



Solvent effect of dioxan, ethanol, chloroform, methanol, acetonitrile on the spectral characteristics of 2-chloro-4-methoxy benzoin

B. Thanuja^{1,*} and Charles C. Kanagam²

¹Department of Chemistry, Sri Sairam Engineering College, Chennai-600044, Tamilnadu, India

²Department of Chemistry, Presidency College, Chennai-60005, Tamilnadu, India

*Corresponding author: revasuku25@gmail.com

Received 16 December 2019, Received in final form 21 December 2019, Accepted 21 December 2019

Abstract

2-chloro-4-methoxy benzoin has been synthesized by the benzoin condensation of 2-chloro benzaldehyde and anisaldehyde in the presence of alcoholic potassium cyanide. The structure of this benzoin ($C_{15}H_{13}ClO_3$) has been elucidated on the basis of UV, fluorescence and IR spectroscopic techniques. Various physico-chemical characteristics such as solubility, colour, absorbance and fluorescence of 2C4MB measured in different solvents like chloroform, acetonitrile, ethanol were reported. In order to investigate solvent effect, UV, fluorescence and IR spectra were studied for 2C4MB in polar and non-polar solvents. The results obtained from the UV, fluorescence and IR spectra of 2C4MB were found to exhibit keto-enol tautomersim.

Keywords: Keto-enol, solvent effect, IR, UV-Vis, fluorescence study.

1. Introduction

Fluorescent compounds are widely useful in chemical sensors, fluorescent labelling, dyes and biological detectors. Benzoin is an excellent chromophore and the substituted benzoin shows strong light emitting properties and long fluorescence lifetimes [1-3]. Among other organic compounds, benzoin compounds are very important, because they are biologically active [4-5]. Many of the benzoin and its derivatives are reported to show interesting NLO properties due to the presence of π -bonds, which helps in the molecular engineering for the tailor made applications [6]. Because of their large optical nonlinearities and chemical, thermal, and optical stability, organic nonlinear optical materials have been the leading practical materials for fabricating optoelectronic devices. In organic system, NLO effects have originated in the virtual electron excitations occurring on the individual molecular unit. Such organic materials are very useful in industry. Most materials with high Second Harmonic Generation (SHG) efficiency show significant absorption in the blue or violet region. Researchers have demonstrated efficient blue-light generation below 400nm using highly efficient organic single crystals [7]. Such organic materials may be used in terabit optical data storage applications. Efficient nonlinear

signal processing in the optical frequency domain requires the development of new families of materials. With this interest, here in report the solvent effects of synthesized 2-chloro-4-methoxy benzoin (2C4MB) using IR, UV, fluorescence study, the molecular design in such way that it has one electron donor (methoxy) and one electron acceptor (carbonyl and chloro) moiety which provides it with a push-pull configuration, which enhances the optical non linearities. 2C4MB crystallizes in the Triclinic crystal structure, with P1 space group [8]. The molecular conformations are of particular interest because they are expected to form intermolecular and intramolecular hydrogen bonding in solution and solid state. So, in addition to the study of important properties like second harmonic generation (SHG), laser damage threshold (LDT), optical and mechanical, assessment of hydrogen bonding also plays important role in optical property. We herein report the synthesis, spectroscopic studies, optical properties crystal structure of the title compound and solvent effect of 2C4MB on NMR, UV-Vis, fluorescence and IR spectra.

2. Materials and methods

2.1 Synthesis of 2C4MB crystal

2-chloro benzaldehyde, 4-methoxy benzaldehyde and potassium cyanide were

purchased from Aldrich. All the reagents used for synthesizing the title compound were of A.R. grade. Solvents were purified by distillation and dried in accordance with the standard procedure [9]. The title compound was synthesized by benzoin condensation using 4 g of KCN dissolved in 75 cc of water in a one litre flask. To this, 6.8g (0.05moles) of anisaldehyde, 7g (0.05moles) of 2-chloro benzaldehyde and 75cc of 95% ethanol were added. The mixture formed a solution at the boiling temperature and was refluxed for one and half hours. Steam was then passed through the solution until all the alcohol and nearly all the unchanged aldehyde was removed. The condensed water was removed by decantation from the product. The product was then pressed to make it as free as possible from oily material on a suction funnel and washed with cold alcohol. In this way about 7.1 g (yield was 60%) of crude product was obtained. The crude mixture was dissolved in hot alcohol and allowed to crystallize slowly. The 2-chloro-4-methoxy benzoin crystal was obtained.

