



# Synthesis and photophysical properties of a novel phthalimide derivative using solvatochromic shift method for the estimation of ground and singlet excited state dipole moments

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## ARTICLE INFO

### Article history:

Received 27 May 2016

Accepted 29 September 2016

Available online xxxx

### Keywords:

Phthalimide

Isoindole

Solvatochromic

TD-DFT

Solvent polarity correlation method

Dipole moment

## ABSTRACT

A novel phthalimide derivative, 2-{4-[(1H-1,2,4-triazol-1-yl)methyl]phenyl}-1H-isoindole-1,3(2H)-dione (TMPID) containing an isoindole moiety was synthesized by the cyclisation of 2-({4-[(1H-1,2,4-triazol-1-yl)methyl]phenyl}carbamoyl)benzoic acid (TMPCB). The absorbance and fluorescence spectra of the derivative were recorded in fifteen different solvents to investigate their solvatochromic behaviour and dipole moments. Different solvent correlation methods, like the Bilot–Kawski, Lippert–Mataga, Bakhshiev, Kawski–Chamma–Viallet and Reichardt methods were employed to estimate the singlet excited and ground state dipole moments. Using multiple regression analysis, solute-solvent, specific and non-specific interactions were analyzed by means of Kamlet–Abboud–Taft and Catalan parameters. Computational studies were performed using time dependent density functional theory (TD-DFT) in order to calculate ground state dipole moment, atomic charges and frontier molecular orbital energies in solvent phase. Experimental and computational studies indicate that the singlet excited state dipole moment of TMPID is greater than the ground state dipole moment. The chemical stability of the derivative was determined by means of chemical hardness ( $\eta$ ) using HOMO–LUMO energies. From TD-DFT computational analysis, reactive centres in the molecule were evaluated based on molecular electrostatic potential (MESP) 3D plots.

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## 1. Introduction

Imide derivatives such as maleimide, succinimide, phthalimide and citraconimide are cyclic organic compounds with general structure ( $-\text{CO}-\text{N}(\text{R})-\text{CO}-$ ), which contain an imide ring. They are an important class of bioactive molecules showing anti-inflammatory, antiviral, antibacterial, anxiolytic, antifungal, analgesic and antitumor properties. Some of the imides are extensively used as a source of functionalized  $\beta$ -lactams, Diels–Alder dienophiles and Michael acceptors in synthetic chemistry. Besides these, phthalimide derivatives are well known for possessing various biological properties that include antimicrobial, anti-malarial, antihypertensive, antiviral and herbicides activity [1]. Phthalimide derivatives like 4-aminophthalimide and *N*-bromophthalimide have been used as a solvatofluorochromic dye in biopolymers, environmentally sensitive molecular probes [2] and oxidative agent catalysts in pharmaceutical and agrochemicals respectively [3,4]. Fluorescent sensors based on phthalimide derivatives have also been synthesized for the detection of cations, achiral and chiral anions and hydrogen

peroxide [5]. In spite of their wide applicability, procedures available for their synthesis are limited [6]. Among them, the most commonly used one is the dehydrative condensation of an anhydride with an amine in the presence of many reagents which yield amic acids containing both carboxyl and amide groups in its structure [7]. When amic acids are treated with suitable dehydrating agents, corresponding cyclic imides are obtained as a result of dehydration and cyclisation. Therefore, a good yield of *N*-alkyl or *N*-arylphthalimides can also be obtained by refluxing a reaction mixture of phthalic anhydride and alkyl or aryl amine in glacial acetic acid [8].

Various fundamental molecular properties can be accessed by observing solvent effects on absorption and fluorescence emission spectra of organic compounds. Dissolved substances are greatly influenced by solvent parameters like dipolarity, hydrogen bond donating and accepting ability which constitute solute-solvent interactions [9]. Solvatochromism refers to changes in electronic absorption spectra with solvent and is gaining momentum in the area of research involving photophysical properties. Depending on polarity of the solvent, position, intensity and shape of the absorption band can vary. Several studies of photophysical properties of organic donor-acceptor molecules suggest intramolecular charge transfer (ICT) and give access to singlet

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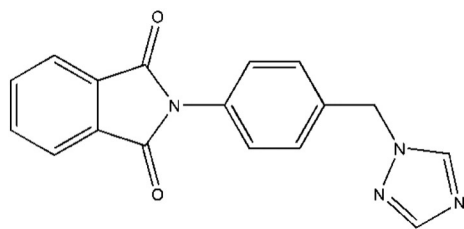


Fig. 1. Molecular structure of TMPID.

excited state characteristics, which allows one to design new molecules and perform in specific applications. These properties include quantum yield, fluorescence decay time, absorption and fluorescence spectral shift [10]. Effect of solvents on absorption and fluorescence spectra is usually used to determine the dipole moments of a fluorescent molecule, from which molecule configuration; changes in electronic distribution upon photo excitation can be studied. Solvent effects vary with change in their dielectric constant, polarity, refractive index and viscosity [11].

