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Solvatochromic Effect on the Absorption Spectra and Fluorescence Spectra and the Estimation of Ground State And Excited-State Dipole Moments Of 4- Methoxycarbonyl)Biphenyl-4-Yl 5-Bromo Thiophene-2-Caboxylate

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Abstract:
The molecule 4-(Methoxycarbonyl)biphenyl-4-yl 5-bromo thiophene-2-caboxylate, is stabilized by a halogen···Oxygen contact, Bromine···Oxygen interaction between the molecules. Crystal is further influenced by C-H ***Pi*** and Pi-Pi interaction. Solvatochromic studies confirm intermolecular charge transfer behaviour with dipole interactions in different solvents. The molecule completely changes its configuration in the excited state due to change in dipole moment. The different solvents used influences the title compound in ground state and in the excited state is studied by solvatochromic method. The overall study of molecular structure, electron density around the molecule in terms of solvatochromic studies provide pivotal understanding of molecular behaviour.

1. Introduction

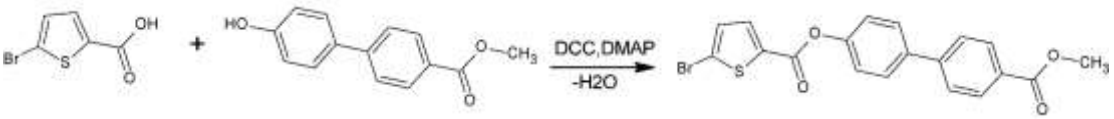
The effect of solvatochromic effect on the absorption and fluorescence properties of any organic compounds is an interesting study[1]. The molecule in the excited state exhibit different conformation due to change in dipole moment. The electronic, molecular structure and photo physical properties of the molecules are revealed by the dipole moment in the excited state. The absorption and emission energy of the title compound is studied with respect to polarity of different solvent. This method involves spectral shift caused due to electrochromic or Solvatochromism phenomena in the excited state. The electronic polarization [2], Stark effect[3], Microwave conductivity[4] and electric dichroism[5] are reliable methods to study the less complex molecules. The solvatochromic methods is based on absorption and fluorescence maxima shifts in different solvents with varying polarity. Koutek [6] work has revealed that, solvatochromic technique gives good results. The absorption and emission spectra of solvent dependent method is used in the estimation of ground state and excited state dipole moment title compound.

The biphenyl and thiophene ring exhibits good properties such as solubility, reactivity and electronic behaviour find its applications in organic electronics, polymer science. The current researchers find significance advances in the field of material science and play key role in the upcoming technological advances. In view of the above, researcher was very much interested to study phot physical properties of the title compound by Solvatochromic method.

MATERIALS AND METHODS/EXPERIMENTAL

Chemicals used

5-bromotetrahydrothiophene-2carboxylicacid, (Sigma-Aldrich,98%), methyl4'-hydroxy bi phenyl-4-carboxylate(Sigma-Aldrich,98%)),4-Dimethylaminopyridine(DMAP), (SpectrochemPurity-99%), Di cyclohexyl carbodiimide (DCC) (Spectrochem, Purity-99%), chloroform (Molychem, Purity-99.8%), acetic acid (Sigma-Aldrich, 98%), sodium sulphate (Sigma-Aldrich, 98%). All reactants used without any further purification.

