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Luminescent properties of chalcone and its aminoderivatives

K.G. Komarova^{a,b,*}, S.N. Sakipov^a, V.G. Plotnikov^{a,c}, M.V. Alfimov^{a,c}^a Photochemistry Center, Russian Academy of Sciences, Novatorov st. 7A, Moscow 117421, Russia^b National Research Nuclear University MEPhI, Kashirskoe shosse 31, Moscow 115409, Russia^c Tomsk State University, 634050 Tomsk, Lenin st. 36, Russia

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ABSTRACT

Excitation energies of singlet and triplet $\pi\pi^*$ and $n\pi^*$ transitions are calculated for chalcone and its aminoderivatives using quantum chemical approach. Solvent impact on the molecular geometry and excited state energies is investigated. Both universal (dipole–dipole) and specific (H-bond formation with C=O group) interactions are taken into account.

Dipole–dipole interactions are shown to stabilize the excited $S_{\pi\pi^*}$ state in the systems studied in the same way as for others heteroaromatic luminophores. Specific interactions in protic solvents cause in addition significant geometry deformation to the non-planar structure of the chromophore. Large intramolecular spin–orbit coupling between the lowest singlet and triplet excited states in the latter case is revealed. It proves that intersystem crossing between these states should be the main channel of fluorescent quenching of 4-(N, N' – dimethylamino)-chalcone in protic solvents.

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1. Introduction

Spectral-luminescent properties of carbonyl derivatives of aromatic compounds are widely investigated and their dependency on the molecular structure and solvent polarity is well established [1–7]. Their luminescent properties mostly correlate with the relative energy of the $n\pi^*$ and $\pi\pi^*$ singlet and triplet excited states [5]. It was shown [6] that intersystem crossing rates for $S_{\pi\pi^*} \rightarrow T_{n\pi^*}$ and $S_{n\pi^*} \rightarrow T_{\pi\pi^*}$ are large, which means that if the energy of singlet or triplet $n\pi^*$ state is lower than the energy of the lowest $S_{\pi\pi^*}$ state then fluorescence quenching occurs. And vice versa, if the lowest singlet and triplet states are $\pi\pi^*$ states fluorescence quantum yield will be significant.

Interaction with protic solvents results in fluorescence activation in the same way as for other heteroaromatic luminophores [7] due to increase of the energy of the $n\pi^*$ states. However, it hardly be said about the properties of chalcone and its amino-derivatives. Due to the flexible $-C=C(-)O$ chain and non-planar structure [8,9] they have distinguishing features, such as fluorescence quenching in protic solvents [4,10–14].

The degree of deviation from planarity for planar chromophores is shown to correlate with intersystem crossing rates due to increase of the magnitude of spin–orbit coupling (SOC) between singlet and triplet states [6,15]. Large deviation from the C_s symmetry induces

the mixing of the π and σ -orbitals in the molecular wave function, which gives rise to the one-center electron integrals in the description of the SOC matrix elements. Thus intersystem crossing as a possible channel of non-radiative decay should be considered if solute–solvent interactions lead to a non-planar geometry of the chromophore [16].

Examining the solvent effect on fluorescent properties of chalcones could be of importance in various fields of photochemistry, biochemistry and pharmaceutical chemistry [17–19]. Chalcone and its derivatives are widely used as fluorescent probes [20,21], materials with significant nonlinear responses [22] and typical chromophore components for photochemical sensors [23]. Charge transfer character of the low-lying $\pi\pi^*$ transition from the phenyl ring to the polyene chain allows one to vary the energy of the intense transition introducing substituents in the phenyl ring [9].

In general solvent–solute interactions are classified in two types: dipole–dipole universal interactions and specific interactions, such as bond formation between chromophore and solvent (usually H-bond formation with protic solvent). Various continuum models (Onsager, COSMO) were efficiently used in order to describe the solvent effect on the photophysical processes of organic chromophores [24–26]. Authors [27] stated out the importance of accounting both types of interactions in order to describe the effect of protic solvents on the energies and relative order of the singlet and triplet $\pi\pi^*$ and $n\pi^*$ excited states.

Electronic structure of chalcone derivatives was explored mostly in their singlet $\pi\pi^*$ states in order to analyze the absorption spectra of substituted chalcones [9,17–19,28]. Substituents in the phenyl ring

* Corresponding author at: Photochemistry Center, Russian Academy of Sciences, Novatorov st. 7A, Moscow 117421, Russia.

