



FLUORESCENCE SPECTRA OF THE NOVEL COMPOUND 2'-CHLORO-4-METHOXY-3-NITRO BENZIL AND 2,2'-DICHLORO BENZIL AT ROOM TEMPERATURE IN DIFFERENT SOLVENTS

KEYWORDS

Solvent effect, emission spectra, photoisomerisation.

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ABSTRACT

Multiple emissions have been observed from 2'-chloro-4-methoxy-3-nitro benzil and 2,2'-dichloro benzil with polar and non polar solvents at room temperature. In non polar solvents, only trapped emission is observed whereas both excitonic and trapped fluorescence occur in polar aprotic solvents. The amount and wavelength of the emitted energy depend on both the fluorophore and the chemical environment of the fluorophore. The cis-skew to trans-planar photoisomerization of both the compounds 2'-chloro-4-methoxy-3-nitro benzil and 2,2'-dichloro benzil in the photoexcited state was in a series of normal solvents at room temperature. The solvent effects on the intramolecular charge transfer bands are discussed using the possible correlations (with advantages and disadvantages) between adsorption/fluorescence maxima and various solvent parameters. The intensity is found to exhibit variably in different solvents. It is revealed that the compound exhibits different geometries in different solvents.

1. Introduction

The conformation of benzil and its substituted analogs of aromatic α -dicarbonyl compound, has been the subject of many spectroscopic, structural, and theoretical investigations since decades[1–14]. The most important and interesting property of benzil and its substituted analogs that has triggered massive scientific exploration is its photoisomerization. The electronic absorption and emission spectra of organic molecules are usually modified in solvation processes. The intensity, frequency or the shape of the absorption and/or fluorescence spectra support modifications when the spectrally active molecules pass from the gaseous phase to the liquid phase. The modifications induced by a solvent in the electronic spectra of molecules can offer information on the local electric field acting on the spectrally active molecule [15-25]. From crystallographic and theoretical studies, the *cis*-skew configuration of the compound is known to be the most stable form in the ground state (S_0). In the triplet state (T_1), however, a photoisomerization takes place from the *cis*-skew to a *trans* planar configuration [18,19,25,26]. The study of solvent effects on the structure and spectroscopic behavior of a solute is essential for the development of solution chemistry [27-31]. The presence of specific and non-specific interaction between the solvent and the solute molecules are responsible for the change in the molecular geometry, electronic structure and dipole moment of the solute. Moreover, for the aromatic diketones, the non radiative singlet to triplet intersystem crossing is reported to be extremely efficient. The corresponding rate constant (k_{isc}) is very high; sometimes leading to the triplet quantum yield to be unity. Thus, k_{isc} is greater than the k_r , where k_r is the rate constant of fluorescence [32]. A glance at the optimized structures of the skew and the *trans* conformations of benzil and its substituted analogs indicates an intrinsic volume change due to photo interconversion. These solute/solvent interactions affect the solute's electronic absorption spectrum and this phenomenon is referred to as solvatochromism [33]. The solvatochromism is one of the few methods that permit to estimate the local field of forc-

es in the interior of liquids, indirectly, by the energy of the intermolecular interactions [34-37]. The solute molecules or ions exert repulsive forces on the solvent molecules at close separations and attractive forces at longer distances. For ionic solute, the attractive forces get importance resulting into a contraction of the solvent molecules by electrostriction. Some electro-optical parameters of the solute molecules can be estimated by spectral means, especially when the solute molecules are active both in absorption and in fluorescence electronic spectra. The compound 2'-chloro-4-methoxy-3-nitro benzil and 2,2'-dichloro benzil is also found to exhibit biological activities such as anti-tumour and anti bacterial activity. The fluorescence study reveals that both the compounds give different fluorescence spectra in different medium. With this background, in the present work, endeavor has been made to study the fluorescence of the molecular system in different polar and non polar solvents with an intention to find the origin of the various emissions.

2. Materials and methods

2.1. Materials.

High-purity spectroscopic and HPLC-grade tetrahydrofuran, acetonitrile, n-hexane, chloroform, were purchased from s.d. fine Chemicals Ltd., Mumbai, India. The solvents that had been purchased were double distilled in the lab. 2'-chloro-3-nitro-4-methoxy benzil and 2,2'-dichloro benzil were synthesised in two steps by crossed benzoin condensation followed by oxidation with conc.HNO₃ (Scheme 1). The structure of the compound was studied by IR, NMR and mass spectra. The molecular conformation was confirmed by single crystal XRD studies. Solvents like tetrahydrofuran, acetonitrile, n-hexane, chloroform (S.D. Fine, India, AR) were dried over molecular sieves. All the binary mixtures were prepared by mass in a dry box and were kept in special air tight bottles.