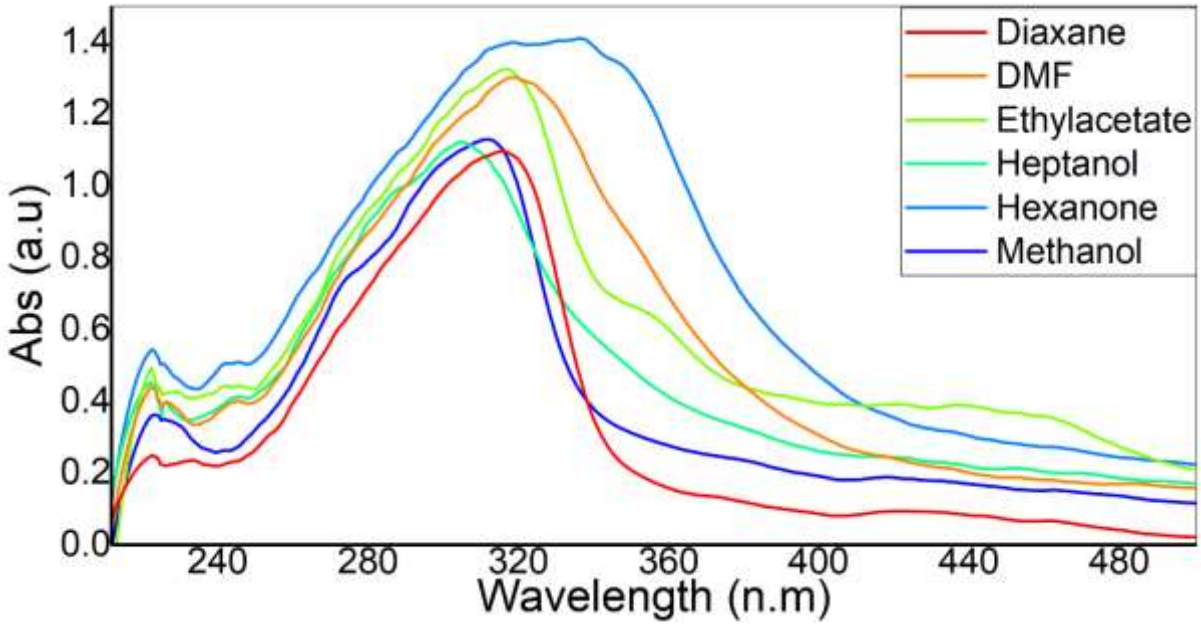


Scheme 1.1 Reaction scheme for the molecule 4'-(methoxycarbonyl)bipenyl-4-yl 5-bromothiophene-2-carboxylate

