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C=O GROUP VERSUS C=C(CN)₂ MOIETY FROM THE VIEWPOINT OF ELECTRONIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY

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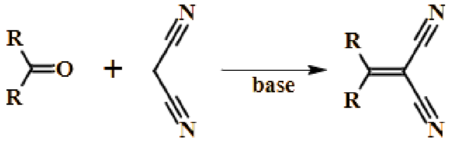
The effect of changing carbonyl group to methylidenepropanedinitrile moiety onto electronic absorption and fluorescence spectra was analyzed theoretically within DFT / TD-DFT scheme. Chalcone (1,3-diphenylpropeneone) was chosen as a model molecular system of this investigation. Methylidenepropanedinitrile moiety was characterized as more suitable for obtaining bright fluorescent products, however, its electron accepting ability was lower compared to carbonyl group, contrary to widespread insights.

Keywords: *chalcone, carbonyl group, methylidenepropanedinitrile, electronic absorption spectra, fluorescence spectra, solvatochromism, intersystem crossing.*

Introduction

Methylidenepropanedinitrile moiety is a popular functional group in organic chemistry community applied in designing of novel fluorescent compounds [1-5]. It is traditionally considered as highly electron accepting center, which introduction results in the enhancement of fluorescence ability, significant long-wavelength shifts both in absorption and fluorescence spectra and appearance of pronounced solvatochromism [2, 6]. Sometimes, such compounds are synthesized entirely with the aim of their consequent chemical modification, see for example, [7]. In several cases $C=C(CN)_2$ moiety can be introduced in position of former carbonyl group even via direct condensation of starting aldehyde or ketone with malonodinitrile under basic catalysis.

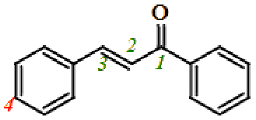


The aim of the current communication is to show, that such expectations are not fully grounded, and to outline the impact of $C=C(CN)_2$ group onto absorption and fluorescence characteristics of the final product of such chemical modification.

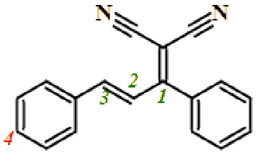
Chalcone core is chosen as model molecular system for the current investigation [8]. This cross-conjugated molecule was thoroughly studied from the second half of 20th century both synthetically and spectroscopically [9-10], however publications on this subject still appear up to last decades [11-13].

Computation methods

Molecular structure of model compounds, 1,3-diphenylpropenone (chalcone, I) and (1,3-diphenylprop-2-en-1-ylidene)propanedinitrile (II) and their 4-dimethylamino derivatives was optimized in DFT scheme (*b3lyp* electron density functional [14] and *cc-pvdz* basis [15]) using Gaussian 09 software [16]. The atom numbering scheme in molecules I and II was unified for readers convenience.



I



II

Electronic absorption spectra were modeled with NWChem 5.0 program pack [17] upgraded with ESSA [18-19] module for analysis of electronic excitations [20]. Spin-orbit coupling of excited states of different orbital nature was analyzed using Orca 5.01 software [21-23]. The above-mentioned combination of electron density functional and orbital basis was chosen owing to good reproducibility of the energies of both singlet and triplet energetic levels [24], which is a critical requirement for the analysis of spin-orbit coupling and intersystem crossing rates on this background.

Results and discussion

According to results of our quantum-chemical modeling, chalcone molecule exists in the most energetically favorable *trans-S-cis* conformation, which is practically planar. Propanedinitrile moiety occupies much more volume than carbonyl group oxygen atom, thus its introduction causes increased steric hindrance and loss of molecule planarity, despite of remaining in conformation typical to chalcone. X-ray structural investigation of compound II was published [25], however, solid state and solution structure can deviate one from another owing to crystalline lattice packing effects. Figure 1 shows the optimized geometry of II, which, in fact appeared quite close with the solid state structure.