A method based on the effect of solvents on absorption and fluorescence maxima can be followed to determine the electric dipole moment, which corresponds to the electron distribution [12] and charge distribution in a molecule [13]. This may result in either increase or decrease of excited state dipole moment when compared to the ground state [14]. When a molecule undergoes excitation, ICT leads to formation of a highly polar singlet excited state. As Donor-Acceptor (D-A) bonds rotate in D-A molecules, microenvironment surrounding the molecule can be analyzed with the help of a fluorophore. On photoexcitation, a fluorophore with D-A nucleus will be accompanied by substantial charge redistribution. This physico-chemical process usually occurs in bulk solutions. In order to study such a phenomenon and evaluate the site of nucleophilic and electrophilic attack in photochemical reactions, ground and singlet excited state dipole moments of organic molecules are used [15]. Most researchers have determined both experimental and theoretical ground state ( $\mu_g$ ) and singlet excited state ( $\mu_e$ ) dipole moments in various organic fluorescent compounds like naphthylimides, coumarins, indoles, purines and fluorescein and some laser dyes [16]. The dipole moment of electronically excited molecules gives useful information for designing nonlinear optical materials and elucidating the nature of the excited states [11].

In the present investigation, we report the synthesis of a novel phthalimide derivative, 2-[4-[(1H-1,2,4-triazol-1-yl)-

1H-isindole-1,3(2H)-dione (TMPID) (Fig. 1) by the cyclisation of 2-([4-[(1H-1,2,4-triazol-1-yl)methyl]phenyl]carbamoyl)benzoic acid (TMPCB) in the presence of acetic anhydride and anhydrous sodium acetate. To the best of our knowledge, the present work is first of its kind for a phthalimide derivative containing an isoindole moiety. The photophysical properties of the phthalimide derivative have been investigated in fifteen different solvents of varying polarities. As a result, absorbance and fluorescence spectra of the derivative were recorded. Using the solvatochromic spectral shift values and theoretical studies, dipole moments of the two electronic states were calculated. All the methods used for solvatochromic studies closely follow Onsager's description of non-specific electrostatic solute-solvent interactions [17a]. The solvatochromism and influence of solvents on absorbance and emission spectra was also studied using Multiple Linear Regression (MLR) analysis. Time dependent density functional theory TD-DFT computations were performed to identify nucleophilic and electrophilic sites of TMPID. The optimized geometry of the molecule in ground state was also performed using Gaussian 09W software (Fig. 2).

## 2. Experimental

### 2.1. Apparatus

Absorption and fluorescence spectral measurements were recorded in  $10^{-5}$  M concentration solutions using Shimadzu UV-visible spectrophotometer (UV-visible 1800) and Shimadzu spectrofluorometer (RF5301PC). The solvatochromic studies were analyzed using Origin 8.0 Professional program. TD-DFT method was followed to perform theoretical studies using Gaussian 09W software program.

### 2.2. Materials

All the chemicals and reagents used were of analytical grade, purchased from Sigma Aldrich Chemical Company and were used without further purification. The synthesized phthalimide derivative was purified by recrystallization using ethanol. A thin layer chromatography (TLC) using silica gel coated aluminium plates (Merck) was performed to ensure the completion of the reaction and check purity of the product. Melting point was measured on Veego melting point apparatus and was uncorrected.

Various solvents of different polarities were used for the study of solvatochromic behavior of the phthalimide derivative. All the solvents were of spectroscopic grade.

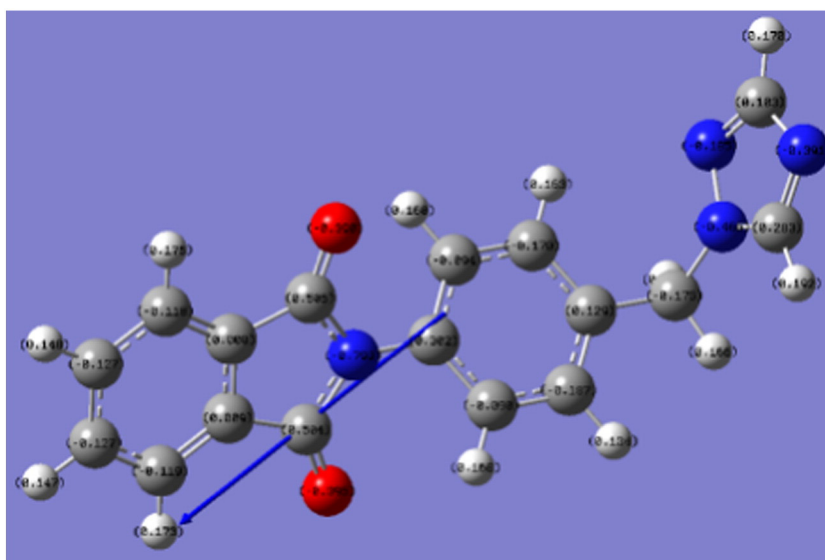


Fig. 2. Ground state optimized geometry of TMPID.

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