

UV-VIS absorption and fluorescent characteristics of some substituted in the styryl fragment synthetic chalcones

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Dedicated to Academician Ivan Juchnovski on the occasion of his 70th birthday

Received December 17, 2007; Revised May 9, 2008

The photophysical properties of a number of synthetic chalcones in different media at 293K are investigated. The effect of the substituents in *p*-position of ring **B** of the studied chalcones on the deactivation processes of their singlet electronically excited state is discussed. It is found that in the case of the *p*-dimethyl-amino substituted compound the relationship between the fluorescent Franck-Condon transition energy and of the fluorescence quantum yield as well, and the ET(30) constants of the solvents is strongly influenced by the proton donating ability of the solvent. These experimental results indicate formation of intermolecular hydrogen bonded solute - solvent complexes in the fluorescent excited state at room temperature in protic solvents. Formation of different tautomeric forms of *p*-hydroxy substituted chalcone in different media is observed as well.

Key words: chalcones, UV-VIS absorption, fluorescence, DFT.

INTRODUCTION

Investigation on the relationship between the structure of electronically excited states of conjugated organic molecules and their absorption and fluorescent properties is one of the main problems of molecular photophysics. Nevertheless, the great number of experimental and theoretical data that is available in the literature specific characteristics for a particular group of compounds is observed in many cases. This holds for the conjugated organic compounds containing hetero-atoms in particular. Their electronic system includes $n\pi^*$ levels that play decisive role in the processes of radiative and nonradiative deactivation of the electronically excited states [1, 2].

Chalcones are natural oxygen-containing aromatic compounds that belong to the group of flavonoids with an open γ -pyrone cycle connecting two benzene fragments. In nature they occur mainly in plants and are also present in food products of plant origin such as propolis, wine, beer, fruit juices and tea. The low content of chalcones in natural raw material and their proved wide-range physiological activities are the reason for the increased interest towards the preparation of new synthetic chalcones with desired properties for application in medicine [3–5]. The synthetic chalcones studied in the present paper possess strong growth inhibitory activity towards the major human pathogen *Candida albicans* [6].

EXPERIMENTAL AND COMPUTATIONS METHODS

Absorption spectra were scanned on a UV-VIS Spectrophotometer Perkin Elmer Lambda 25 and the fluorescence spectra – on a Perkin Elmer LS 55 spectrofluorimeter. The fluorescence quantum yield (Q_F) was determined relative to that of the dye Rhodamine 6G ($Q_F = 0.95$ in ethanol) [7]. All measurements were performed at room temperature. The solvents used are of fluorescent grade.

The ground state geometry of two tautomers of *p*-hydroxy chalcone (hydroxy and oxo) were optimized by applying density functional theory (DFT) at the B3LYP/6-311+G** level. The nature of the potential energy surfaces was determined using harmonic vibrational analyses. The absence of imaginary frequencies confirmed that the stationary points correspond to minima on the potential energy surfaces. Self-consistent reaction field (SCRf) theory was employed to optimize the tautomers in the aqueous phase. The optimized geometries were used to compute electronic vertical singlet transition energies at the time-dependent density functional theory (TDDFT) level using the B3LYP functional. All calculations were performed using GAUSSIAN 98 suite of program [8].

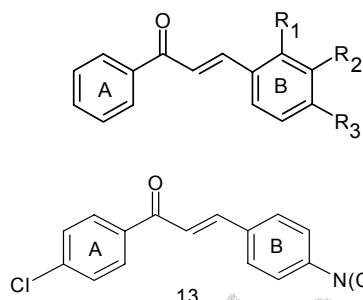
RESULTS AND DISCUSSION

The investigated compounds are presented in Table 1. The longest wavelength absorption maxima of the studied chalcones in ethanol at room tempe-

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ture are in the region of 33000–23000 cm^{-1} and move to the red with increasing the solvent polarity passing from benzene through acetonitrile to ethanol. The molar absorptivity in ethanol is between 12000 and 30000 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. The type of the substituent in *p*-position of the phenyl ring B has a strong influence on the energy of the longest wavelength absorption Frank-Condon transitions. A bathochromic shift by 3500 cm^{-1} is observed upon increasing its electron donating ability in the sequence methyl-, methoxy- and hydroxy- group. On the contrary, the cyano group possessing strong electron withdrawing abilities increases the energy of the S_0 - S_1 absorption transition by 400 cm^{-1} . The presence of dimethylamino group in *p*-position of ring B leads to the appearance of a second red shifted absorption band in ethanol with a maximum around 23000 cm^{-1} . This experimental result could be explained by the strong charge transfer transition between the electron withdrawing carbonyl group and the electron donating dimethylamino one in the molecule of compound **5** [9] (Table 2).