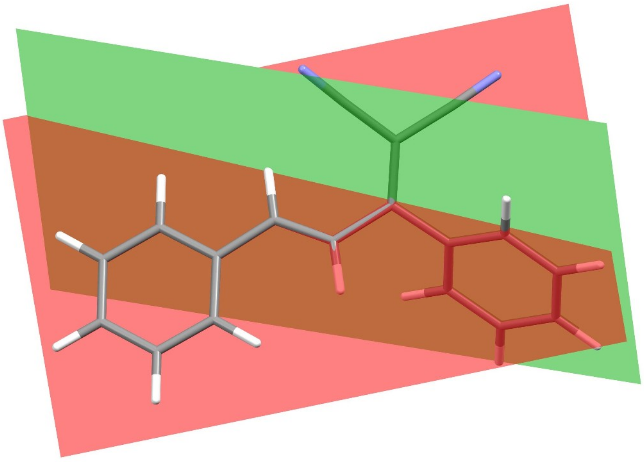
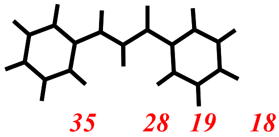
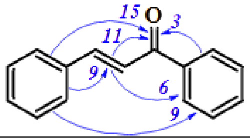
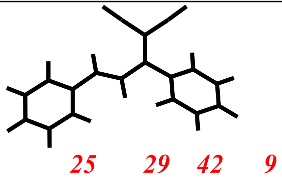
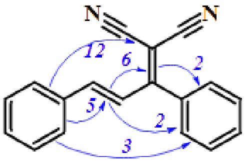
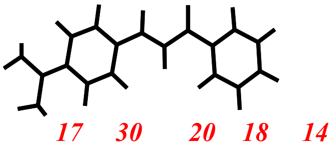
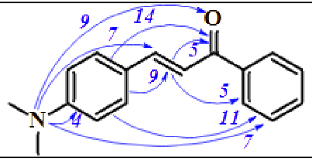
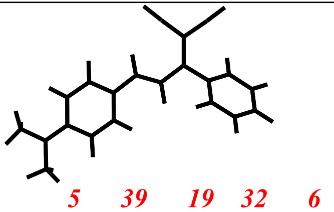
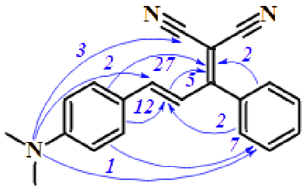


Figure 1. Molecular structure of compound II (*b3lyp/cc-pvdz* optimization). Two planes drawn through its benzene rings are shown in red and green colors.

Three planar sub-fragments are clearly seen (Figure 1): styryl moiety (*a*, red), rigid methylidenepropanedinitrile (*b*, not shown for clarity) and phenyl-1 (*c*, green) with the angles between their planes: $\angle ab \sim 35^{\circ}$ and $\angle bc \sim 50^{\circ}$. This means that conjugation of phenyl-3 with dinitrile group is slightly deviated (torsion angle ~28°), while as dinitrile conjugation with phenyl-1 is significantly weakened (torsion angle ~46°). All the above features are regulated by the rigidity of methylidenedinitrile moiety and its close spatial location near phenyl-1. Absence of a general planarity of compound II and its dimethylamino derivative does not affect principally their optical properties, many chromophoric molecules with the same acceptor unit are non-planar as well [26].

The electronic excitations forming the long-wavelength part of their UV/Vis absorption spectra in the molecules of investigated compounds were analyzed in ESSA approach [18-19], recently adapted for TDDFT calculations (Table 1). ESSA requires calculation of special quantum-chemical indices – localization numbers (L_i) and charge transfer numbers (l_{ij}) [27]. To simplify the presentation of results, several submolecular fragments were selected: dimethylamino group in phenyl-3 (if present), phenyl-3, C=C double bond, carbonyl/methylidenepropanedinitrile group and phenyl-1. Table 1 includes data for well-resolved absorption bands, which are forming long-wavelength part of absorption spectra of investigated compounds. Chalcone is the exception, its first electronic transition is of nπ* type, low-intensive, forbidden by overlap selection rule. This band can be observed experimentally only in concentrated solutions. The role of nπ* states in electronic spectroscopy of chalcones is discussed in the final part of the present paper.

Table 1. Singlet electronic excitations forming the long-wavelength part of their UV/Vis absorption spectra in molecules of investigated compounds analyzed within ESSA approach.

State	Transition parameters	Localization numbers, L_i	Charge transfer numbers, l_{ij}
S_2	316 nm 31630 cm^{-1} $f \sim 0.725$ Δμ 9.9 D		
S_1	377 nm 26540 cm^{-1} $f \sim 0.552$ Δμ 5.3 D		
S_1	383 nm 26110 cm^{-1} $f \sim 0.786$ Δμ 20.0 D		
S_1	448 nm 22330 cm^{-1} $f \sim 0.860$ Δμ 16.4 D		

Here f – oscillator strength, Δμ – excited-to-ground state dipole moments vector difference (charge transfer quantitative characteristic). Localization numbers are summarized over the given moiety (% of whole-molecular excitation) are shown below the structural subunits on the corresponding diagrams, the red circles radii are proportional to atomic L_i. Charge transfer numbers are shown near the arrows, which denote the direction of redistribution of electron density (% of the electric charge of electron).

