FLUORESCENCE OF 4- AND 5-NITRO ISOCARBOSTYRYL DERIVATIVES REVISITED

L.V. Chepeleva[a], A.O. Doroshenko[b]

V. N. Karazin Kharkiv National University, 4 Svobody sq., Kharkiv, 61022, Ukraine

   a) ✉ *ludmilachepeleva@karazin.ua*   ⓘ *https://orcid.org/0000-0003-3188-3179*
   b) ✉ *andrey.o.doroshenko@karazin.ua*   ⓘ *https://orcid.org/0000-0002-9643-9549*

Spectral properties of several selected nitro substituted isocarbostyrils (I, isoquinoline-2H-1-ones) were discovered in our research group several decades ago. These relatively small molecules demonstrated unusual spectral behavior: they were highly solvatochromic and 5-nitro-I appeared fluorescent in solvents of intermediate-to-high polarity. UV-vis spectra of the title compounds were studied previously both experimentally and theoretically, however, on the quite low level of quantum theory (π-electronic approximation). The aim of the current communication is to reconsider them on DFT/TDDFT level with the account of the $n\pi^*$ states localized on NO_2-group spin-orbit coupling analyses and radiationless intersystem crossing (ISC) process, which regulates the fluorescent properties of nitro-substituted aromatic compounds.

Keywords: isoquinoline-2H-1-one, isocarbostyril, nitro group, UV-vis absorption and fluorescence spectra, radiationless decay, intersystem crossing, ESSA approach.

Introduction

Isoquinoline-2H-1-one derivatives, known also as isocarbostyrils [1-2], had been discovered in 20th century first of all as potentially biologically active compounds [3-4], because many of them have their natural analogs, see for example [5-7].

However, our research group studied their spectral properties as well [8-9], such an optical investigations in this series are quite rare [10]. Special attention was focused just on the nitro-substituted isocarbostyrils [9]. By the general considerations, nitro group is not the best substituent to introduce in the aromatic core aiming to obtain highly fluorescent products [11]. From the middle 20th, this substituent is widely recognized as intramolecular fluorescence quencher. Pioneer works of Ernst Lippert formulated the principle, that observation of fluorescence of nitro-compounds below 500 nm is not possible [12-13]. The initial hypothesis of Lippert was about the population of the pre-dissociative state of nitro group, which results in the fast radiationless decay of the excited state. Nowadays explanation of the nitroaromatics photophysics include the fast radiationless deactivation of their lower singlet excited state via the efficient intersystem crossing (ISC) process with participation of the low-lying triplet $n\pi^*$ levels of the nitro group [14-19], situated near the above-mentioned "Lippert's margin, 500 nm". Such behavior is in line with the well-known El-Sayed rule [20-22] concerning the increased spin-orbit coupling of the excited states of different orbital type ($\pi\pi^*$ and $n\pi^*$) and multiplicity (singlet and triplet). However, there exist a lot of examples of highly fluorescent nitro-compounds seemingly deviating with the general insights [23-25].

4- and 5-nitro-substituted isocarbostyrils (compounds II and III) demonstrated principally different emissive behavior, first of them is non-fluorescent, while as the second is characterized by low-to-intermediate quantum yields in polar aprotic solvents [9] with maximal value in acetone. Our initial paper was theoretically grounded on the available for that period π-electronic quantum-chemical calculations, which are unable to model very important for the examined case excited states of $n\pi^*$ type. The main aim of this communication is to review the spectral behavior of the title nitro-isocarbostyrils using more contemporary quantum chemical approaches.
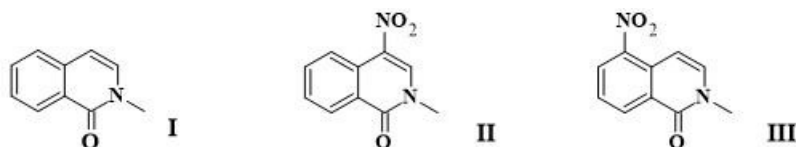
Experimental part

The title 4- and 5-nitro-substituted isocarbostyrils were synthesized by the procedures described in [3-4], 2-methyl derivatives were selected for the current investigation owing to their increased solubility in non-polar solvents. Extended review in the field of synthesis of isoquinolones can be found in [26].