2.2. Solubility

Compound 2C4MB is found to be soluble in polar aprotic solvents like dioxan, acetonitrile, dichloromethane, tetrahydrofuran, ethyl acetate, acetone and in non-polar solvents like chloroform and benzene. The compound is also soluble in polar protic solvents like ethanol and methanol and is completely insoluble in water.

2.3. Characterization

The electronic spectra were recorded by UV-1601 Shimadzu UV-Visible spectrophotometer in different solvents in the range of electronic absorbance between 200 and 800 nm. The fluorescence emission spectra were recorded using Perkin Elmer LS55 fluorescence spectrophotometer using the excitation wavelength of the respective absorption maxima for different solvents. The infrared spectra were recorded using Perkin Elmer spectrometer in the frequency range 4000-450 cm^{-1} using KBr pellet method.

3. Results and discussions

3.1. UV-vis spectra

The absorption bands around 200–350 nm is characteristic peak of carbonyl moiety, the absorption maximum and extinction coefficient values are given in Table 1. The effect of solvent polarity on the absorption and emission spectra is termed as solvatochromism [10]. The absorption maximum values (λ_{max}) increase with increase in the solvent polarity (Fig 1a & 1b.). This compound shows bathochromic (red) shift in highly polar

solvents. As a result, the compound has low $\pi \rightarrow \pi^*$ transition energy in polar solvents. Because, the excited state is more polar than the ground state and the electronic transition energy decreases with increase in the polar solvent [11].

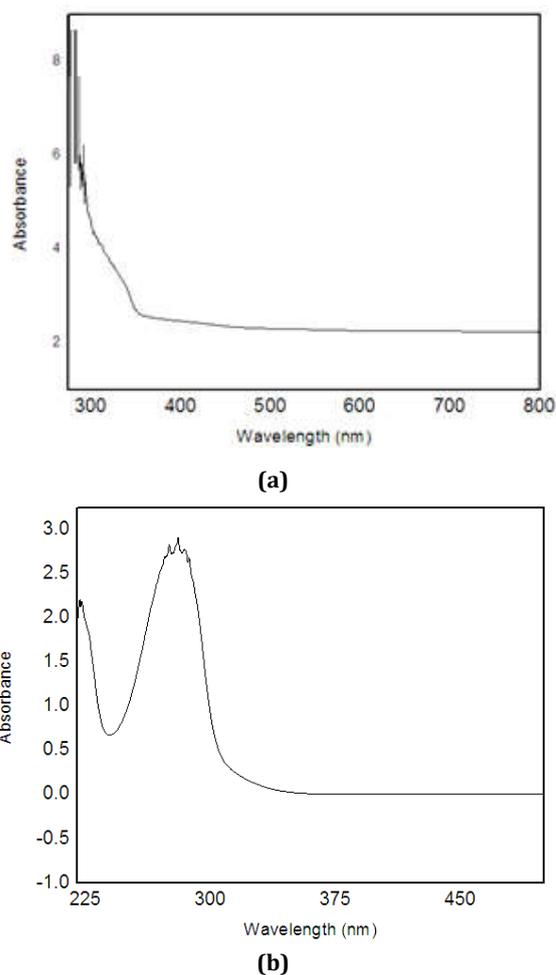


Fig. 1. UV spectra of 2C4MB in (a) ethanol and (b) Chloroform

Table 1. Absorption maximum of 2C4MB in different solvents.