Well-resolved long-wavelength absorption bands in spectra of the investigated molecules are formed mainly by electronic transitions of ππ* type. Chromophoric fragments forming long-wavelength region of absorption spectra of compounds I and II are similar in their nature, this follows from the ESSA analysis of electronic excitations (two upper rows of Table 1). They are preferably located on the same structural subunits – phenyl-3, double bond and propenone/propenylidene moiety. In the earlier investigations of UV-Vis spectroscopy of chalcones the above mentioned units were considered as the main chromophore in chalcone series [28-30]. Phenyl-1 becomes a part of chromophoric fragment for some higher-energy absorption bands, which are not considered in the current communication. Participation in electronic excitation of both C≡N groups in molecule II and its dimethylamino derivative is not high, probably this is the reason of close analogy of its spectral behavior and that of chalcone.

Electronic excitation on carbon atom in *para*-position of phenyl-3 is relatively high, thus, substituent introduced there will result in batochromic shift and increase in intensity of corresponding absorption band. The nature of electronic transitions of dimethylamino substituted molecules I and II remains practically the same, as they are in unsubstituted compound (classical auxochrome behavior).

The main acceptor unit in chalcone molecule is its carbonyl group: 0.26*e* electron density moves to it at electronic excitation. The secondary acceptor is phenyl-1, to which definite amount of excessive electron density migrates from phenyl-3 and C=C double bond. Totally, Δμ vector reaches 9.9 D.

The electron density redistribution at excitation of compound II looks quite similar, however in this case amount of electric charge increasing on methylidene propane dinitrile group is lesser, 0.18*e* only. Increase of electron density on phenyl-1 is nearly half lower as well. This decrease in excited state charge transfer reflects also lower Δμ~5.3 D. Spatial dimensions of compounds I and II are practically the same, thus the discussed vector differences characterize entirely electric charges redistributions.

When a strong electron donor, dimethylamino group, appears in the investigated molecules, all the conclusions formulated for unsubstituted compounds remain nearly unchanged.

In dimethylamino chalcone electron density redistributes between one main electron donor, $N(CH_3)_2$-C_6H_4-, and two electron withdrawing centers, carbonyl group and phenyl-1. Corresponding amount of charge removal is 0.28*e* and 0.22*e* correspondently. The resulting Δμ reaches 20 D, this allows to classify the formed excited state as "charge transfer", for example, for classical "push-pull" molecule (see [26] for description of this term), 4-dimethylamino-4'-nitro-stylbene Δμ vector reaches 25 D (up to 0.3-0.4*e* being transferred).

Dimethylamino-substituted compound II seemingly demonstrate comparable charge transfer, main acceptor unit has got 0.37*e*, however secondary acceptor, phenyl-1, is significantly weaker, it obtains 0.08e but loses 0.04e. Finally, Δμ in this case is 16.4 D – this is a bit lower compared to dimethylamino-chalcone.

The above analyses allows to come to conclusion, that $C=C(CN)_2$ group is a weaker electron acceptor moiety in comparison with carbonyl group. This supposition somewhat contradicts with common insights of organic chemists working in new dyes design, who introducing this group with the aim of increasing of push-pull and optical non-linear parameters of their novel compounds.

Undoubtful effect of methylidenepropane dinitrile moiety is significant long-wavelength spectral shift in respect to initial carbonyl compounds. For a pair of title compounds, I and II, batochromic shift reaches ~5100 cm^{-1}, while as for their dimethylamino derivatives it is even somewhat lower, ~3800 cm^{-1}. This is in line with our conclusion concerning lesser electron accepting ability of methylidenepropane dinitrile moiety compared to carbonyl one.

In the middle 20th century, when methods of quantum chemistry were in their early development period, empiric additive theory of electron spectroscopy was developed by Woodward [31] and Fieser [32]. Contributions of functional groups introduced into conjugated molecules were summarized to get the maximum absorption wavelength (nm) without using computers, which were generally absent that time. According to Woodward and Fieser, contribution of a double bond (extending conjugation chain) to position of the long-wavelength absorption band is ~30 nm.

If we convert the shifts mentioned in the above paragraph into the wavelength scale, we will get 67 nm for a pair of compounds I and II, while as for their dimethylamino derivatives analogous shift will be 65 nm. Looks like a classical additive scheme! Carbonyl group and methylidenepropane dinitrile moiety differs one from another on two triple bonds -C≡N, only one π-component of each of them extends conjugation. Thus, long-wavelength shift of absorption spectra in the discussed case is no more than the general effect of the extending of a conjugation chain length (32-33 nm), which is not regulated by the seemingly increased electron accepting properties of $C=C(CN)_2$ moiety.