E-mail address: kgvladi@gmail.com (K.G. Komarova).

conjugated with $-C=C-$ group affect the absorption maximum with a greater extent than those in the phenyl ring conjugated with $-C(=O)-$ group [9]. Both electron-donor and electron-acceptor (except highly polar CF_3 and Cl) substituents cause a decrease in the energy of the $S_{\pi\pi^*}$ - state. The largest shift (0.8 eV) corresponds to the 4-(N, N' - dimethylamino)-chalcone, which is shown to have also high fluorescence quantum yield (0.6 in dimethylformamide) when compared to the non-fluorescent chalcone [12,14]. In paper [8] the energies of singlet and triplet $\pi\pi^*$ and $n\pi^*$ excited states were simulated using quantum chemical approach for 4-(N, N' - dimethylamino)-chalcone and its complex with water molecules in a gas phase. However, dipole-dipole interactions were not taken into account, so the obtained results can be compared only to spectral properties in binary mixture of non-polar solvent with small amount of water.

The aim of the present work is to study the solvent effect on the geometry and energies of the low-lying excited states of chalcone (Ch) and its amino-derivatives 4-aminochalcone (ACh) and 4-(N, N' - dimethylamino)-chalcone (DMACH). The special attention is paid for spin-orbit interaction between the lowest singlet and triplet states for cases where fluorescence quantum yield is not negligible. The energies of singlet and triplet $\pi\pi^*$ and $n\pi^*$ excited states are calculated using RI-CC2 quantum chemical approach. Both universal dipole-dipole and specific interactions are taken into account. In order to describe specific interactions for protic solvents (H-bond formation) we consider complex of each chromophore with 1 ethanol molecule. The solvent effect on the geometries due to universal dipole-dipole interactions is taken into account during the geometry optimization within the COSMO model [29]. Then the energy shifts induced by dipole-dipole interaction with the medium are calculated within Onsager approach [27] for the electronic states under the consideration. It will be demonstrated that geometry changes due to solvent-solute interaction affect the spin-orbit coupling between the low-lying singlet and triplet excited states.

2. Computational details

We use second order approximate coupled cluster (CC2) method [30] within resolution of the identity approximation [31–33] for quantum chemical calculations of the excited state energies and equilibrium geometries as implemented in Turbomole program package [34]. Excitation energies and dipole moments were obtained for ground state and $S_{\pi\pi^*}$ state equilibrium geometries. The effect of universal interactions on excitation energies is simulated within COSMO and Onsager-Liptay theory [35,36] for the set of solvents: cyclohexane ($\epsilon = 2$), N,N-dimethylformamide (DMF, $\epsilon = 36.7$), and ethanol ($\epsilon = 22.4$). All the calculations use cc-pVDZ basis set [37,38].

The energy shifts of electronic states, caused by dipole-dipole interaction, are estimated based on the Onsager-Liptay theory as follows:

$$\vec{E}_R = f\vec{\mu} = (f_{ind} + f_{or})\vec{\mu}; \quad \vec{\mu} = \vec{\mu}_0 + \alpha\vec{E}_R,$$

$$f_{or} = \frac{2}{a^3} \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right),$$

$$f_{ind} = \frac{2}{a^3} \left(\frac{n^2 - 1}{2n^2 + 1} \right), \quad (1)$$

where a - the solute cavity radius; ϵ , n - the static dielectric constant and the refractive index of medium; $\vec{\mu}$ - the vector of the dipole moment of dissolved molecule; f_{or} , f_{ind} - orientation and induction polarity functions, respectively; and $\vec{\mu}_0$, α - dipole moment vector and polarizability tensor of the molecule in a gas

phase. The radii a are fitted in order to qualitatively reproduce the energies of the $S_{\pi\pi^*}$ state (see Supporting Information, Table 2).

The energy difference between r and s states of the molecule in the solvent reaction field with fast component f_{ind} corresponding to the s state and slow component corresponding to the r state is given by

$$\Delta_{rs} = \Delta_{rs}^0 - \frac{1}{2}f_{ind}(\vec{\mu}_r^T - \vec{\mu}_s^T)(1 - f_{ind}\alpha)^{-1}(\vec{\mu}_r - \vec{\mu}_s) - f(\vec{\mu}_r^T - \vec{\mu}_s^T)(1 - f_{ind}\alpha)^{-1}\vec{\mu}_s, \quad (2)$$

where Δ_{rs}^0 , Δ_{rs}^0 - the energy difference between the states for molecule in the reaction field and isolated molecule, respectively; $\vec{\mu}_r$, $\vec{\mu}_s$ - the vector of dipole moments of the isolated molecule in r and s states, respectively; $\vec{\mu}_r^T$, $\vec{\mu}_s^T$ - transposed vectors of dipole moments of the isolated molecule in r and s states, respectively. This expression is correct under the condition that solvent relaxation (10^{-12} s) can take place within the limited lifetime of excited state, e.g. for liquid solvents of low viscosity [36].