Electronic absorption spectra of the title compounds in hexane were measured on Agilent Cary 3500 UV-Vis Multicell Spectrophotometer. Deconvolution of the experimental spectra onto individual absorption bands were made by non-linear LSM method with approximation of a band shape by un-symmetric log-normal function [27].

Quantum-chemical calculations with optimization of molecular geometry in DFT/TDDFT approximation were conducted in b3lyp/cc-pvdz [28-29] scheme using Gaussian 09 program [30]. Elements of Bader's AIM (atoms-in-molecule) theory were used to analyze molecular structure and redistribution of electron density [31-32]. Energies of a weak H-bonds were estimated within semiempirical Espinosa approach [33]. Electronic absorption spectra and the nature of the excited states of different multiplicity were analyzed within ESSA approach [34-35] using NWChem software [36]. Spin-orbital interaction was modeled using Orca 5.0.4 [37-38] software.

Results and discussion

The molecular structure of isocarbostyrils in the study was optimized in DFT scheme. Obviously, we did not expect any deviations of planarity for unsubstituted compound I. Its methyl group in position 2 takes the most energetically favorable conformation. Also, its rotation around N-C bond is not expected to have significant effect on the electronic spectra.

Compounds II and III were analyzed from the viewpoint of their planarity as well. Calculations result in practically coplanar NO_2-group and isocarbostyril core of compound II. However, such molecular geometry requires definite in-plane distortions of valence angles at introduced substituent (Fig. 1): the angle C3-C4-N_{nitro} appeared decreased to 114°. Such a feature is regulated by intramolecular non-covalent interactions between the nitro group oxygen atoms and neighboring hydrogen atoms, which can be considered as non-conventional intramolecular hydrogen bonds. Corresponding distances O···H are of the order of 2Å (O···H-C3 2.23Å, O···H-C5 2.13Å). The energies of unconventional intramolecular H-bonds estimated by Espinosa expectedly were not so high: ~5.3 kcal/mol both. However, these seem quite enough to keep nitro group in the plane of isocarbostyril core.
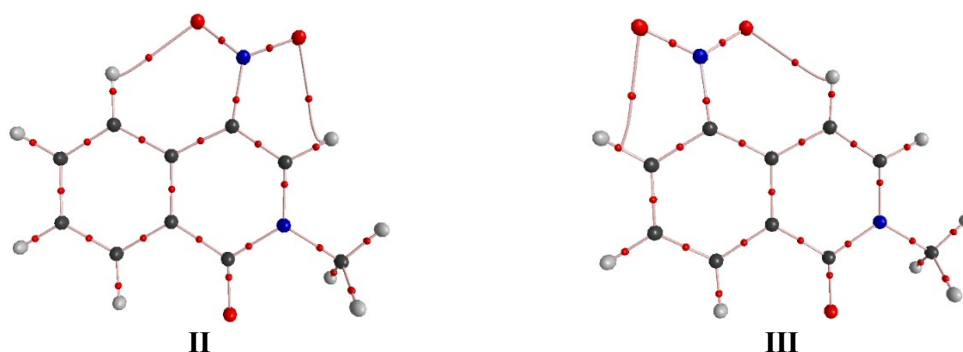

Figure 1. Molecular geometry of 4- and 5-nitro substituted isocarbostyrils (*b3lyp/cc-pvdz* calculations). Bond paths [39] and bonds critical points of (3,-1) type (AIM theory) are shown as well.

Compound III demonstrated definite non-planarity. Its nitro group rotates out of the isocarbostyril core plane on ~16°. Such a relatively small value indicates the absence of violations in ππ-conjugation in this molecule. Distances between nitro group oxygens and neighboring hydrogen atoms are of the order of 2Å as in the case of 4-substituted isomer (O···H-C5 2.14Å, O···H-C6 2.29Å), this corresponds to H-bonds energies of the same 5.0-5.2 kcal/mol. The latter is insignificantly lower in comparison with compound II. In-plane distortions of valence angles, for example, C5-C6-N_{nitro} ~115° takes place as well.

Thus, we have to conclude that there are no fundamental differences in molecular structure of compounds II and III.