The intramolecular donor-acceptor interaction at the discussed functional groups replacement would only decrease, this reduces the push-pull character of dyes and expectations for obtaining pronounced non-linear optic effects at such a structural modification.

From the point of view of fluorescent properties, carbonyl group has a negative feature – its nπ* levels inducing radiationless decay in the electronically excited organic molecules. According to classical El-Sayed rule [33-34], singlet and triplet excited states of different orbital nature (nπ* and ππ*) are characterized by the increased spin-orbit coupling (SOC). This increases the rate of intersystem crossing (ISC) between them, which concurs with fluorescence emission and is the main reason for dramatic fluorescence quantum yields decrease of organic molecules.

Let's consider molecular photophysics of carbonyl and methylidenepropane dinitrile compounds from the viewpoint of spin-orbit interactions. Table 2 represents the results of quantum-chemical calculations of the energies of two lowest singlet (nπ* and ππ*) and all the lower-lying triplet excited states, which are responsible for molecular photophysics.

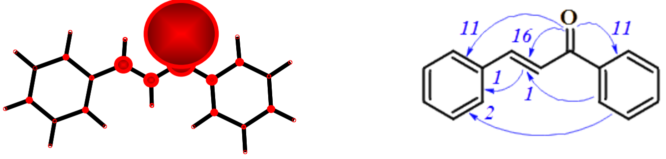
Table 2. Electronically excited states, which are responsible for efficient ISC process owing to increased spin-orbit coupling (SOC), in chalcone and its dimethylamino derivative. TDDFT calculations *in vacuo*.

Excited state	Energy (*intensity*)	SOC, cm^{-1}	k_{ISC}, s^{-1}
Chalcone, I			
$S_1(n\pi^*)$	385 nm / 25970 cm^{-1} (f~0)		
$T_3(\pi\pi^*)$	387 nm / 25870 cm^{-1}	18.3 (S_1-T_3)	$4.9\cdot10^{13}$
$T_2(n\pi^*)$	444 nm / 22500 cm^{-1}	-	-
$T_1(\pi\pi^*)$	522 nm / 19160 cm^{-1}	19.2 (S_1-T_1)	$5.1\cdot10^{10}$
4-N(CH_3)$_2$-chalcone			
$S_2(n\pi^*)$	379 nm / 26400 cm^{-1} (f~0)		
$S_1(\pi\pi^*)$	383 nm / 26110 cm^{-1} (f~0.786)		(k_f~$3.6\cdot10^8$)*
$T_3(\pi\pi^*)$	381 nm / 26220 cm^{-1}	20.9 (S_2-T_3)	$4.4\cdot10^{13}$
$T_2(n\pi^*)$	435 nm / 22980 cm^{-1}	9.5 (S_1-T_2)	$1.2\cdot10^{11}$
$T_1(\pi\pi^*)$	582 nm / 17170 cm^{-1}	17.7 (S_2-T_1)	$1.5\cdot10^{10}$

* Fluorescence emission rate constant calculated from the oscillator strength and wavenumber (cm^{-1}) of S_1 state by the common equation: $k_f \sim 2/3\cdot f\cdot\nu^2$.

Calculations of spin-orbit coupling and Robinson-Frosch [35-36] intersystem crossing rate constant estimations are given there as well (SOC and ΔE in cm^{-1}): $k_{ISC} = 0.71\cdot10^{12}\cdot SOC^2\cdot\exp(-0.25\Delta E^{0.4})$. Carbonyl group nπ* states are easily identifiable within ESSA approach, typical example of localization and electron density redistribution at S_0-S_1(nπ*) electronic transition is given below (Scheme 1).

nπ*:



Scheme 1

Contrary to other electronic transitions, nπ* ones are strictly localized on a functional group with unshared electron pairs, electron density redistribution is directed from its heteroatom to the nearest carbon atoms.

The lowest singlet excited state in chalcone molecule is of nπ* type, it is characterized by strong spin-orbit coupling with the lower-lying triplet ππ* states. This is the reason for the fact that unsubstituted chalcone is non-fluorescent at room and even at liquid nitrogen temperatures. The S_1 and T_3 states are close in energy, their positions could insignificantly deviate due to solvent effects, however, this will not change photophysics of chalcone principally.

