



Luminescent properties of chalcone and its aminoderivatives



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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

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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:

$$\begin{aligned} \vec{E}_R = f\vec{\mu} &= (f_{ind} + f_{or})\vec{\mu}; \quad \vec{\mu} = \vec{\mu}_0 + \alpha\vec{E}_R, \\ f_{or} &= \frac{2}{a^3} \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right), \\ f_{ind} &= \frac{2}{a^3} \left(\frac{n^2 - 1}{2n^2 + 1} \right), \end{aligned} \quad (1)$$

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

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

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

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