The effect of non-specific interactions using COSMO is included only for the started Hartree-Fock wave functions of the molecules. This is quite a rough approximation, because the absolute value of dipole moment of the excited state is larger than one of the ground state (they are co-directional though). Nevertheless, energies calculated within this approximation are in good agreement with values obtained using Onsager-Liptay theory (Eqs. (1) and (2), see Supporting Information, Table 3). We believe that this fact approves the use of such approximation even for excited states geometry optimization.

The spin-orbit coupling effects are taken into account within the multi-configurational wave-function approach (MCSCF). State-averaging over 10 low-lying states (both singlet and triplet) is used for the optimal wave function construction. Active space consists of 6π and $1n$ occupied orbitals and 3 vacant π orbitals. All the calculations use 6-311G(d,p) Gaussian basis set. The matrix elements of the effective spin-orbit coupling operator H_{SO} are calculated for 4 low-lying singlet and triplet states within perturbation theory with full Breit-Pauli Hamiltonian [39] as implemented in the GAMESS program package [40]. The calculated values are listed in the table (see Supporting Information, Table 6). The only largest matrix element is shown for triplet states with different magnetic quantum numbers. The value for others appears to be lower by two orders of magnitude.

3. Results and discussion

Chalcone and its derivatives have non-planar structure in the ground state. There are two flexible torsion angles: (i) θ - twisting of the ring A and (ii) ϕ - twisting of the ring B (Fig. 1). The θ -angle appears to be larger than ϕ , which supports the fact that phenyl ring B is more conjugated with the $-C=C(-)O$ chain than phenyl ring A.

Our calculations show that dipole-dipole interactions weakly affect the θ -angle in the ground state geometry of the molecules studied, even for highly polar media. For example, changes about $|\delta\theta| = 3^\circ$ are observed for the aminochalcone starting from cyclohexane ($\epsilon = 2$) to dimethylformamide ($\epsilon = 36.7$). Effect of specific interactions in protic solvent (ethanol, $\epsilon = 22.4$) appears to be much larger for aminochalcone - $|\delta\theta| = 11^\circ$, however for other chalcones studied the effect does not exceed $|\delta\theta| = 6^\circ$ (Fig. 2).

Media effect on the ϕ torsion angle is less straightforward and differs for chalcone and its aminoderivatives. The changes of $|\delta\phi| = 5^\circ$ are observed for chalcone in aprotic solvents starting from cyclohexane to DMF, however for the aminoderivatives $|\delta\phi| < 1^\circ$ is found. Taking into account specific interactions result in decrease of the ϕ torsion angle in chalcone ($|\delta\phi| = 4.6$), weakly

increase of it in aminochalcone ($|\delta\phi| = 1$) and dramatic increase of it in 4-(N, N' – dimethylamino)-chalcone – $|\delta\phi| = 11^\circ$. Significant mixing of the π and σ -orbitals in the molecular wave function in the latter case is observed.

Solvent affects the geometry of the amino-group in amino-derivatives of chalcone ($|\delta\psi| < 5^\circ$). For aminochalcone it stays non-planar even in ethanol, while for DMACH in ethanol it is planar (see details in Supporting Information, Table 1).

Changes of the chromophore geometry upon non-specific interactions weakly influence the tensor of polarizability, however H-bond formation with ethanol molecule leads to a 20% increase of the polarizability in the systems studied.

Excited state energies calculated for the ground state geometry and reactive field correspond to the energies of the vertical vibronic transitions. On account of the fact that the band width is much smaller than the transition energy we believe that calculated values correlate with the maxima of the corresponding absorption band.

It is important to remind of the correctness of the classification of electronic excited states. The usage of common $\pi\pi^*$ and $n\pi^*$ designations for excited states of planar molecules in the case of the chalcone and its amino-derivatives is not rigorous because of deviation of their structure from planarity. Nevertheless we use these designations below, because of two facts. As our calculations reveal, the composition of the low-lying excited state wave

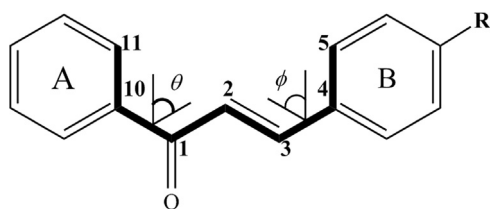


Fig. 1. Structure of the chalcone and its aminoderivatives R = H, NH₂, N(CH₃)₂. θ – the torsion angle C11–C10–C1–C2, ϕ – the torsion angle C2–C3–C4–C5.