At introduction of dimethylamino group in position 4 of chalcone molecule, an inversion of singlet nπ* and ππ* states takes place. However, high efficiency of radiationless decay remains in this case as well. 4-N(CH_3)$_2$-I is non-fluorescent in low polar solvents like cyclohexane. Calculations result in close proximity of the energies of S_1(ππ*) and S_2(nπ*) states of this compound (energy difference ~0.2 kcal/mol). Estimation according to Arrhenius results in their nearly equal equilibrium populations (0.55:0.45). This means that both lowest singlet excited states can be involved in radiationless deactivation processes, which finally lead to population of non-emissive in fluid solutions triplet states: the first of them starts from S_1 while as the second starts from the thermally activated S_2. In Table 2 both these decay pathways are considered.

In polar protic solvents fluorescence of 4-N(CH_3)$_2$-I appeared owing to solvatochromic lowering the energy of S_1 state, however, even at such conditions fluorescence quantum yields remain quite low [8, 12], no higher than several percents.

Nitrile group has its own nπ* levels, however they are located at much higher energy in respect to S_1 state and thus have no influence on fluorescence ability. Thus, all the lowest singlet and triplet states of nitrile-substituted compounds should be of ππ* type. From another side, compound II is not planar, this induces slight enhancement of spin-orbit coupling. Basing on these considerations, we decided to make analogous analyses also for compound II and its dimethylamino derivative (Table 3).

Table 3. Lowest singlet and triplet excited states of compound II and its dimethylamino derivative, spin-orbit coupling and ISC rates in their molecules. TDDFT calculations *in vacuo*.

Excited state	Energy (*intensity*)	SOC, cm^{-1}	k_{ISC}, s^{-1}
(1,3-diphenylprop-2-en-1-ylidene)propanedinitrile, II			
$S_1(\pi\pi^*)$	377 nm / 26540 cm^{-1} (f~0.552)		(k_f~$2.6\cdot10^8$)*
$T_2(\pi\pi^*)$	429 nm / 23300 cm^{-1}	0.67 (S_1-T_2)	$5.6\cdot10^{10}$
$T_1(\pi\pi^*)$	688 nm / 14550 cm^{-1}	0.28 (S_1-T_1)	$1.3\cdot10^6$
4-N(CH$_3$)$_2$-II			
$S_1(\pi\pi^*)$	448 nm / 22330 cm^{-1} (f~0.859)		(k_f~$2.9\cdot10^8$)*
$T_2(\pi\pi^*)$	471 nm / 21230 cm^{-1}	0.29 (S_1-T_2)	$9.7\cdot10^8$
$T_1(\pi\pi^*)$	774 nm / 12920 cm^{-1}	0.18 (S_2-T_1)	$1.4\cdot10^6$

* See note to Table 2.

Spin-orbit coupling caused by violations in planarity is not too strong, thus we are expecting much higher fluorescence ability for both investigated dinitriles. Rough estimation of their fluorescence quantum yields based on theoretically predicted photophysical processes rate constants gives 0.32 for compound II and 0.23 for its dimethylamino derivative in non-polar surrounding. This satisfactory matches with the experimental data.

Conclusions

Carbonyl group demonstrates itself as stronger electron accepting moiety compared to methylidenepropane dinitrile one, thus C=O causes higher solvatochromism and more pronounced non-linear optic effects. From another side, carbonyl group brings into a system of energetic levels of conjugated organic molecules their own singlet and triplet nπ* states, which can be the reason of partial or even complete intramolecular fluorescence quenching by the mechanism of intersystem crossing. Long-wavelength shifting of both absorption and fluorescence spectra at introduction of C=C(CN)$_2$ moiety is caused not by appearance of a new strong electron-withdrawing center, but entirely by the enlargement of π-conjugated system of the core molecule by two triple bonds of nitrile groups.

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А. О. Дорошенко. Група С=О у порівнянні з угрупованням С=С(CN)$_2$ з точки зору електронної абсорбційної та флуоресцентної спектроскопії.

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Ефект заміни карбонільної групи на метиліденпропандінітрильний фрагмент у електронній абсорбційній та флуоресцентній спектроскопії було проаналізовано теоретично за схемою DFT/TD-DFT. Як модельну молекулярну систему для цього дослідження було обрано халкон (1,3-дифенілпропенон). Метиліденпропандинітрильний фрагмент був охарактеризований як більш сприятливий для отримання продуктів з яскравою флуоресценцією, однак його електроноакцепторна здатність виявилася помітно нижчою у порівнянні з карбонільною групою, всупереч поширеній у науковій спільноті думці.

Ключові слова:. *халкон, карбонільна група, метиліденпропандінітрил, електронні спектри поглинання, спектри флуоресценції, сольватохромія, інтеркомбінаційна конверсія.*

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