

Structural and photophysical properties of alkylamino substituted 2-arylidene and 2,5-diarylidene cyclopentanone dyes



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ABSTRACT

A series of alkylamino substituted 2-arylidene and 2,5-diarylidene cyclopentanone compounds were synthesized. Spectroscopic and photophysical properties of these compounds have been measured in a variety of solvents. Absorption and fluorescence maxima have been correlated with the Empirical Scale of Solvent Polarity ($E_T(30)$). Theoretical TD-DFT spectral calculations and Lippert–Mataga analysis support the internal charge transfer (ICT) nature of the $S_0 \rightarrow S_1$ excitation for these compounds, with higher degrees of ICT depicted for the alkylamino substituted 2,5-diarylidene cyclopentanones. Photophysical properties consisted of measuring the fluorescence quantum yields (Φ_f) and lifetimes (τ_f) in a variety of solvents. Radiative and nonradiative decay constants have been determined from the Φ_f and τ_f data. Variation with solvent in the nonradiative rate of decay is interpreted in terms of a competition between internal conversion and intersystem crossing. Lastly, two compounds presented have been shown to undergo excited state protonation in glacial acetic acid.

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1. Introduction

The class of organic compounds called diarylidene cycloalkanones are ketocyanine dyes that have received attention in their use as photosensitizers for various electron energy transfer processes [1], fluorescent solvent polarity probes [2], fluoroionophores [3], and nonlinear optical materials [4], particularly in their use as chromophores in undergoing two photon absorption.

Previous work has been done in our lab studying the structural and spectroscopic properties of C_{2v} unsubstituted 2,5-diarylidene cyclopentanones, namely (2E,5E)-2,5-dibenzylidene cyclopentanone (1), (2E,5E)-2,5-dicinnamylidene cyclopentanone (2), and (2E,5E)-2,5-bis(5-phenyl-penta-2,4-dienylidene) cyclopentanone (3) [5,6]. It was found that fluorescence was not observed for 1 in any of the solvents studied (protic and aprotic). Fluorescence was observed for 2 only in protic solvents, and in a number of protic and aprotic solvents for 3. Solvents which were able to induce fluorescence in compounds 2 and 3 were believed to do so by inverting the order of $^1(n, \pi^*)$ and $^1(\pi, \pi^*)$ states. It was also demonstrated that 2 and 3 undergo excited state protonation in glacial acetic acid, with a signature of dual emission in the

fluorescence spectra. Additional work in our lab involved studying the photophysical properties of an asymmetrically substituted 2,5-diarylidene cyclopentanone dye, namely (2E,5E)-2-(4-cyanobenzylidene)-5-(4-dimethylaminobenzylidene) cyclopentanone, in a variety of solvents [7]. This asymmetric push–pull compound exhibits efficient two photon absorption (TPA) when dissolved in chloroform and is known to have potential for applications in TPA [4e]. Lastly, recently published work on the photochemistry of compound **1** in oxygenated and deoxygenated solutions has been conducted [8]. The testing of **1** as a direct photosensitizer of singlet state oxygen ($^1\Delta_g$), a strong oxidant used in photodynamic therapy in destroying targeted tumor and cancerous cells in living organisms, was also carried out in these studies.

This manuscript provides a presentation and discussion of the structural, spectroscopic, and photophysical properties of a series of alkylamino substituted 2-arylidene and 2,5-diarylidene cyclopentanone compounds. These class of ketocyanine compounds are of interest due to their electron “push–pull” structures. The two alkylamino substituted 2-arylidene cyclopentanones presented are examples of D–A compounds and the four alkylamino substituted 2,5-diarylidene cyclopentanones are examples of D–A–D compounds (where D is an electron donor group and A is an electron acceptor group). The presence of electron donor groups bonded to the polyene chain should have an effect of the electronic structure

