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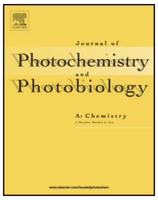

Intramolecular charge transfer in coumarin based donor-acceptor systems: Formation of a new product through planar intermediate

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ABSTRACT

Fluorescence behavior and intramolecular charge transfer (ICT) property of *N*,*N*′-dimethylamino substituted anil derivative of coumarinyl amine was studied by steady state and time-resolved fluorescence spectroscopy in combination with density functional theory calculation. Quantitative analysis of the effect of solvent hydrogen bonding on several spectral parameters was done using multiple regression analysis based on Kamlet–Taft model. The present system shows an additional long wavelength fluorescence band almost instantaneously in presence of methanol in sharp contrast to the model unsubstituted analogue. This new fluorescence band is believed to be due to the formation of a new isomer (*cis*-type) through a planar intermediate. While there is a substantial barrier ($\sim$50 kJ mol^{-1}) in the ground state, the isomerization process in the excited state in polar-protic environment proceeds very fast and believed to be catalyzed by hydrogen bond formation at the imine nitrogen atom in combination with stabilization of the resulting species through ICT.

1. Introduction

Derivatives of 1,2-benzopyrone, more commonly known as coumarins, are widely occurring in nature. It was first isolated in 1820 from a specific variety of bean, and many other coumarin derivatives found in a wide range of plants [1–3]. Compounds of the coumarin series are known to be active as fluorescent dyes and also materials for dye lasers [4,5]. Coumarins exhibit interesting fluorescence properties, including a high degree of sensitivity to their local environment like polarity and viscosity. This sensitivity has led to their widespread application as sensitive fluorescent probes of a wide range of systems, including homogeneous solvents and mixtures, and heterogeneous materials [6–8]. Coumarin derivatives can also be used for anticoagulant, antibacterial, antifungal, antihelminitic, hypothermal properties and vasodilatory action [9,10]. Recent studies have shown that several coumarin derivatives can act as efficient anticancer agents [11–15]. For example, a simple compound like 7-hydroxycoumarin inhibits the release of Cyclin D1, which is over expressed in many types of cancer.

Photochromism in aromatic anils is an active field of contemporary research mostly due to its potential and practical applications [16–19]. The anils of salicylaldehyde (salicylideneaniline, SA) and its derivatives are known to show additional absorption as well as fluorescence property due to the formation of a stable photochromic species. The process is initiated within ultrafst time scale in the excited state; but, also known to be occurring in the ground state in presence of alcoholic solvents [20–22]. The mechanism of SA photochromism is controversial with two different viewpoints (Scheme 1): one involves a preceding hydrogen atom transfer step followed by the formation of *cis* and *trans* keto isomer; whereas, the other mechanism involves the transfer of a hydrogen ion with the formation of *cis* and *trans* zwitterionic species [23–25]. Nevertheless, in both the cases, the presence of *o*-hydroxy group seems indispensable for the formation of the photochromic species.

Although new syntheses and studies on photophysical behavior of substituted coumarins have attracted a lot of attention in recent times [26–29], to the best of our knowledge, there is no report on the fluorescence properties derived from the anils of coumarinylamine. Furthermore, the electron deficient coumarinyl moiety can serve as an efficient acceptor, if coupled with suitable donor system. With this intention, we have synthesized two anil products of substituted *para*-amino benzaldehyde with 6-amino coumarin (structures of the compounds are given in Chart 1) and