Solvent	$\pi \rightarrow \pi^*$ (nm)	$n \rightarrow \pi^*$ (nm)
Ethanol	285	293
Chloroform	240	293

3.2. Fluorescence spectra

The emission maxima and its intensity in different solvents for compound 2C4MB are given in Table 2. λ_{em} emission of compound 2C4MB in polar solvents like ethanol and acetonitrile is very high (403 nm and 410 nm) when compared to the non-polar solvent chloroform (380 nm). The difference between the emission maxima and excitation maxima (Stokes shift) [12] is higher in the polar

solvents like acetonitrile and ethanol whereas lesser in chloroform. Compound 2C4MB also showed maximum intense emission and λ maxima of emission in solvent ethanol. Its emission maxima (λ em) are 382 nm and 384 nm respectively (Fig. 2).

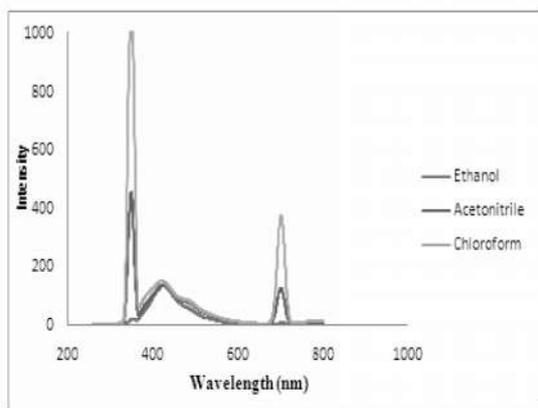


Fig. 2. Fluorescence spectra of 2C4MB

The emission spectra showed gradual red shift when the solvent polarity was changed from lower to higher. This is due to the fact that the excited state of the compound is more stabilized in highly polar solvents when compared to that in less polar solvents. The difference between the energy of emission and excitation is higher for polar protic solvent than for nonpolar solvent. This shows that ground state is also stabilized because of strong intermolecular interaction between the solute and the solvent. The energy difference is a measure of the intermolecular interaction. The differences between the forms of 2C4MB present in each solvent lead to different excitation and emission wavelengths of fluorescence for each solution. Solvent effects due to hydrogen bonding of 2C4MB with protic and aprotic solvents are also evident in the fluorescence spectra of 2C4MB. This experimental study reveals additional information about the effect of hydrogen bonding on fluorescence of the 2C4MB molecule in different solvents.

Table 2. Fluorescence data of 2C4MB with different solvents.

Solvent	λ_{max} (nm)	Intensity	Excitation
Chloroform	438	158	290
Acetonitrile	430	204	290
Ethanol	425	188	240

3.3. IR spectra

The infrared spectra of 2C4MB are shown in Fig. 3. The strong band at 1666 cm^{-1} corresponds to C=O stretching and shows a doublet at 3469 and

3060 cm^{-1} correspond to a OH stretching frequency, indicating the presence of intramolecular hydrogen bonding.

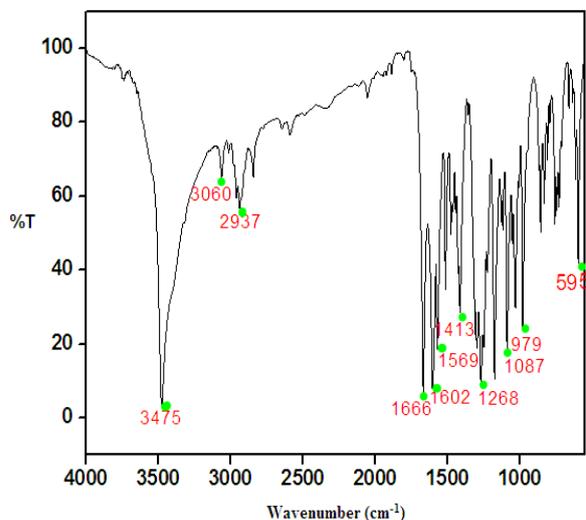
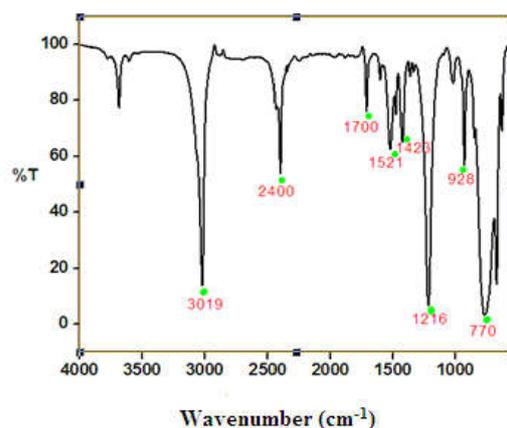
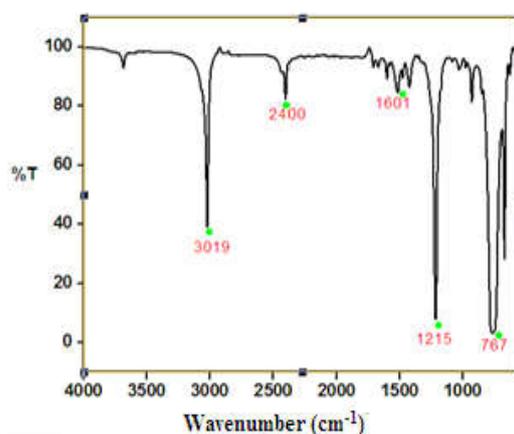