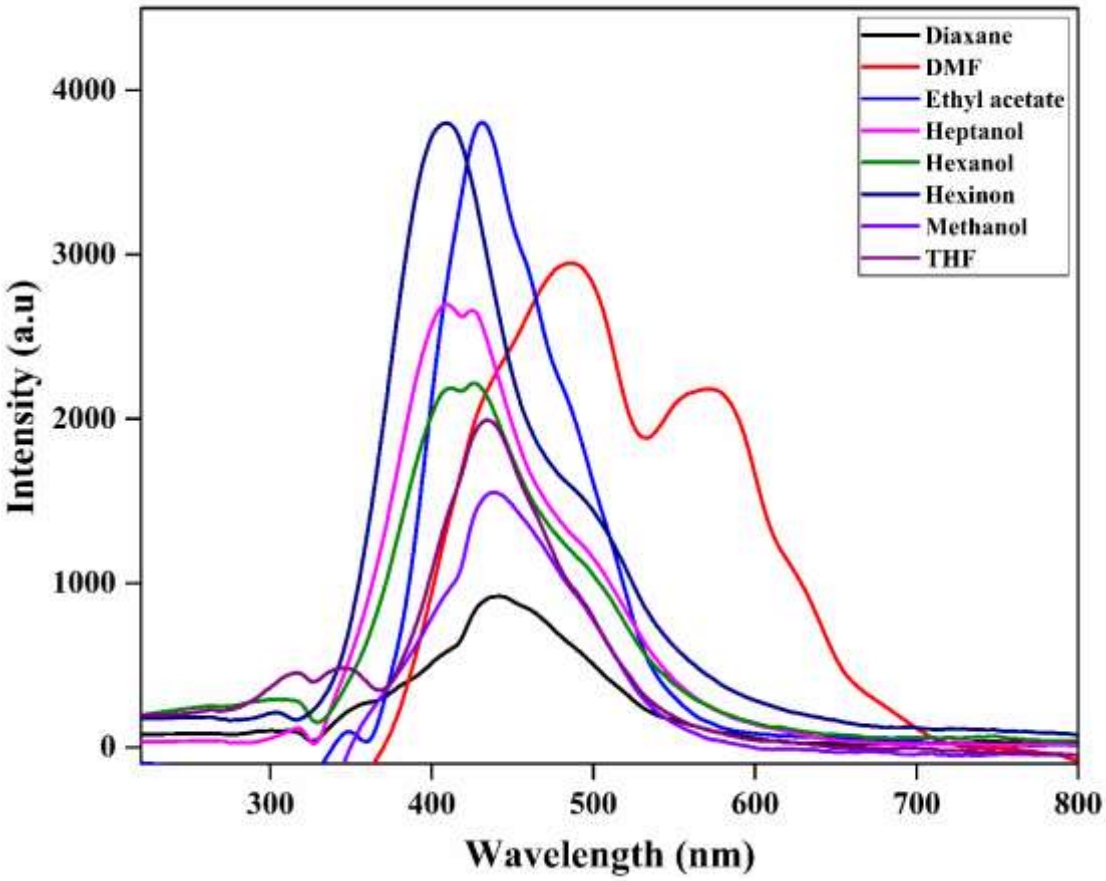
1.4 Photophysical properties

1.4.1 Solvent effect on absorption and fluorescence

The absorption spectra of the title compound were recorded between 200 to 900 nm. The solvent polarity influences the absorption wavelength and shape of absorption bands of title compound , particularly it influences on the molecules undergoing transitions from ground
state to the excited state. If the solvent attains stability with respect to one state than other, the energy gap changes hence absorption wave-length shifts to longer wavelength (red shift).



(a)



(b)

Figure 1.1: Graph plotted between absorbance vs wavelength (a) and fluorescence vs wavelength of the title compound dissolved in different solvent.

1.4.2 Experimental and theoretical ground-state dipole moments

The ground state and experimental excited dipole moments were determined by solvatochromic method using Lippert equation, Bakhshiev equations and Kawski-Chamma-Viallet equation [7-9]. The dipole moments of the title compound were determined using Lippert equation, Bakhshiev equations and Kawski-Chamma-Viallet equation. i.e.,

Lippert equation

$$\bar{\gamma}_a - \bar{\gamma}_f = m_1 F_1 + Constant \qquad \text{..... (1)}$$

Bakhshiev's equation

$$\bar{\gamma}_a - \bar{\gamma}_f = m_2 F_2 + Constant \qquad \text{..... (2)}$$

Kawski-Chamma-Viallet equation

$$\frac{\bar{\gamma}_a + \bar{\gamma}_f}{2} = -m_3 F_3 + Constant \qquad \text{..... (3)}$$

where $\bar{\gamma}_a$ and $\bar{\gamma}_f$ are wavenumbers of absorption and fluorescence maximum wavelength in cm^{-1}. m_1, m_2 are the slopes of equations (1) and (2). F_1, F_2 F3 Bakhshiev and Bilot–Kawski polarity functions and are given by

$$F_1(\varepsilon, n) = \left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right] \quad \text{.....(4)}$$

$$F_2(\varepsilon, n) = \frac{2n^2+1}{n^2+2}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] \quad \text{.....(5)}$$

$$F_3(\varepsilon, n) = \left[\frac{2n^2+1}{2(n^2+2)}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) + \frac{3(n^4-1)}{2(n^2+2)^2}\right] \quad \text{.....(6)}$$

where ε_r and n are the relative permittivity and the refractive index of the solvent respective

The graph of $(\bar{\upsilon}_a - \bar{\upsilon}_f)$ vs $F_1(\varepsilon, n)$, $(\bar{\upsilon}_a - \bar{\upsilon}_f)$ vs $F_2(\varepsilon, n)$ and $(\bar{\upsilon}_a + \bar{\upsilon}_f)/2$ vs $F_3(\varepsilon, n)$ gives linear slope values m_1, m_2 and m_3 respectively which is as shown in **Figure 1.1**

$$m_1 = \frac{2(\mu_e-\mu_g)^2}{hca^3} \quad \text{.....(7)}$$

$$m_2 = \frac{2(\mu_e-\mu_g)^2}{hca^3} \quad \text{..... (8)}$$

$$m_3 = \frac{2(\mu_e^2-\mu_g^2)}{hca^3} \quad \text{..... (9)}$$

where μ_e is excited state dipole moment, μ_g is ground state dipole moments, h is Planck's constant, c is velocity of light. Using Suppans's equation Onsager cavity radius 'a' is determined [10]. During molecular transition from ground state to excited state, symmetry of the molecule does not change. Therefore, molecules remain parallel in both ground state and excited state. The ground state and excited state dipole moments are given by