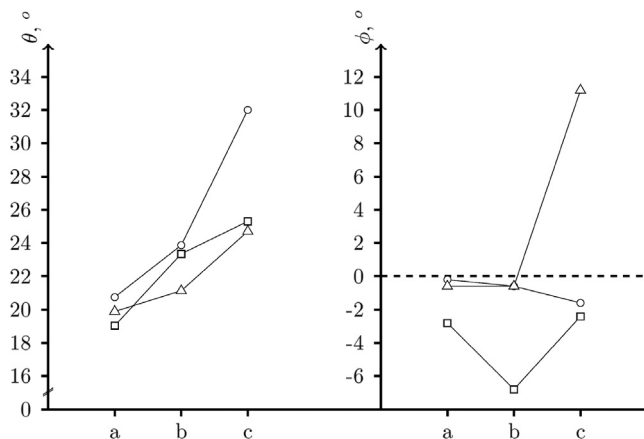


Fig. 2. Changes of the twisting angles θ and ϕ (see Fig. 1) in the ground state geometry of the chalcone (rectangles), aminochalcone (circles) and 4-(N, N' – dimethylamino)-chalcone (triangles) in various solvents: (a) cyclohexane ($\epsilon = 2$), (b) DMF ($\epsilon = 36.7$), and (c) ethanol ($\epsilon = 22.4$).

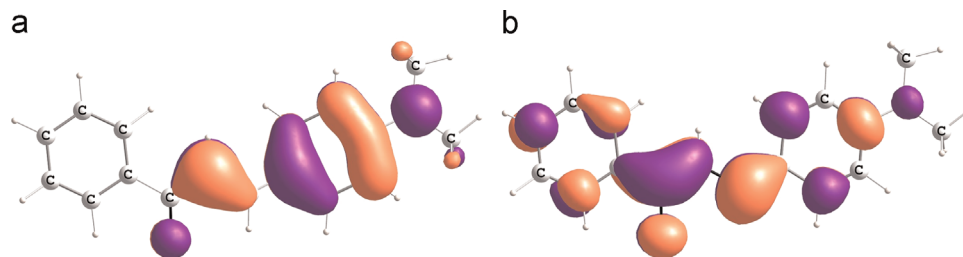


Fig. 3. Molecular orbitals involved in the lowest $\pi\pi^*$ – transition in 4-(N, N' – dimethylamino)-chalcone: (a) HOMO and (b) LUMO.

functions is dominated by the one of the two configurations of $\pi\pi^*$ and $n\pi^*$ nature for structures with torsion angle θ lower than 30° . The second fact corresponds to the significant difference between the oscillator strengths of the so-called $S_0 \rightarrow S_{\pi\pi^*}$ and $S_0 \rightarrow S_{n\pi^*}$ transitions in the systems studied (see details in Supporting Information, Table 2). For the first type the calculated oscillator strength is about ≈ 1 and for the second one it is less than $\approx 10^{-2}$.

The excited state energies for chalcone, aminochalcone and 4-(N, N' – dimethylamino)-chalcone calculated for various solvents within Onsager–Liptay theory in the ground state equilibrium geometry and reactive field are shown in Figs. 4–6, respectively. Let us consider the nature of the excited electronic states of the systems studied. The low-lying excited states are intramolecular charge transfer states. In the $n\pi^*$ – states the transition corresponds to the charge transfer from the carbonyl-group to the π -electronic system of the molecule. Charge transfer in the $\pi\pi^*$ excitations takes place from the aromatic subsystem on the phenyl ring B to the π -electronic system localized on the $-C=C-C(-)=O$ chain (see Fig. 3). Large increase of the calculated dipole moment of the $S_{\pi\pi^*}$ excited state is observed compare to the dipole moment of the ground state (see Supporting Information, Table 4). This leads to a bathochromic shift of the $S_{\pi\pi^*}$ absorption bands with the increase of the solvent polarity.

Along with the noted before-mentioned large difference of the oscillator strengths of the $S_0 \rightarrow S_{\pi\pi^*}$ and $S_0 \rightarrow S_{n\pi^*}$ transitions the salient feature of the $\pi\pi^*$ and $n\pi^*$ states is the extent of the singlet–triplet splitting [1,2,5–7]. As can be seen from the calculated results, similar to the other heteroaromatic compounds, the singlet–triplet splitting for the $n\pi^*$ states of chalcone and its amino-derivatives is about ≈ 0.2 – 0.3 eV, while for the $\pi\pi^*$ states it is ≈ 1 – 1.5 eV. This fact supports the correctness of the usage of $n\pi^*$ and $\pi\pi^*$ designations. It is interesting to notice that introducing amino-groups to the chalcone structure leads to a decrease of the singlet–triplet splitting for the $\pi\pi^*$ states (from ≈ 1.56 eV to ≈ 0.9 eV). This fact indicates the increase of the charge transfer character of the transition for chalcones with electron-donating substituents in the phenyl ring B.