At the same time, optical characteristics of the studied nitro-substituted isocarbostyrils differ principally. Compound III is a deeper-colored and fluorescent in low-to-intermediately polar aprotic solvents.
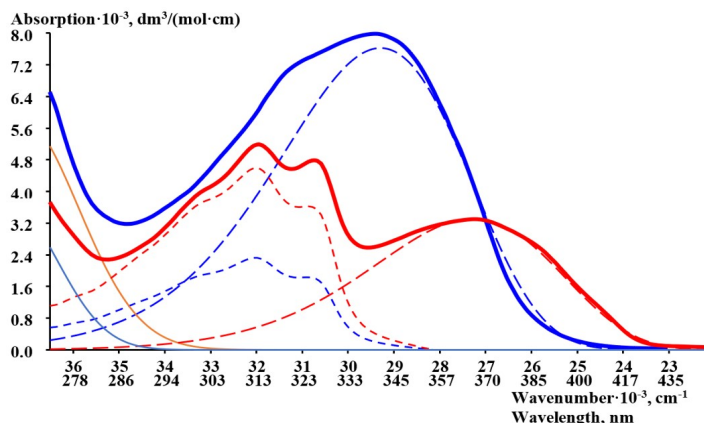

Figure 2. Electronic absorption spectra of title nitro-isocarbostyrils in hexane (thick solid lines) deconvoluted into individual absorption bands (dashed lines: long-wavelength band – long dashes, second absorption band – short dashes, other absorption bands are not shown). Compound II – blue, compound III – red).

Electronic absorption spectra of title compounds in hexane are presented in Figure 2. Obviously, only the most intensive bands of $\pi\pi^*$ type are observed experimentally, low-intensive bands of forbidden $n\pi^*$ transitions are hidden below them. Thus, to let just approximate location of their positions, one can use the results of quantum-chemical modeling.

The electronic transition forming the long-wavelength absorption band of both examined nitro-compounds are of the charge-transfer origin. It was formed with the participation of highest bonding molecular π-orbital of a core molecule (HOMO of isocarbostyril, I) and lowest vacant orbital of NO_2-group (LUMO) [9]. Thus, in our initial paper on this subject we characterized such electronic transitions as "new" in respect to other ones in the spectrum of compound I. This assumption is supported by the data of quantum-chemical modeling (both in π-electronic [9] and full-valent approximations, current communication) and by the similarity of a shape of the second resolved band in the spectra of nitro-compounds with the long-wavelength band in the spectrum of unsubstituted molecule I (Figure 2).

Charge-transfer character of the S_0-S_1 electronic transition experimentally manifests itself in the expressed solvatochromism of compounds II and III [9] and the results of ESSA [34-35] analyses presented in Figure 3 and in Table 1. To simplify the description of the excited state electron density redistribution, several intramolecular fragments were selected in the core molecules, namely: annealed benzene ring, C_3-C_4 double bond, amide nitrogen with the attached methyl group, carbonyl group and finally - nitro-substituent (compounds II-III).
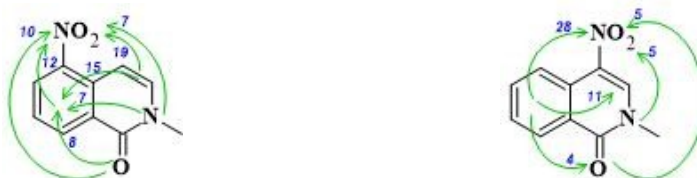