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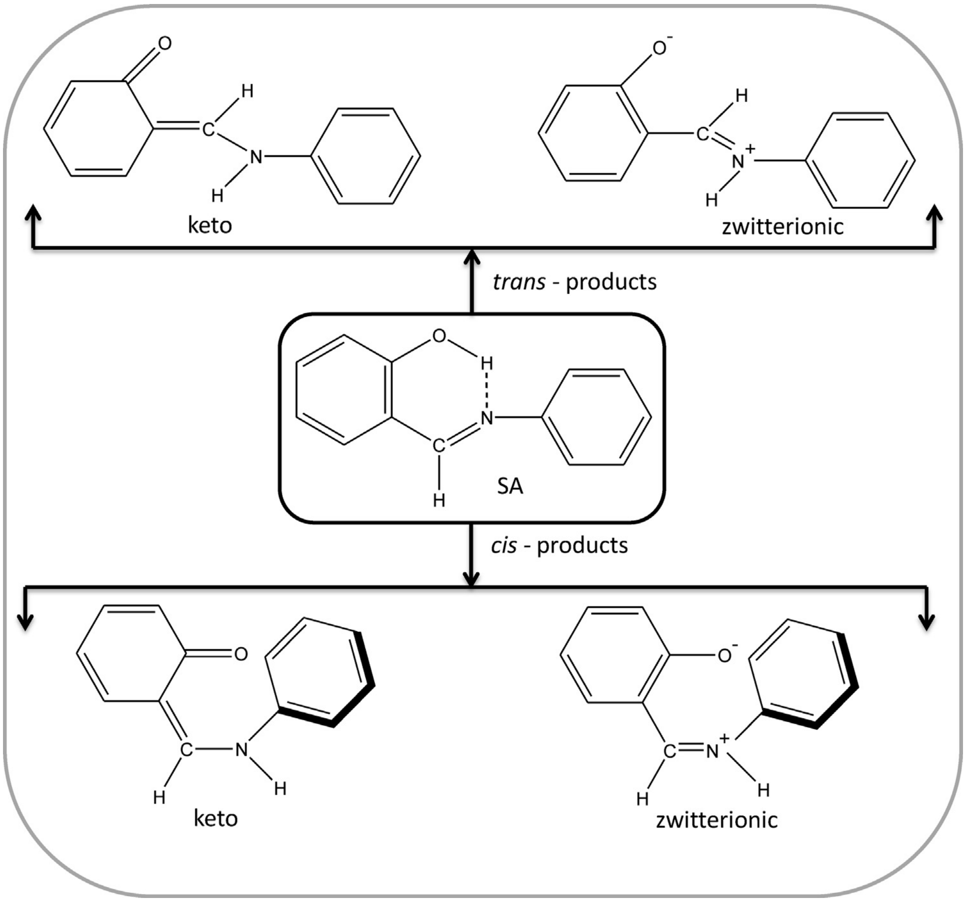

Scheme 1. Structure of different *cis*- and *trans*-photoproducts resulting from salicylideneaniline (SA) photochromism.

investigated the photophysical behavior with steady state and time resolved fluorescence spectroscopy in combination with density functional theory (DFT) calculation. The dimethylamino substituted anil (**II**) is capable to undergo intramolecular charge transfer and is expected to show additional excited state photophysics in comparison with its model unsubstituted counterpart, **I**. The current study intends to give idea on photon induced ICT process between covalently linked donor–acceptor groups built within highly fluorescent coumarin framework. The moderately twisted donor–acceptor linked coumarin (**II**) give high fluorescence quantum yields with large Stoke-shift which is proposed to be due to the formation of a final photoproduct. The rapid formation of a new fluorescence band in polar protic solvent for **II** can show promising application in designing "turn-on" fluorescence sensor for protic environment. Furthermore, almost full charge separation in the excited state of strongly twisted donor–acceptor provides the possibility of electron transfer initiated photocatalysis.

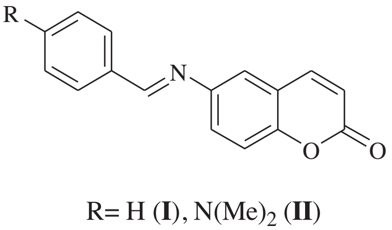

Chart 1. Structure of the substituted coumarin derivatives investigated in the present study.

2. Experimental

*2.1. Synthesis and characterization of the substituted coumarin derivatives (**I**–**II**)*

The synthesis procedure of the investigated compounds is given in Scheme 2. In brief, 6-amino coumarin (**3**) has been synthesized according to the literature procedure [30] from **1** via **2**. A mixture of **3** (1 mmol) and respective aryl aldehydes **4a**-**b** (1 mmol) was taken in a round bottle flask, 5 mL of anhydrous ethanol was added to it. The reaction mixture was stirred at room temperature for 2 h. After completion of the reaction (monitored by thin layer chromatography, TLC), the solvent was removed under high vacuum and crude reaction mass was washed with diethyl ether and hexane to get the pure product **I** or **II**.

(E)-6-(Benzylideneamino)-2H-chromen-2-one (**I**): M.p. – 150–152 °C [31]. ^{1}H NMR (acetone-d$_6$, 400 MHz) $\delta = 8.70$ (s, 1H), 8.04–7.98 (m, 3H), 7.59–7.38 (m, 6H), 6.48 (d, $J = 9.2$ Hz, 1H). (E)-6-((4-methylbenzylidene) amino)-2H-chromen-2-one (**II**): M.p. – 195–197 °C [31]. ^{1}H NMR (CDCl$_3$, 400 MHz) $\delta = 8.26$ (s, 1H), 7.71–7.64 (m, 3H), 7.34–7.20 (m, 3H), 6.68 (d, $J = 8.8$ Hz, 2H), 6.38 (d, $J = 9.6$ Hz, 1H), 3.00 (s, 6H). Single crystal of compound **II** was obtained by careful recrystallization from methanol, and the structure was unambiguously confirmed by X-ray crystallography. In the supplementary section, Fig. 1S shows the ORTEP diagram of compound **II** with probability ellipsoids representation (30%) and