The lowest singlet excited state of chalcone is of $n\pi^*$ nature in the solvents studied. Changes in solvent polarity do not affect the order of the excited states (see Fig. 4). For comparison, the energy of the $S_{\pi\pi^*}$ -state in various solvents calculated within COSMO is: (a) cyclohexane – 4.46 eV, (b) DMF – 4.32 eV, and (c) ethanol – 4.17 eV. Experimental value of the excitation energy to the $S_{\pi\pi^*}$ state is 4.1 eV, to the $S_{n\pi^*}$ -state is 3.4 eV in the iso-octane ($\epsilon \approx 2$) [5], calculated energies are in qualitative agreement with the experimental values.

Large difference between the energies of the $S_{\pi\pi^*}$ and $S_{n\pi^*}$ states in chalcone (>0.8 eV) in the ground state should stay of the same order in the excited $S_{\pi\pi^*}$ state. This fact confirms the fluorescence quenching of chalcone [6] due to the fast process of the $S_{\pi\pi^*} \rightarrow T_{n\pi^*}$ and $S_{n\pi^*} \rightarrow T_{\pi\pi^*}$ intersystem crossing.

Calculated energies of the electronic states of aminochalcone show that in aprotic solvents quenching is dominated by the $S_{\pi\pi^*} \rightarrow T_{n\pi^*}$ and $S_{n\pi^*} \rightarrow T_{\pi\pi^*}$ intersystem crossing. In the ethanol the energy of the $S_{n\pi^*}$ state is higher than the energy of the $S_{\pi\pi^*}$ state, however their energies are close to each other and the lowest excited state optimization

results in the $n\pi^*$ main configuration of the wave function. This fact explains negligible fluorescence quantum yield of aminochalcone in polar solvents [4]. For comparison, the energy of the $S_{n\pi^*}$ state calculated within COSMO is: (a) 3.86 eV, (b) 3.57 eV, and (c) 3.45 eV.

In 4-(N, N' – dimethylamino)-chalcone the $S_{\pi\pi^*}$ and $S_{n\pi^*}$ states are quasi-degenerate in the non-polar solvent (cyclohexane), so the fluorescence quenching occurs through the $S_{\pi\pi^*} \rightarrow T_{n\pi^*}$ and $S_{n\pi^*} \rightarrow T_{\pi\pi^*}$ intersystem crossing. The energy of the $S_{\pi\pi^*}$ state becomes lower than the energy of $S_{n\pi^*}$ state for $\epsilon = 36.7$ (dimethylformamide), however the energies of the triplet states are lower. For comparison, excitation energy to the $S_{\pi\pi^*}$ state calculated within COSMO approach is: (a) 3.52 eV, (b) 3.21 eV, and (c) 3.01 eV. Experimental values of the energy of the $S_{\pi\pi^*}$ transition are: 3.19 eV in heptane, 3.06 eV in toluene, 2.97 eV in acetone and 2.94 eV in dimethylformamide [3,12].

Solvent effect on luminescent properties of the systems studied can be demonstrated in the same way as for ground state for the molecular geometry, corresponded to the potential energy surface minimum of the $S_{\pi\pi^*}$ excited state. Calculations reveal that $S_{\pi\pi^*}$

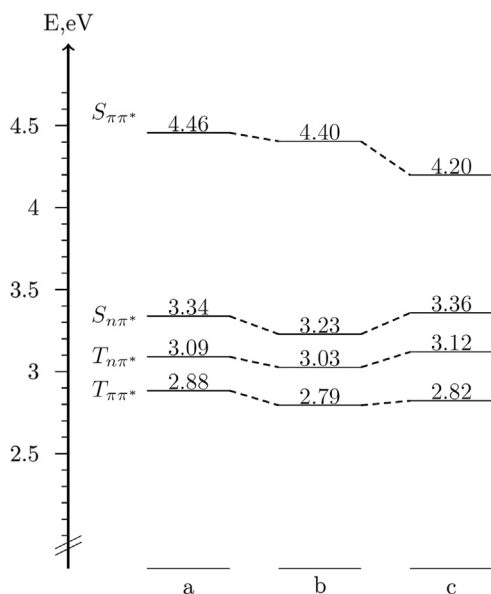


Fig. 4. Excitation energies for chalcone calculated for various solvents within Onsager–Liptay theory in the ground state equilibrium geometry and reactive field for the set of solvents: (a) cyclohexane ($\epsilon = 2$), (b) DMF ($\epsilon = 36.7$), and (c) ethanol ($\epsilon = 22.4$).