Figure 3. Excited state electron density redistribution at long-wavelength electronic transitions of nitro-isocarbostyrils (ESSA approach, charge-transfer numbers [% of electron charge]).
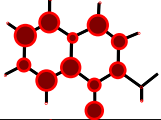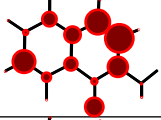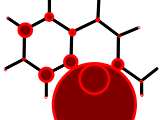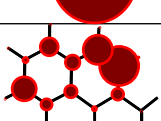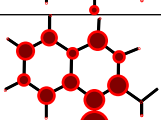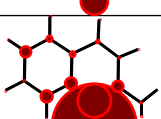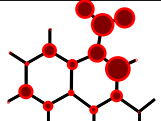
The character of the electron density redistribution at S_0-S_1 electronic excitation in the molecules of two nitro-substituted isocarbostyrils is quite different and depends on the nitro group position. In the case of position 4, when the electron withdrawing group is introduced into the heterocyclic moiety of isocarbostyril core, the role of the main source of electron density plays the annealed benzene ring with totally redistributed of up to *0.43 e* charge. In the case of isomeric 5-nitro-isocarbostyril the situation changes to near opposite – the electron density redistributes from the heterocyclic unit to annealed benzene ring, in which the concrete NO_2-group is not the main electron acceptor. Totally, at
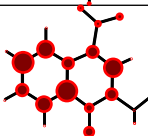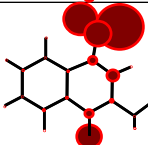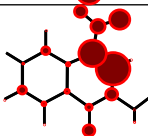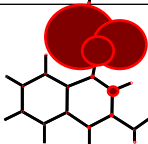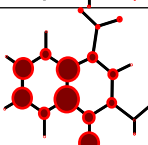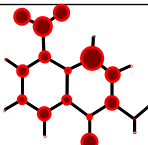
electronic excitation of compound III, electron density redistribution reaches up to *0.78 e*. This allows us to consider the more expressed effect of the introduced nitro group in position 5. And this statement is qualitatively supported by the experimental absorption spectra – compound III has a longer–wavelength position of the S_0-S_1 band compared to compound II, however, electronic transition with higher charge-transfer character has lower intensity.
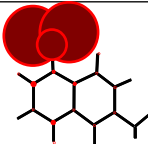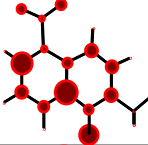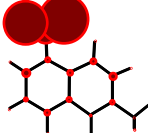
The next electronic transition of both nitro-substituted compounds has "isocarbostyril nature", its localization looks like that for unsubstituted molecule I.

Another feature of the calculated spectra are positions of $n\pi^*$ bands. Such electronic transitions and excited states formed in such a way are typical to functional groups with unshared electron pairs: amide carbonyl and nitro groups in the title molecule. Energies of the carbonyl $n\pi^*$ states are quite high owing to the influence of neighboring electronegative N atom. They can not influence the formation of fluorescent characteristics, contrary to low-energetic $n\pi^*$ states of NO_2 moiety. That is why, the latter are in focus of this investigation. Especially this is important to triplet states of $n\pi^*$ type, they are characterized by increased spin-orbit interaction with higher lying singlet $\pi\pi^*$ states of the molecules on study and can be a reason for high rates of intersystem crossing (ISC), the main factor of radiationless decay in (hetero)aromatic organic molecules.
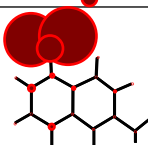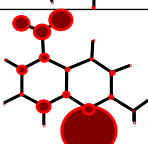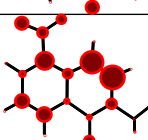
Table 1. Calculated several long-wavelength electronic transitions in UV/Vis absorption spectra of title isocarbostyrils (TDDFT, b3lyp/cc-pvdz) and the results of their ESSA analyses.

Transition	Energy (WN/WL) cm^{-1}/nm	Intensity	Localization	$\Delta\mu$ (D)	SOC cm^{-1}
Compound I					
S_0-S_1, $\pi\pi^*$	33330/300	0.049		6.04	-
S_0-S_2, $\pi\pi^*$	35184/284	0.170		5.34	-
S_0-S_3, $n\pi^*$ C=O	37580/266	0.0002		*9.2*	-
S_0-T_1, $\pi\pi^*$	23730/421	forbidden		1.12	0
S_0-T_2, $\pi\pi^*$	26150/382	forbidden		4.72	0
S_0-T_4, $n\pi^*$ C=O	34730/288	forbidden		*8.03*	16
Compound II					
S_0-S_1, $\pi\pi^*$	29960/334	0.142		9.79	-