$$\mu_g = \frac{|m_3-m_2|}{2}\left(\frac{h\,c\,a^3}{2\,m_2}\right)^{\frac{1}{2}} \quad \text{.....(10)}$$

$$\mu_e = \frac{|m_3+m_2|}{2}\left(\frac{h\,c\,a^3}{2\,m_2}\right)^{\frac{1}{2}} \quad \text{.....(11)}$$

Dividing Eq. (8) by Eq. (7)

$$\frac{\mu_e}{\mu_g} = \frac{|m_2+m_3|}{|m_3-m_2|} \quad \text{For } m_3 > m_2 \quad \text{.....(12)}$$

Table 1.1 clearly says that band shift of 4-(Methoxycarbonyl)biphenyl-4-yl 5-bromo thiophene-2-caboxylate with different solvents of different polarities. A graph is plotted between ($\bar{\upsilon}_a$- $\bar{\upsilon}_f$) vs $F_1(\varepsilon, n)$ ($\bar{\upsilon}_a$- $\bar{\upsilon}_f$) vs $F_2(\varepsilon, n)$ and ($\bar{\upsilon}_a + \bar{\upsilon}_f/2$ vs $F_3(\varepsilon, n)$, From these graphs slopes m_1, m_2 and m_3 were determined. The slopes, intercept and correlation coefficients are obtained by linear square fitted methods and tabulated in the **Table 1.2.** The good correlations obtained in all the cases. The literature survey shows that m_3 is negative, one has to consider modulus of the slope, similar to findings in the previous work. The excited state and ground state dipole moment of the title compound is determined with the using equations (10) and (11) and tabulated in the **Table. 1.3**

Table.1.1 Solvatochromic data of the title compound with calculated values of F_1, F_2 and F_3

Solvent	$\bar{\gamma}_a$ **(cm^{-1})**	$\bar{\gamma}_f$ **(cm^{-1})**	$\bar{\gamma}_a - \bar{\gamma}_f$ **(cm^{-1})**	$(\bar{\gamma}_a + \bar{\gamma}_f)/2$	**F_1 (ϵ,n)**	**F_2(ϵ,n)**	**F_3(ϵ,n)**
1NN Dimethyl formamide	34246.5753	28571.4285	5675.1468	31409.0020	0.2731	0.8343	0.7117
Acetone	30395.1367	29411.7647	983.3720	29903.4507	0.2797	0.7864	0.6457
THF	32258.0645	22988.5057	9269.5588	27623.2851	0.2120	0.5521	0.5479
Benzene	34246.5753	27937.6431	6308.9322	31092.1093	0.2421	0.6091	0.5383
Ethyl acetate	34843.2055	28028.4769	6814.7286	31435.8413	0.1899	0.4765	0.5099
Choloroform	34246.5753	28028.4769	6218.0984	31137.5261	0.1434	0.3632	0.4936
Methanol	35087.7193	22988.5057	12099.2140	29038.1125	0.3170	0.8605	0.6395
Heptanol	33333.3333	24096.3855	9236.9478	28714.8594	0.2485	0.6802	0.6058
Hexinone	29916.8312	24509.8039	5407.0273	27213.3176	0.2602	0.7217	0.6231