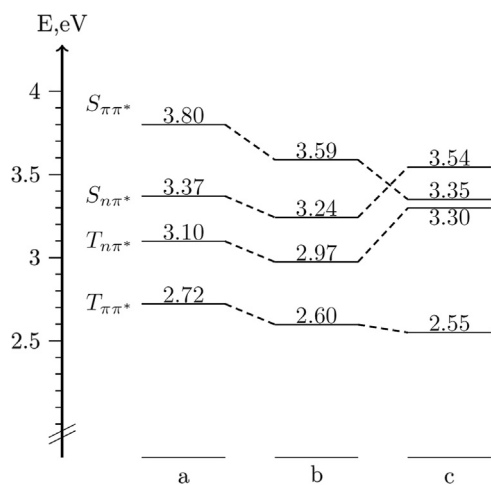


Fig. 5. Excitation energies for aminochalcone calculated for various solvents within Onsager–Liptay theory in the ground state equilibrium geometry and reactive field for the set of solvents: (a) cyclohexane ($\epsilon = 2$), (b) DMF ($\epsilon = 36.7$), and (c) ethanol ($\epsilon = 22.4$).

excited state is the lowest for 4-(N, N' – dimethylamino)-chalcone. In the $S_{\pi\pi^*}$ excited state decrease of the torsion angles θ and ϕ is observed compare to the ground state geometry in cyclohexane and DMF (see Supporting Information, Table 1). Taking into account both universal and specific interactions (in the case of ethanol) results in significant twisting of both phenyl rings ($\theta = 21^\circ$, $|\phi| = 16.2^\circ$). Geometry turns into non-planar structure, which induces the mixing of the π and σ -orbitals in the molecular wave function.

The energy of singlet and triplet $n\pi^*$ states is lower than the energy of $S_{\pi\pi^*}$ state (Fig. 7) in aprotic solvents with low polarity (cyclohexane). For such a case considerable probability of the fluorescence quenching should be expected via intersystem crossing from $S_{n\pi^*}$ to $T_{\pi\pi^*}$ state [6]. This fact explains low fluorescence quantum yield for 4-(N, N' – dimethylamino)-chalcone in cyclohexane [4,12]. Increase of the solvent polarity (DMF, $\epsilon = 36.7$) causes changes in the relative order of the excited states. It is found that the lowest states in the latter case are $\pi\pi^*$ singlet and triplet states, so the probability of the intersystem crossing tends to be negligible. This is confirmed in experiment – considerable increase of the fluorescence quantum yield is observed for 4-(N, N' – dimethylamino)-chalcone in DMF [4,12].

Spin-orbit coupling matrix elements of $S_{\pi\pi^*}$ state with $T_{n\pi^*}$ and $T_{\pi\pi^*}$ states were calculated for 4-(N, N' – dimethylamino)-chalcone in order to demonstrate the changes of the intersystem crossing rates due to solvent effect (see Supporting Information, Table 6). In the $S_{\pi\pi^*}$ excited state geometry in aprotic solvents the SOC matrix elements for $\pi\pi^*$

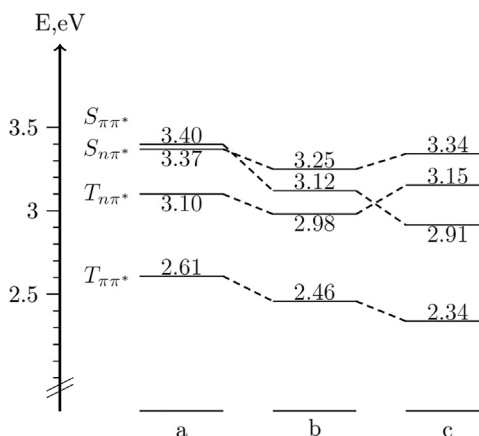


Fig. 6. Excitation energies for 4-(N, N' – dimethylamino)-chalcone calculated for various solvents within Onsager–Liptay theory in the ground state equilibrium geometry and reactive field for the set of solvents: (a) cyclohexane ($\epsilon = 2$), (b) DMF ($\epsilon = 36.7$), and (c) ethanol ($\epsilon = 22.4$).

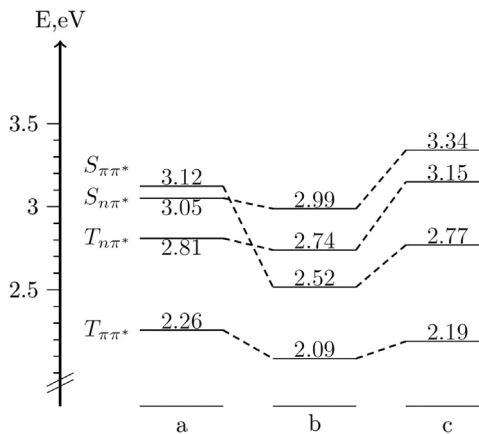


Fig. 7. Excitation energies for 4-(N, N' – dimethylamino)-chalcone calculated for various solvents within Onsager–Liptay theory in the $S_{\pi\pi^*}$ excited state equilibrium geometry and reactive field for the set of solvents: (a) cyclohexane ($\epsilon = 2$), (b) DMF ($\epsilon = 36.7$), and (c) ethanol ($\epsilon = 22.4$).

singlet and triplet states are small ($1\text{--}2.2\text{ cm}^{-1}$), which provides low intersystem crossing rates between them. In the protic solvent (ethanol) significant mixing of the $n\pi^*$ and $\pi\pi^*$ states is observed, the SOC matrix element for $\pi\pi^*$ states increases to 6 cm^{-1} . This fact explains the low fluorescence quantum yield of 4-(N, N' – dimethylamino)-chalcone in protic solvents. It shows that non-planar structure of the chromophore in the lowest excited state leads to the significant increase of the spin-orbit coupling between $\pi\pi^*$ states (see Supporting Information, Table 6), and results in fluorescence quenching.