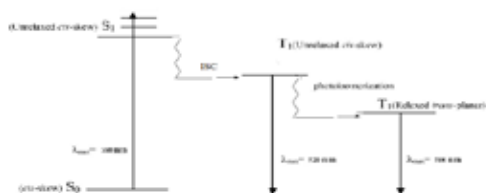
2.2. Lifetime measurements

The fluorescence lifetime measurements were done using a Jobin–Yvon–Horiba Fluorolog III time correlated single

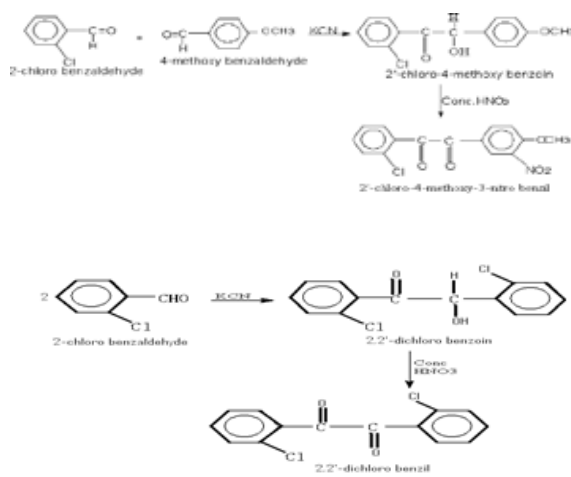
photon counting fluorometer attached with a pulsed diode laser. A 405 nm diode laser was used as excitation source. The detector used was R-928 operating at a voltage of 950 V. The fluorescence decay was acquired with a peak preset of 10,000 counts. The decay data was analyzed using Data Analysis Software.

3. Result and discussion

At room temperature, upon photoexcitation at its lowest energy $n\pi^*$ absorption band (380 nm and above) occurs in all the solvents. Both the emission bands are rather weak in intensity as well as unstructured, if the molecule is to move to a new vibrational level during the electronic transition, this new vibrational level must be instantaneously compatible with the nuclear positions and momenta of the vibrational level of the molecule in the originating electronic state. The absorption is well extended to the visible region in all solvents under study. A loss of the vibrational fine structure was observed on going to more polar solvents. There is appreciable change in the energy of transitions in the different solvents suggesting that solvent stabilization of ground state species is significant. The absorption spectrum in each solvent is very broad and the presence of more than one shoulder probably indicates the presence of more than one isomeric form in the ground state [38,39]. The lowest energy emission does not show any solvent effect in terms of shifting of the band position. The emission spectra in both the polar and non polar solvents change their patterns when the same system is excited at the $\pi\pi^*$ absorption band at 400 nm. The much stronger fluorescence peak at 420 nm is observed. Intensity of this emission is strong enough to mask the above mentioned 400–430 nm fluorescence, if it persists at all at this excitation. Both the compounds were practically insoluble in water at neutral and medium acidic pH, while soluble in both polar and non-polar organic solvents. It is more soluble in alkaline solvents and in extremely acidic solvents, presumably due to the diketo groups, or due to the degradation or change in each dissociated form from cis diketo to trans diketo configuration. Fluorescence have been observed from both the unrelaxed (skew) and the relaxed (trans-planar) conformations of the system. The polar aprotic solvent tetra hydro furan and acetonitrile shows higher intensity than the non polar solvents n-hexane, chloroform for both the compounds 2'-chloro-4-methoxy-3-nitro benzil and 2,2'-dichloro benzil (fig. 1&3). Based on solvent media, the absorption maxima of both the compounds 2'-chloro-4-methoxy-3-nitro benzil and 2,2'-dichloro benzil were found to be located in different wavelength region in THF, acetonitrile, hexane and chloroform. A large bathochromic shift of absorption maximum was observed for the compounds in tetra hydro furan and acetonitrile suggesting a red shift in absorption maxima for more polar solvents, positive solvatochromism. However, in the case of non polar solvents hexane and chloroform a blue shift was observed negative solvatochromism.



