupling between the ^1L_b and ^1L_a states. Hence, the use of various hydrogen-bonding ligands makes room for the capacity to regulate the strength of the coupling [8]. In another study of isolated gas-phase, 3-methylindole was used to give a good insight into the factors governing the fluorescence wavelength of simple proteins comprising a single tryptophan residue. Furthermore, the resulting information can be quantitatively used to suggest the fluorescent properties of different proteins or protein mutants via a tryptophan probe implanted in certain key positions [9]. In another report, the studies on the photophysics of 2-methylindole in different environment revealed that ^1L_a and ^1L_b states are very closely spaced [10].

Report has shown that the fluorophore for tryptophan, an important amino acid with big size is indole. This indole has similar structural property with 3-methylindole, thus having an in-depth knowledge about spectroscopic properties of 3-methylindole provides opportunity of using it in probing amino acid tryptophan, an essential parameter to understanding of protein functionality. Consequently, the objective of this work is to study spectroscopic behaviours of 3-methylindole in different solvents and also to examine how these properties are affected due to positional change of methyl group in 2-methylindole.

2. Methods

2.1. Experimental

2-Methylindole, 3-methyindole, spectroscopic grade 1-propanol, methanol, acetonitrile, ethylacetate, 1,4-dioxane, benzonitrile and chlorobenzene were all procured from Fluka and used as received. The absorptions of 1×10^{-4} M of the samples were measured at room temperature by a Jenway Spectrophotometer from Bibby Scientific Limited, UK. Then the absorption maxima of 2-methylindole and 3-methyindole in the five selected solvents were recorded. The steady-state fluorescence emission spectra of 1×10^{-4} M of the samples were recorded using FLS920 Spectroflourimeter from Edinburg Instruments, UK. The excitation wavelengths for the solution of both 2-methylindole and 3-methyindole in the five solvents were chosen based on their absorption maxima obtained from the previous absorption measurement. The fluorescence intensities of different concentrations of the quenchers in 1×10^{-4} M of 2-methylindole and 3-methyindole in acetonitrile and propanol solution were recorded. The excitation wavelength was set at 290 nm for all the solutions with the quenchers.

2.2. Computation

The structures of the indolic compounds were fully optimized using GAUSSIAN09 program [11]. Frequency calculation was carried out to ensure that all the frequencies were positive and also for vibrational analysis for which the scaling factor of 0.958 was used for frequencies above 1700 cm^{-1} while 0.983 was use for 1700 cm^{-1} and below [12]. Moreover, the interactions with the solvents were examined using Polarizable Continuum Model (PCM) via the Integration Equation Formalism variant while Time-dependent (TD) DFT using linear response (LR) together with PCM solvation model was used for UV calculation for emission spectra. The hydrogen bonding investigation was accomplished using counterpoise corrected method with Basis Set Superposition Error (BSSE). This computational study was accomplished using M06L method developed by Truhlar group [13,14] with basis set of 6-311++g(d,p) (Fig. 1).

3. Results and Discussions

3.1. Vibrational Spectra

The proper assignment of vibrational mode to a particular frequency is guided by the knowledge of molecular symmetry which is better obtained from density functional theory (DFT) calculation. In line with this, the symmetries of the two indolic compounds were theoretically predicted to be Cs (Table 2S) while, with the aid of GaussView [15] vibrational assignment was meticulously done. Although the calculation

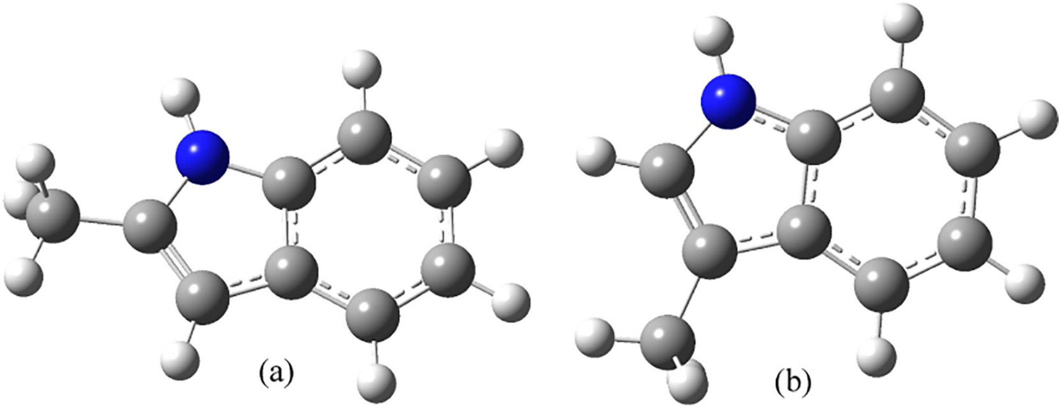

Fig. 1. Structures of 2-methylindole (a) and 3-methylindole (b).