4. Conclusions

Results show some key features of the $\pi\pi^*$ and $n\pi^*$ charge transfer states in chalcones. Electron-donating substituents in the B-phenyl-ring lower the energy of the $\pi\pi^*$ excited singlet and triplet states and slightly increase the energy of $n\pi^*$ states. Such a dependence known earlier for other types of heteroaromatic molecules [41,6] is shown to be true for chalcones.

In the excited $S_{\pi\pi^*}$ state charge transfer from the amino-group to the π -subsystem of the molecule results in a significant increase of the dipole moment of the excited state when compared to the ground state. This leads to a bathochromic shift of the $S_{\pi\pi^*}$ absorption bands with the increase of the solvent polarity.

It is established that fluorescence quenching in non-polar solvents (cyclohexane) is observed due to fast intersystem crossing $S_{\pi\pi^*} \rightsquigarrow T_{1\pi\pi^*}$ or $S_{n\pi^*} \rightsquigarrow T_{n\pi\pi^*}$ processes. Increase of the solvent polarity results in the interchanging between the $\pi\pi^*$ and $n\pi^*$ excited states and in the case of 4-(N, N' – dimethylamino)-chalcone considerable fluorescence quantum yield is to be expected for aprotic solvents with large dielectric constant (≈ 38 , DMF).

Table 1

Structural parameters for chalcone (Ch), aminochalcone (ACh) and 4-(N, N' – dimethylamino)-chalcone (DMACH) in various solvents: θ – torsion of the phenyl ring A, ϕ – torsion of the phenyl ring B, ψ – pyramidalization of the amino-group, $l(\text{C}=\text{O})$ – the bond length C=O.

Molecule, State	Cyclohexane	DMF	Ethanol
Ch, ground state			
θ	19	23	25
ϕ	–2.9	–7.1	–2.5
ψ	–	–	–
$l(\text{C}=\text{O}), \text{\AA}$	1.25	1.27	1.27
ACh, ground state			
θ	21	24	32
ϕ	–0.1	–0.5	–1.5
ψ	22.2	19.7	18
$l(\text{C}=\text{O}), \text{\AA}$	1.25	1.28	1.28
DMACH, ground state			
θ	20	21	25
ϕ	–0.5	–0.5	11.2
ψ	5.2	4.9	0
$l(\text{C}=\text{O}), \text{\AA}$	1.26	1.28	1.28
DMACH, $S_{\pi\pi^*}$ ground state			
θ	11	13	21
ϕ	–1.4	–0.5	–16.2
ψ	0	0	0
$l(\text{C}=\text{O}), \text{\AA}$	1.29	1.32	1.32

Table 2

Onsager radii for chalcone (Ch), aminochalcone (ACh) and 4-(N, N' – dimethylamino)-chalcone (DMACH).

Molecule	Ground state	Ground state (complex with ethanol)	$S_{\pi\pi^*}$
Ch	5.6	5.65	–
ACh	5.65	5.7	–
DMACH	5.7	5.8	6.1

The solvent considerably affects the geometry of the chalcone and its aminoderivatives. Increase of the torsion angles of the phenyl rings and $-\text{C}=\text{C}-\text{C}(-)=\text{O}$ chain is observed upon increase of the solvent polarity. The effect of specific interactions with protic solvent on the spin-orbit coupling due to changes of the molecule geometry is revealed. It proves that intersystem crossing between $\pi\pi^*$ states causes fluorescence quenching of 4-(N, N' – dimethylamino)-chalcone in protic solvents.

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Appendix A. Supporting information

A.1. Structural parameters in various solvents

See Table 1.

A.2. Onsager radii

See Table 2.

A.3. Energies of $\pi\pi^*$ and $n\pi^*$ states calculated within COSMO approach

See Table 3.

Table 3

Energies of the $\pi\pi^*$ and $n\pi^*$ states for chalcone (Ch), aminochalcone (ACh) and 4-(N, N' – dimethylamino)-chalcone (DMACH) in various solvents, calculated within COSMO approach.