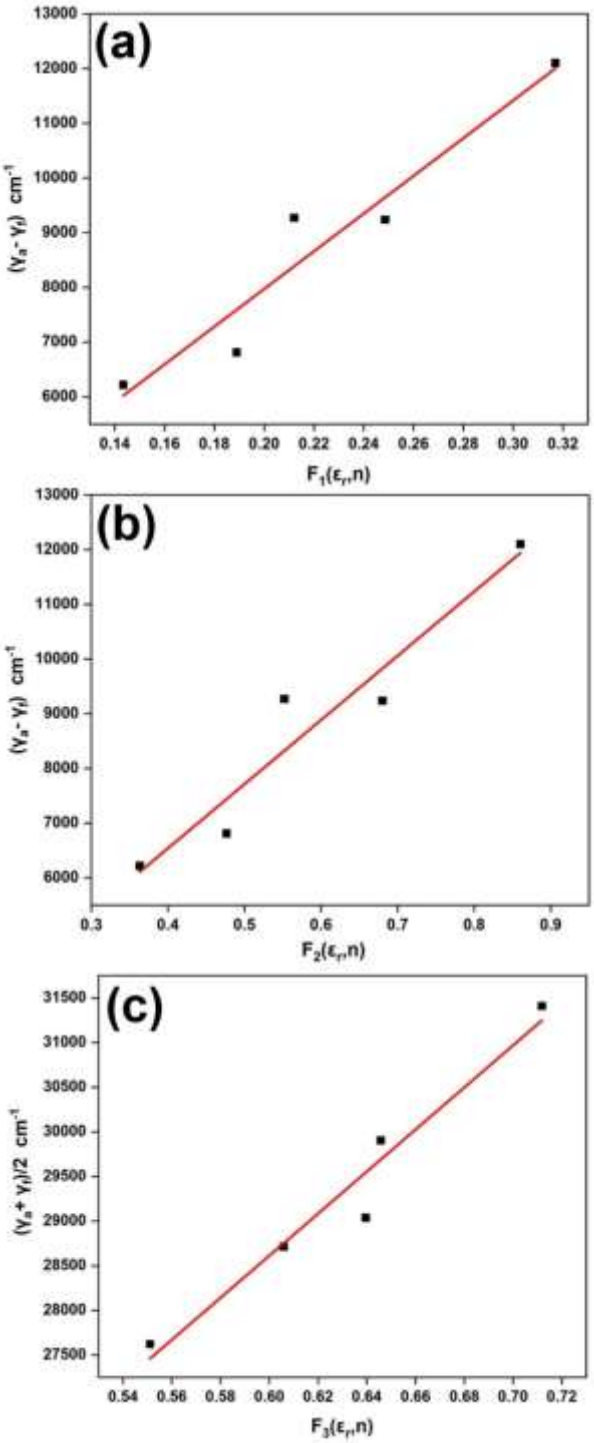


Figure 1.2 The variation of Stokes shift according to the (a)Lippert, (b)Bakshiev and(c)Bilot–Kawski–Chamma–Viallet function with different solvents.

Table 1.2 statistical treatment of the correlations of solvent spectral shifts of title compound

Method	Slope	Intercept	Correlation coefficient	Number of data
Lippert's correlation	**34444**	**1080**	**0.93**	**5**

Bakhshiev's correlation	**11726**	**1849**	**0.92**	**5**
Kawaski-Chamma-Viallet correlation	**23554**	**14479**	**0.96**	**5**

Table 1.3 Ground and excited states Dipole moments of (I) (in Debye)

Molecule	Radius a (A°)	μ_g[b] (D)	μ_g[c] (D)	μ_e[d] (D)	(μ_e/μ_g)[e]
Compound (IV)	4.63	1.6126	4.8908	13.4873	2.7876

[a] 1 Debye (D) = 10^{-18} esu = 3.33564 × 10^{-30} Coulomb meter (C-m).
[b] Theoretical μ_g value obtained from Gaussian program.
[c] Experimental μ_g value calculated from Eq. (10).
[d] Experimental μ_e value calculated from Eq. (11).
[e] The ratio μ_e/μ_g is calculated from equation (12).

Conclusion

In the synthesised molecule 4-(Methoxycarbonyl)biphenyl-4-yl 5-bromo thiophene-2-caboxylate, the molecular arrangement is stabilized by a halogen···Oxygen contact, Bromine···Oxygen interaction between the molecules. Crystal is further influenced by C-H ***Pi*** and Pi-Pi interaction. Solvatochromic studies confirm intermolecular charge transfer behaviour with dipole interactions in different solvents. The overall study of molecular structure, electron density around the molecule in terms of solvatochromic studies provide pivotal understanding of molecular behaviour.

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