It is important to note that the energy of this emission band is higher than the lowest energy absorption of both the compounds corresponding to the S_0-S_1 transition. This observation clearly signifies that when the compound is promoted to an excited singlet state higher than the S_1 . The higher intensity of this fluorescence band also points to its origin from a $\pi\pi^*$ transition in contrast to the low intensity S_1 fluorescence with a transition of $n\pi^*$ character (fig. 2&4). Emission of a fluorescence photon from the vibrational ground state of the first excited singlet state constitutes a spontaneous process that contains information about the environment of the fluorophore and its interactions. From this emission it is clear that Kasha's rule which states that emission occurs from the lowest excited state of a given multiplicity and is independent of the excitation wavelength occurs. The absorbance of both the compounds strongly depended on the solvent polarity. The absorption band obtained in the 350–450 nm regions could be attributed to the S_0-S_1 transition, which is intensified at the cost of absorption intensities of other transitions. In the transition from S_0-S_1 state it emits from both the relaxed cis skew to unrelaxed cis skew form. However, while it returns to the ground state it exhibits relaxed planar trans form.



schematic representation of 2'-chloro-4-methoxy-3-nitro benzil and 2,2'-dichloro benzil

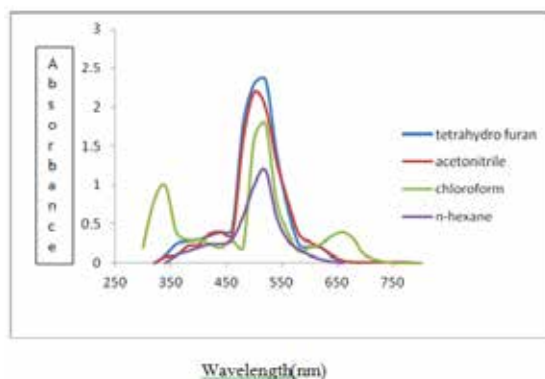
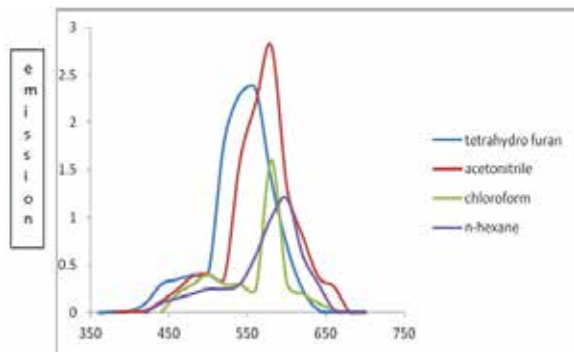
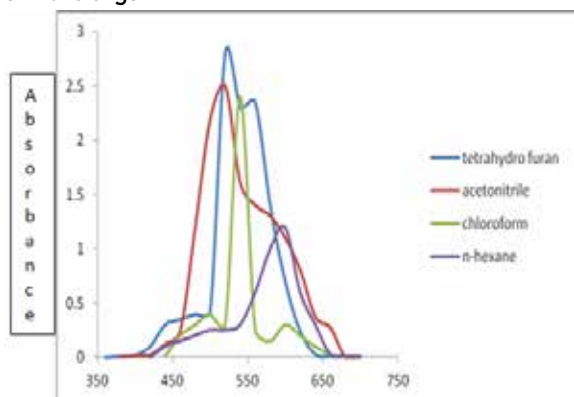


Fig. 1. Absorption spectra for the compound 2'-chloro-4-methoxy-3-nitro benzil



wavelength(nm) must be labelled for x axis for the above graph and Fig 2 emission spectra for the compound 2'-chloro-4-methoxy-3-nitro benzil at the bottom of wavelength



wavelength (nm) should be given as label for x axis and fig 3. absorption spectra of 2,2'-dichloro benzil must come below

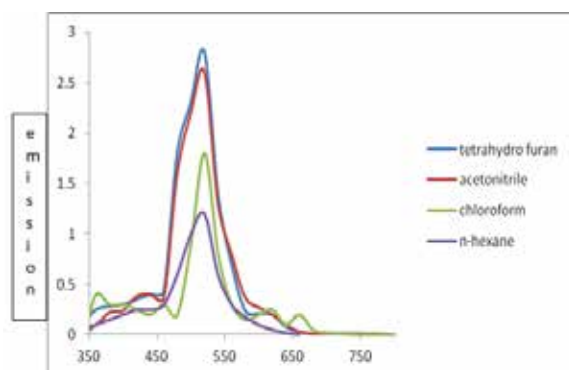


Fig 4. Emission spectra of 2,2'-dichloro benzil

Conclusion

The present work provides a comprehensive insight into the fluorometric behavior of the substituted aromatic α -dicarbonyl molecule, 2'-chloro-4-methoxy-3-nitro benzil and 2,2'-dichloro benzil in different solvent medium. The study also pertains to the idea about solvent solute interactions in polar and non polar solvents. The emission intensity of the compounds in different solvent medium is explained. The work reveals that in fluid media, depending on the excitation wavelength, the compound 2'-chloro-4-methoxy-3-nitro benzil and 2,2'-dichloro benzil fluoresces from both the S1 and S2 states.

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