Molecule	Transition	Cyclohexane	DMF	Ethanol
Ch, ground state	$S_{\pi\pi^*}$	4.46	4.32	4.17
	$S_{1\pi\pi^*}$	3.41	3.43	3.47
	$T_{\pi\pi^*}$	2.90	2.86	2.84
	$T_{1\pi\pi^*}$	3.15	3.20	3.23
ACh, ground state	$S_{\pi\pi^*}$	3.86	3.57	3.45
	$S_{1\pi\pi^*}$	3.43	3.42	3.62
	$T_{\pi\pi^*}$	2.73	2.61	2.57
	$T_{1\pi\pi^*}$	3.17	3.18	3.38
DMACH, ground state	$S_{\pi\pi^*}$	3.52	3.21	3.01
	$S_{1\pi\pi^*}$	3.42	3.42	3.45
	$T_{\pi\pi^*}$	2.63	2.47	2.38
	$T_{1\pi\pi^*}$	3.17	3.17	3.23
DMACH, $S_{\pi\pi^*}$ excited state	$S_{\pi\pi^*}$	3.18	2.89	2.77
	$S_{1\pi\pi^*}$	3.12	3.10	3.34
	$T_{\pi\pi^*}$	2.27	2.19	2.19
	$T_{1\pi\pi^*}$	2.89	2.90	3.15

A.4. Dipole moments of the $\pi\pi^*$ and $n\pi^*$ states

See Table 4.

Table 4

Dipole moments of the $\pi\pi^*$ and $n\pi^*$ states in a gas phase for chalcone (Ch), aminochalcone (ACh) and 4-(N, N' – dimethylamino)-chalcone (DMACH) in the equilibrium ground state geometries in various solvents.

Molecule	Solvent	S_0	$S_{\pi\pi^*}$	$S_{1\pi\pi^*}$	$T_{\pi\pi^*}$	$T_{1\pi\pi^*}$
Ch, ground state	Cyclohexane	2.5	8.2	1.8	2.4	1.1
	DMF	2.7	8.4	1.9	1.6	1.3
	Ethanol	3.8	10.1	1.8	4.1	1.6
ACh, ground state	Cyclohexane	4.7	14.4	1.5	6.6	1.8
	DMF	4.8	14.6	1.7	6.5	2.1
	Ethanol	7.5	17.3	2.7	9.8	2.9
DMACH, ground state	Cyclohexane	5.7	17.6	2.3	9.2	2.5
	DMF	6.1	17.7	2.4	9.2	2.9
	Ethanol	8.0	18.2	5.4	12.1	4.0
DMACH, $S_{\pi\pi^*}$ excited state	Cyclohexane	6.9	17.5	2.6	9.5	2.7
	DMF	6.9	18.2	3.0	9.6	3.3
	Ethanol	9.7	12.5	14.1	13.8	5.1

A.5. Oscillator strengths of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions

See Table 5.

A.6. Spin-orbit coupling

See Table 6.

Table 5

Oscillator strengths of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, calculated within RI-CC2 and COSMO approach for chalcone (Ch), aminochalcone (ACh) and 4-(N, N' – dimethylamino)-chalcone (DMACH) in various solvents.

Molecule	Solvent	$S_0 \rightarrow S_{\pi\pi^*}$	$S_0 \rightarrow S_{1\pi\pi^*}$
Ch, ground state	Cyclohexane	0.8810	0.0006
	DMF	0.8927	0.0022
	Ethanol	0.9251	0.0004
ACh, ground state	Cyclohexane	0.9765	0.0020
	DMF	0.9701	0.0331
	Ethanol	1.0369	0.0345
DMACH, ground state	Cyclohexane	0.9783	0.0770
	DMF	1.0555	0.0261
	Ethanol	1.1430	0.0042
DMACH, $S_{\pi\pi^*}$ excited state	Cyclohexane	1.1023	0.0004
	DMF	1.0359	0.0037
	Ethanol	1.0765	0.0285

Table 6

Spin-orbit matrix elements for $\pi\pi^*$ and $n\pi^*$ states of the 4-(N, N' – dimethylamino)-chalcone in the equilibrium geometry of the ground and $S_{\pi\pi^*}$ excited state in various solvents.

Geometry	Solvent (θ, ϕ)	$ \langle S_{\pi\pi^*} \hat{H}_{SO} T_{\pi\pi^*} \rangle $	$ \langle S_{\pi\pi^*} \hat{H}_{SO} T_{n\pi^*} \rangle $
Ground state	Cyclohexane (20, 0.5)	5.5	1.7
	DMF (21, 0.5)	7.4	3.6
	Ethanol (25,11.2)	15.8	3.5
Excited $S_{\pi\pi^*}$ state	Cyclohexane (11, 1.4)	24.2	1.2
	DMF (13, 0.5)	28.0	2.2
	Ethanol (21,16.2)	17.2	6.2

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