Table 1. Investigated compounds.



Ccompound	R ₁	R ₂	R ₃
1	H	H	H
2	H	H	CH ₃
3	H	H	OCH ₃
4	H	H	OH
5	H	H	N(CH ₃) ₂
6	H	H	Cl
7	H	H	CN
8	OH	H	H
9	H	OH	H
10	H	OH	OH
11	H	- O - CH ₂ - O -	
12	H	OCH ₃	OCH ₃

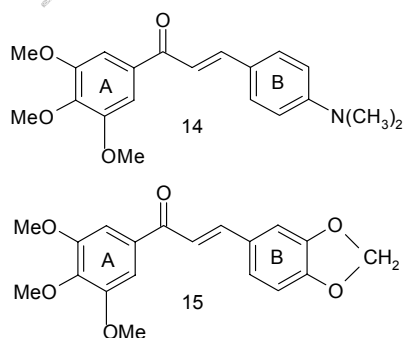


Table 2. Absorption characteristics of the investigated chalcones at 293 K: $\tilde{\nu}_{\text{ABS}}$ – energy of the longest wavelength absorption Franck-Condon transitions in cm^{-1} ; ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) – molar absorptivity. The numbers of the compounds correspond to those given in Table 1.

Compound	Benzene	Acetonitrile	Ethanol	
	$\tilde{\nu}_{\text{ABS}}$	$\tilde{\nu}_{\text{ABS}}$	$\tilde{\nu}_{\text{ABS}}$	ϵ
1	32790	32260	32050	13000
2	31250	30960	30490	19350
3	29590	29410	28990	17510
4	29760	29410	28570	13330
5	24510	24390	28270	26000
6	31750	32260	31750	12850
7	33330	32790	32470	12000
8	29410	28990	28170	14800
9	32790	32470	32790	15000
10	28570	28170	27030	14860
11	28170	28170	28090	16380
12	28170	27930	27620	17100
13	24270	23810	23260	24320
14	24100	23920	23260	30000
15	28410	27780	27620	17200

In the case of compounds **4** and **10** (Table 1), where the substituent R₂ is a hydroxyl group, a specific interaction with protic solvents in S₀ state is observed (Fig. 1) that is most probably due to the oxo-hydroxy tautomerism of these compounds [10].

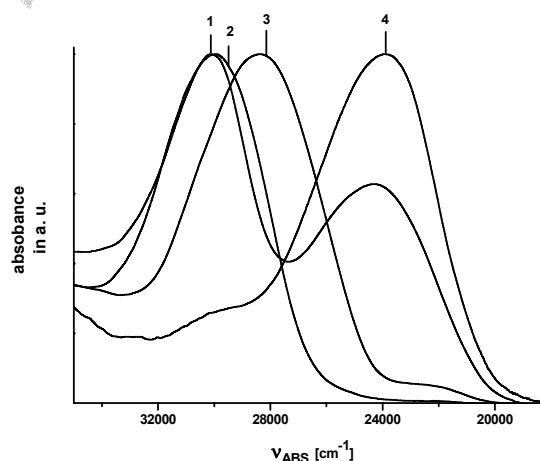


Fig. 1. Absorption spectra of compound **4** in solution at 293 K in: benzene - curve 1; ethanol - curve 2; water at pH 7 - curve 3; water at pH 9 - curve 4.

The assignment of the bands between 33000 and 20000 cm^{-1} to the absorption of the hydroxy and the oxo form is performed on the basis both of experimental results in benzene, ethanol, water at pH 7 and water at pH 9, and quantum chemical calculations as well.

The longest wavelength absorption band of **4** in benzene has a maximum at 29760 cm^{-1} . It could be related to the presence of a hydroxy form. A new bathochromically shifted band with maximum at

around 24000 cm^{-1} appears in ethanol and water at pH 7. It could be assigned to the possible formation of another tautomeric form of *p*-hydroxy substituted chalcones – namely an oxo form. Equilibrium between oxo and hydroxy tautomeric forms in ethanol and water (pH 7) is observed, while in water at pH 9 the oxo tautomeric form is mainly present. Computed transition energies were found in a good agreement with the corresponding experimental data as well. Calculation predicts singlet $\pi\text{-}\pi^*$ electron transition at 29400 cm^{-1} for hydroxy and at 24800 cm^{-1} for oxo tautomeric forms, respectively.