Fig. 3. IR spectrum of 2C4MB in solid form



(a)



(b)

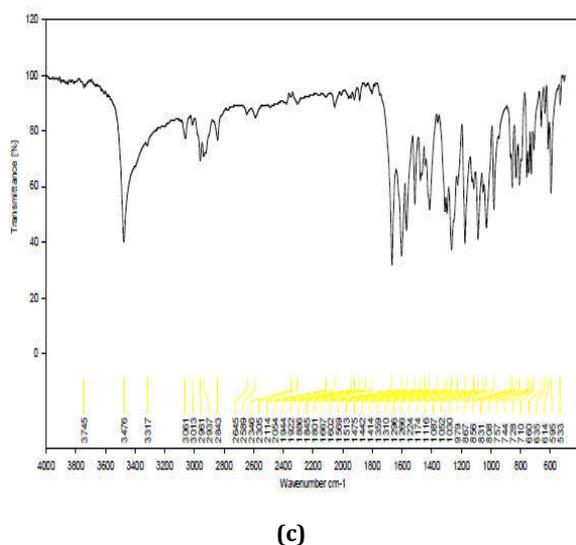


Fig. 4. IR spectra of 2C4MB in ethanol at (a) higher & (b) lower concentration and (c) in n-hexane

Absorption at 1586 cm^{-1} and at 1602 cm^{-1} corresponds to aromatic hydrocarbon C=C stretching frequency. The two weak absorptions at 957 cm^{-1} and 859 cm^{-1} are assigned to C-H deformation of mono-substituted benzene. Benzoin belongs to the compounds having α -ketols are found to exhibit a kind of equilibrium between isomers called 'Tautomerism' [13-15]. In the solid state, the title compound exists as a molecule with a carbonyl group, a $-\text{CH}-\text{OH}$ group, with intermolecular hydrogen bonding and the benzene rings. The study of IR spectra in solvents (ethanol) of different polarity and in solution of different concentrations indicates the presence of the enolic form. As shown in Figs. 4 (a & b), the lowering of intensity of the carbonyl absorption can be observed as the dilution increases. It is also observed that the breadth of $-\text{OH}$ bond increases with decreasing of polarity of solvent. The IR spectra was taken in non-polar solvent (hexane), there is no changes in the intensity of carbonyl absorption (Fig. 4(c)), this proves the hydrogen bonding in the compound has a solvent effect, as the polarity of the solvent changes.

4. Conclusion

In this present study, we have synthesized a 2C4MB based fluorescent compound. The absorbance, emission, color, intensity of fluorescence and solubility of both the compounds were investigated in different organic solvents. The compound 2C4MB showed the emission maximum in ethanol acetonitrile, chloroform. The solvent effect is also proved by IR analysis. Intramolecular

hydrogen bonding disappears as the polarity of the solvent changes.

Acknowledgements:

The authors are grateful to acknowledge SAIF, IIT-Madras for Supporting in all the spectroscopic studies. We thank Dr. Kutti Rani, Department of chemistry, Abdur Rahman university, for her support in this work.