S_0-S_2, nπ* NO$_2$	30810/325	0		*4.46*	-
S_0-S_3, $\pi\pi$*	34630/289	0.031		2.74	-
S_0-S_6, nπ* NO$_2$	35670/280	0		*2.03*	-
S_0-T_1, $\pi\pi$*	20950/477	forbidden		5.02	0.03
S_0-T_2, nπ* NO$_2$	24190/413	forbidden		3.24	0.06
S_0-T_3, nπ*	24760/404	forbidden		4.04	9.5
S_0-T_4, $\pi\pi$* NO$_2$	25440/393	forbidden		1.47	0.06
Compound III					
S_0-S_1, $\pi\pi$*	25110/398	0.097		13.04	-
S_0-S_2, nπ* NO$_2$	29880/335	0.003		*3.74*	-
S_0-S_3, nπ* C=O	32590/307	0		4.26	-
S_0-S_5, nπ* NO$_2$	34650/289	0.008		0.73	-
S_0-T_1, $\pi\pi$*	20020/500	forbidden		6.74	0.19

S_0-T_2, nπ* NO$_2$	23140/432	forbidden		*3.12*	1.08
S_0-T_3, ππ*	24760/404	forbidden		3.64	1.65
S_0-T_4, nπ* NO$_2$	25440/393	forbidden		*2.49*	3.09

Intensity = oscillator strength of given electronic transition.

Δμ – vector difference of the excited state and the ground state dipole moments of a molecule. High values for nπ* are owing to a diametrically opposite change in the excited state dipole moment spatial direction in respect to that in the ground state. Normally polarity of nπ* states are lower than that for ππ* ones.

SOC – spin-orbit coupling between the fluorescent state S_1 and a given triplet state.

Table 1 contains data mainly for the lowest excited singlet (fluorescent) state S_1 and several singlet and triplet nπ* states, which are important for molecular photophysics.

For unsubstituted compound I, lowest excited singlet state is of ππ* origin, as the next singlet state S_2. They are localized on carbon and nitrogen atoms of isoquinolone core. S_3 is the nπ* state of carbonyl group, at its formation electron density redistributes from the lone pairs of its oxygen atom to neighboring carbon atoms. Analogous triplet nπ* state is T_4, it is characterized by significant spin-orbit coupling with S_1 state, thus intersystem crossing (ISC) between them should be rather efficient. However, by the energy T_4(nπ*) state lies ~1400 cm^{-1} above the fluorescent state S_1, so ISC between them can only be thermally activated. By this reason, compound I is fluorescent, however its quantum yield does not exceed 0.1 at room temperature.

Introduction of nitro-group in positions 4 or 5 of isoquinolone core causes appearance of two additional nπ* states, localized on NO$_2$-group. For each of them, electron density redistributes from lone pairs of oxygen atoms to neighboring nitrogen and carbon atoms. Initially, there should be two isoenergetic levels, however in reality they are energetically splitted to avoid degeneration.

Excited ππ* states of compounds II and III have analogous localization with the core isoquinolone molecule, probably, except S_1 states, which have significant contribution of (π-bonds of) nitro groups, which enlarges the isoquinolone conjugated system. Generally, this results in the lowering of an energy, and the discussed cases are not the exception. The effect of NO$_2$ group introduction is ~3000 cm^{-1} for S_1 state of compound II and ~8000 cm^{-1} for compound III in comparison with unsubstituted isoquinolone. Probably, this is a consequence of higher charge-transfer character of S_0-S_1 electronic transition in molecule III.

In calculated absorption spectra of compound II nitro group nπ* levels are S_2 and S_6 both lying above the S_1 state. Triplet nπ* states are significantly less splitted in energy (<1000 cm^{-1}). As it was already reported in one of our previous papers [25], only one of the discussed $T_{nπ*}$(NO$_2$) demonstrates high spin-orbit coupling with singlet ππ* states, resulting in higher ISC rates and finally – fluorescence quenching. The same is typical to compound II, which demonstrates increased spin-orbit interaction (*β*=9.5 cm^{-1}) of T_3 state with S_1. The ISC in this case should be rather rapid, moreover, triplet nπ* lies substantially below S_1 state. ISC rate can be roughly estimated by the Robinson-Frosch equation, $k_{ISC} \sim 0.71 \cdot 10^{12} \cdot \beta^2 \cdot \exp(-0.25 \cdot \Delta v^{0.4})$,[40] and is equal in this case to $3.1 \cdot 10^{10}$ s^{-1}. Owing to relatively slow fluorescence emission (estimated as $k_f \sim 2 \cdot f \cdot v^2/3$, $8.5 \cdot 10^7$ s^{-1}), the resulting quantum yield of II should be less than 1%. In reality, no fluorescence was detected for compound II at all. The above estimations are conducted *in vacuo*, any solvatochromic lowering of S_1 state decreases its energy gap with $T_{nπ*}$(NO$_2$) and correspondingly strengthens ISC.