In order to explain the obtained experimental results a detailed theoretical study of the molecular geometry of the species studied was performed. The solvent effect was studied by SCRF theory. The relative stability of the hydroxy and oxo tautomers in gas phase and in water ($\epsilon = 78.39$) was determined. Comparison of the energy values of the studied tautomers indicates that in gas phase the hydroxy tautomer is more stable by 15.7 kcal/mol , while in water solution the oxo tautomer is only slightly less stable (less than 1 kcal/mol). Therefore, it could be concluded that *p*-OH chalcones will be present mainly in their hydroxy tautomeric form in gas phase while in aqueous media both hydroxy and oxo forms exist. The obtained results are in good agreement with the corresponding experimental ones.

The unsubstituted chalcone does not fluoresce in solution at room temperature. The absence of fluorescence is due to the fact that its longest wavelength absorption transition lies around $27\,000\text{ cm}^{-1}$ and like in the case of other carbonyl-containing compounds is of $S_0\text{-}S_1(\pi\pi^*)$ type [11]. This transition cannot be observed in the absorption spectrum of compound **1** as it is overlapped by an intensive $S_0\text{-}S_1(\pi\pi^*)$ band. Radiation $S_1(n\pi^*)\text{-}(S_0)$ transitions in carbonyl compounds are forbidden and that is why the compound does not have a fluorescence of its own [1].

The presence of electron donating substituent in *p*-position of ring **B** such as methoxy- or hydroxy-group leads to a bathochromic shift of the longest wavelength absorption transition. The energy of lowest lying $S_1(\pi\pi^*)$ and $S_1(n\pi^*)$ levels becomes similar. These compounds do not fluoresce in aprotic solvents. However, in protic solvents the so-called “activated fluorescence” [1, 2, 12] with maxima in the range of $25000\text{-}23000\text{ cm}^{-1}$ and low fluorescent quantum yields is observed.

In the case of the *p*-dimethylamino substituted in ring **B** chalcone a specific interaction with protic solvents in excited state is observed, namely formation of intermolecular solute-solvent hydrogen bonds (Fig. 2).

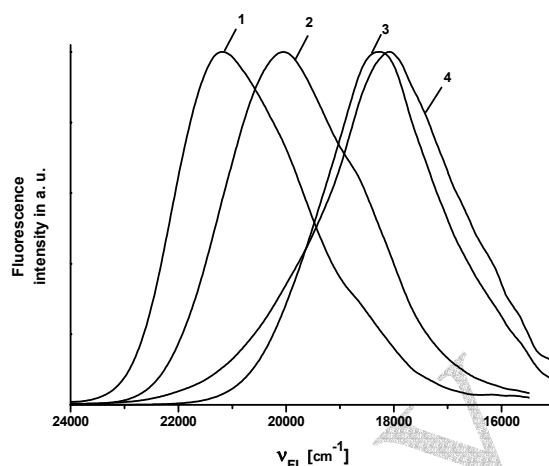


Fig. 2. Fluorescent spectra of compound **5** in solution at 293K in: benzene - curve 1; ethylacetat - curve 2; acetonitrile - curve 3; ethanol - curve 4.

The fluorescent maximum of compound **5** moves to the red with increasing the polarity and proton donating ability of the solvents. The fluorescent quantum yield increases with increasing the solvent polarity in the case of aprotic solvents. On the contrary, the Q_F decreases drastically in protic solvents in comparison to aprotic ones despite their high polarity.

The assumption for formation of hydrogen bonds in excited state is confirmed by the investigations on the relationship between the ET(30) constants of the solvents and the energy of the fluorescent maxima and the Q_F value, respectively [13].

Two different linear correlations – one for protic and one for aprotic solvents – for the relationship between the energy of the fluorescent transition and ET(30) constants of the solvents are observed. The presence of two different linear correlations shows that the nature of the fluorescent species in protic and in aprotic solvents is different [14, 15] (Fig. 3).

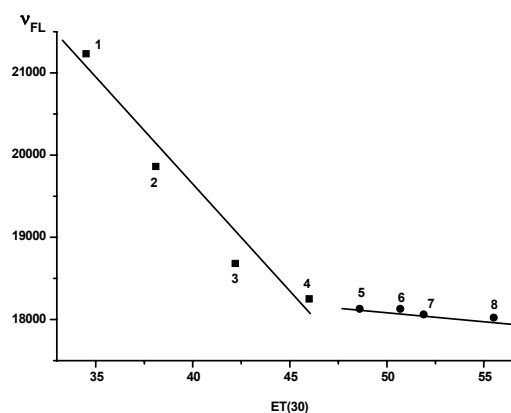


Fig. 3. Energy of the fluorescent maxima ν_{FL} in cm^{-1} of compound **5** vs the solvent polarity parameter ET(30) in: benzene - 1; ethylacetate - 2; acetone - 3; acetonitrile - 4; *n*-butanol - 5; *i*-propanol - 6; ethanol - 7; methanol - 8.