References:

- [1]. Y. Wang, C. Sa, F. Li, L. Liu, Y. Pan, X. Wu, H. Wang, "Syntheses, characterization and fluorescent properties of two series of dehydroabiatic acid C-ring derivatives", *Spectrochim. Acta A* 76 (2010) 328.
- [2]. Z. Yongliang, Z. Fengying, L. Qiang, G. Deqing, "Synthesis, Characterization and Fluorescence Properties of Europium, Terbium Complexes with Biphenyl-4-Carboxylic Acid and o-Phenanthroline", *J. Rare Earths* 24 (2006) 18.
- [3]. M. Costro, J. Sanchis, S. Gil, V. Sanz, J. A. Gareth Williams, "Poly(amine) biphenyl derivatives as fluorescent sensors for anions and cations", *J. Mater. Chem.* 15 (2005) 2848.
- [4]. Aysel Hande Olceroglu, Pinar Calik, Levent Yilmaz, "Chiral separation of racemic benzoin via enzyme enhanced ultrafiltration", *Desalination* 200 (2006) 464.
- [5]. H. Q. Li, J. Y. Xue, L. Shi, S. Y. Gui, H. L. Zhu, "Synthesis, crystal structure and antimicrobial activity of deoxybenzoin derivatives from genistein", *Eur. J. Med. Chem.* 43(2008) 662.
- [6]. Christopher C. Harding, J. S. Shane Rountree, David J. Watkin, Andrew R. Cowley, Terry D. Butters, Mark R. Wormald, Raymond A. Dwekc, George W. J. Fleetb, "2-Acetamido-N-benzyl-1,4-imino-1,2,4-trideoxy-L-arabinitol 0.33hydrate", *Acta. Cryst. E* 61 (2005) 1683.
- [7]. L. A. Hornak, Marcel Dekker (1992) "Polymers for Light Wave and Integrated Optics" (14th Edition, 1993) New York, USA.
- [8]. B. Thanuja, Charles C. Kanagam, G. Nithya, "Study of molecular interactions in binary mixtures of 2-chloro-4-methoxy benzoin with various solvents through ultrasonic speed measurements", *Indian J. Phys.* 87(2013)1225.
- [9]. A. I. Vogel, "Textbook of Practical Organic Chemistry" (5th Edition, 1989) Longman, London.
- [10]. S. K. Gularyan, G. E. Dobretsov, O. M. Sarkisov, F. E. Gostev, V. Y. Svetlichny, "The lipophilic fluorescent probe 4-dimethylaminochalcone: factors responsible for the fluorescence yield", *Biofizika* 50 (2005) 780.

- [11]. S. K. Gularyan, G. E. Dobretsov, B. M. Polyak, V. Y. Svetlichny, N. E. Zhukhlistova, B. M. Krasovitskii, L. I. Kormilova, V. E. Zavodnik, "4-Dimethylaminochalcone as a fluorescent probe: Quantum chemical calculations of its interaction with the environment", *Russ. Chem. Bull.* 55 (2006) 1737.
- [12]. V. Tomeckovaa, M. Poskrobovaa, M. Stefanisinovaa, P. Perjesi, "Some fluorescence properties of dimethyl aminochalcone and its novel cyclic analogues", *Spectrochim. Acta A* 74 (2009) 1242.
- [13]. R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, G. T. Davis, "Fluorine Nuclear Magnetic Resonance Shielding in p-Substituted Fluorobenzenes. The Influence of Structure and Solvent on Resonance Effects", *J. Amer. Chem. Soc.* 85(1963) 3146.
- [14]. C. D. Ritchie, E. S. Lewis, "On the Solvent Dependence of Substituent Effects on Reactivities", *J. Amer. Chem. Soc.* 84 (1962) 591.
- [15]. C. D. Ritchie, B. A. Bierl, R. J. Honour, "The Solvation of Polar Groups. I. A Study of Solvent Effects on Infrared Band Intensities", *J. Amer. Chem. Soc.* 84(1962) 4687.