Compound III has analogous location of its nitro group nπ* levels, while as spin-orbit coupling between S_1 and both $T_{nπ*}$(NO$_2$) states is weaker (correspondingly, 1 and 3 cm^{-1} for low-lying and higher-energetic triplet nπ*, Table 1). Rough estimation of ISC rate (~$6 \cdot 10^{11}$ s^{-1}) results in this case in

a very low quantum yield. Indeed, compound III is not fluorescent in non-polar media. However, high solvatochromism rapidly decreases S_1 state energy, it downshifts lower than practically solvent-insensitive triplet $n\pi^*$ states, this increases fluorescence quantum yield of compound III [9] in solvents of intermediate-to-high polarity (ethyl acetate, acetone, acetonitrile). Inversion of singlet and triplet excited state of different orbital character usually leads to improvement of fluorescent characteristics.

The molecular geometry of structurally relaxed electronically excited molecule of compound III estimated in TDDFT scheme does not change principally: the angle between nitro group and isoquinolone core remains nearly the same. However, the energy of structurally relaxed fluorescent state lowers dramatically – up to 20800 cm^{-1} ($\Delta\nu \sim$5000 cm^{-1}). Below the lowest excited singlet state remains only one $n\pi^*$ state located on the nitro-group, thus ISC rate falls to $\sim 5 \cdot 10^{10}$ s^{-1} (Robinson-Frosch) and the quantum yield of compound III even without accounting of additional solvatochromic effects should increase on at least an order of magnitude.

Conclusions

4- and 5-nitro substituted isoquinolones were reconsidered theoretically basing on TDDFT calculations aimed to locate the singlet and triplet NO_2-groups $n\pi^*$ states and elucidate their spin-spin coupling with the potentially fluorescent S_1 $\pi\pi^*$ state of title compounds.

Difference in fluorescent properties of isomeric 4- and 5-derivatives were attributed to:
1) lower energy of S_1 state of compound III and its relative location in respect to $T_{n\pi^*}(NO_2)$,
2) its more pronounced solvatoichromism owing to an expressed S_1 state charge-transfer character and
3) lesser spin-orbit coupling with $n\pi^*$ states of nitro groups.

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Л.В. Чепелєва, А.О. Дорошенко. НОВИЙ АНАЛІЗ ФЛУОРЕСЦЕНТНИХ ВЛАСТИВОСТЕЙ 4- ТА 5-НІТРОПОХІДНИХ ІЗОКАРБОСТИРИЛУ.

Харківський національний університет імені В.Н. Каразіна, хімічний факультет, майдан Свободи, 4, Харків, 61022, Україна

Спектральні характеристики 4- і 5-нітрозаміщених ізокарбостирилів (I, ізохінолін-2Н-1-онів) були досліджені нашою науковою групою декілька десятиліть тому. Ці відносно невеликі за розмірами молекули продемонстрували незвичайну спектральну поведінку: вони були високосольватохромними, а 5-нітро-I демонстрував помітну флуоресценцію у розчинниках середньої та високої полярності. Ультрафіолетові спектри поглинання заголовних сполук були досліджені у той час експериментально, а також і теоретично, але на досить низькому рівні квантової теорії (π-електронне наближення). Метою даної публікації є більш глибокий аналіз на рівні DFT/TDDFT з урахуванням nπ* станів, локалізованих на нітрогрупі, а також оціночні розрахунки спін-орбітального зв'язку нижнього синглетного стану та триплетних nπ* рівнів NO_2-групи, а також оцінка швидкості безвипромінювального процесу інтеркомбінаційної конверсії (ISC), який у значному ступені регулює флуоресцентні властивості нітро-заміщених ароматичних сполук.

Ключові слова: *ізохінолін-2Н-1-он, ізокарбостирил, нітрогрупа, спектри поглинання та флуоресценції в УФ та видимому діапазонах, безвипромінювальний розпад, інтеркомбінаційна конверсія, метод ESSA.*