In corroboration of the assumption for formation of intermolecular hydrogen bonds is the presence of two linear correlations $ET(30)/Q_F$ that are obtained for protic and aprotic solvents, respectively. The quenching of fluorescence in protic solvents is most probably due to vibrations of the hydrogen bonds between the molecules of the solute and the protic solvent in excited state, thus acting as an additional channel for radiationless deactivation (Fig. 4).

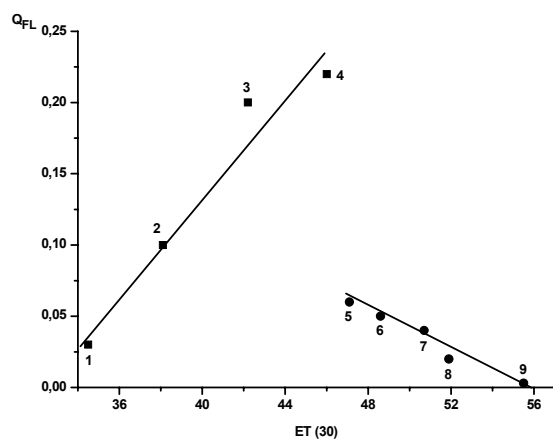


Fig. 4. Fluorescent quantum yield Q_{FL} of compound **5** vs the solvent polarity parameter $ET(30)$ in: benzene - 1; ethylacetate - 2; acetone - 3; acetonitrile - 4; *n*-butanol - 5; *i*-butanol - 6; *i*-propanol - 7; ethanol - 8; methanol - 9.

CONCLUSIONS

It is shown that the nature of the substituent in *p*-position of the benzene ring **B** has a strong influence on the position of the longest wavelength absorption maxima of the investigated chalcones. The presence of electron donating groups like methoxy- and hydroxy- ones leads to its bathochromic shift, while the introduction of electron withdrawing substituent, namely cyano group leads to a blue shift of this maximum. The occurrence of strong charge transfer in the case of *p*-dimethylamino-substituted chalcone is observed. The ability of *p*-hydroxy-substituted chalcone to exist in different tautomeric forms, namely oxo and hydroxy ones, in solvents of different polarity and proton donating ability is proved by experimental data and quantum chemical calculations. The main fluorescent characteristics of the studied chalcones are determined at room temperature and it is shown that the absence of fluorescence in some cases is due to the fact that their lowest lying S_1 state is of $n\pi^*$ type. A specific interaction – formation of intermolecular hydrogen bonds in excited state between the *p*-dimethylamino-substituted chalcone and protic solvents is

proved on the basis of the relationship between the energy of the Fluorescent Frank Condon transition and the $ET(30)$ constants of the solvents.

Acknowledgement: The financial support by the Bulgarian Council of Scientific Research for Project X-1514 is politely acknowledged.

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АБСОРБЦИОННИ И ФЛУОРЕСЦЕНТНИ ХАРАКТЕРИСТИКИ В УВ-ВИДИМАТА ОБЛАСТ НА НЯКОИ ЗАМЕСТЕНИ В СТИРИЛНИЯ ФРАГМЕНТ СИНТЕТИЧНИ ХАЛКОНИ

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Посветена на акад. Иван Юхновски по повод на 70-та му годишнина

Постъпила на 17 декември 2007 г.; Преработена на 9 май 2008 г.

(Резюме)

Изучени са фотофизичните отнасяния в различни по полярност и протонодонорни свойства разтворители при 293К на една група синтетични халкони. Проследен е ефектът на природата на заместителя на *p*-място във фенилното ядро **V** на изследваните халкони върху процесите на дезактивация на възбудените им синглетни електронни състояния. Установено е, че в случая на *p*-диметиламино-заместеният халкон протонодонорните свойства на разтворителите оказват съществено влияние върху зависимостите между енергията на флуоресцентния Франк Кондонов преход и флуоресцентния квантов добив от една страна и ET(30) константата на разтворителите от друга. Тези експериментални резултати са индикация за формирането на свързани с междумолекулни водородни връзки комплекси между разтвореното вещество и протния разтворител във възбудено състояние при стайна температура. На базата на експериментални резултати от абсорбционните спектри в УВ-видимата област в различни разтворители и на квантово-химични пресмятания е доказано наличието на различни тавтомерни форми на *p*-хидрокси заместения халкон.