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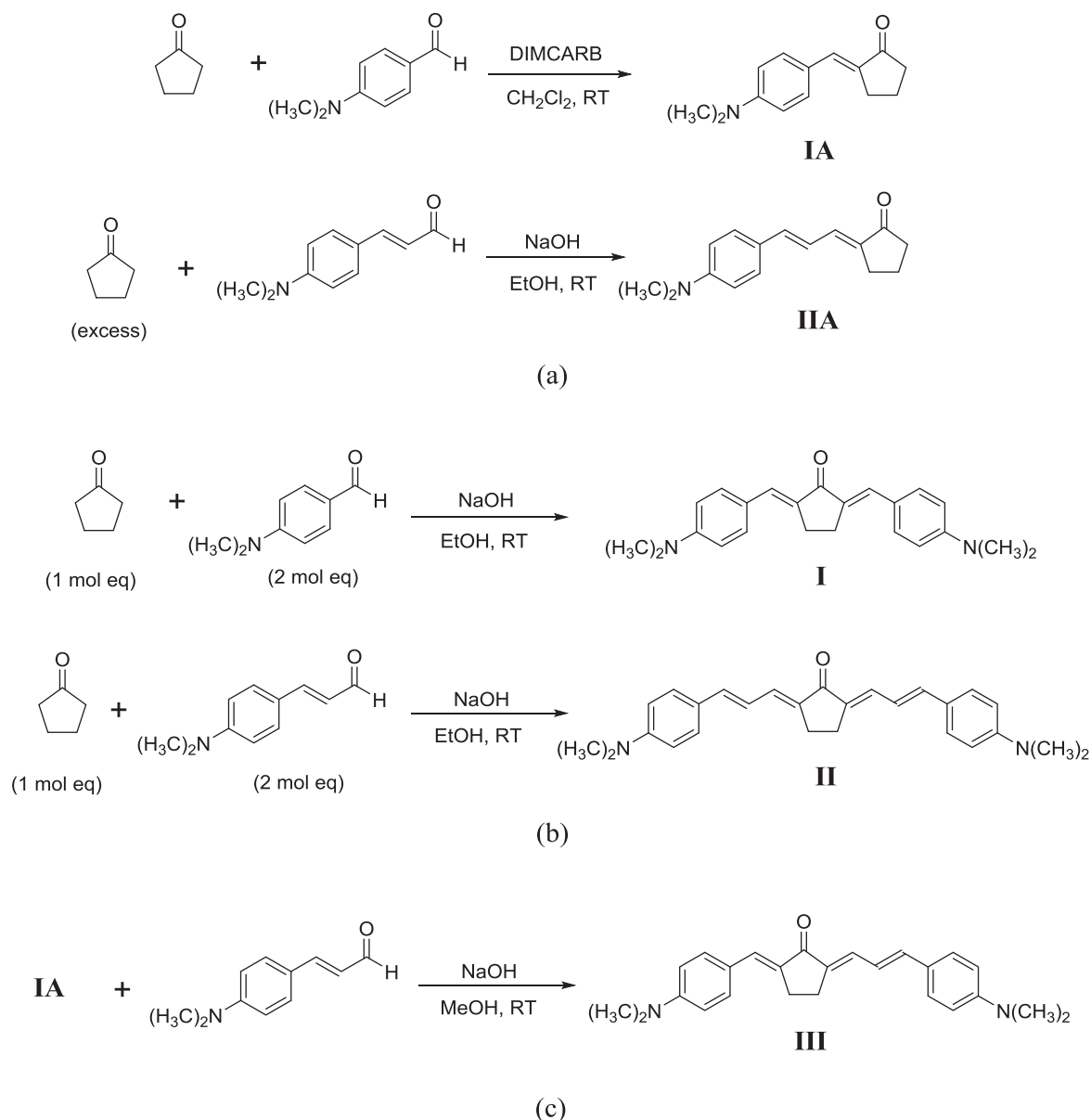


Fig. 1. Reaction schemes for the preparations of (a) **IA** and **IIA**, (b) **I** and **II**, and (c) **III**.

and photophysical properties, making this particular set of compounds different than the compounds presented in Ref. [5]. In addition, several of the compounds presented have longer π conjugated chains compared to compound **1** in Ref. [5] and compound **I** in Ref. [7]. The length of a π conjugated chain also has an effect on electronic structure, spectroscopic and photophysical properties.

A unique feature of these types of electron “push–pull” polyene compounds are their photoinduced internal charge transfer (ICT) properties. The ICT state is an excited state characterized by the transfer of electron density from the electron donor end of the molecule upon photoexcitation. The nature of ICT excited states gives rise to lower energies of fluorescence than the locally excited (LE) states. In other words, the fluorescence of an ICT state is red shifted relative to the LE state. A special type of ICT state is termed the twisted internal charge transfer (TICT) state, where the plane of a dimethylamino group is at a twisted angle with respect to the rest of the molecule due to rotation about the C–N bond. TICT states form in highly polar

solvent environments and their fluorescence is quenched and red shifted relative to the LE state. A section of this manuscript compares the structural and spectroscopic properties of compounds **II** and **IV**. Compound **II** contains free-moving dimethylamino groups substituted on the aryl moieties and can potentially undergo the formation of a TICT state. On the contrary, compound **IV** is spatially restricted on the aryl moieties due to the presence of closed, saturated ring systems that structurally prevent it from having a TICT state. Comparisons of the spectroscopic and photophysical properties of these two compounds will lead to determining whether or not **II** undergoes the formation of a TICT state.

Furthermore, the work presented in this manuscript is expected to be of importance to those interested in studying the structural, spectroscopic, and photophysical properties of these class of compounds and related compounds. A thorough understanding of the properties of these compounds is pertinent to examining their applications.

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