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Pyrazolyc 3-hydroxychromones: Regulation of ESIPT reaction by the “flavonol-like” intramolecular hydrogen bonding to carbonyl group oxygen, which dominates over the “alternative” H-bond to heterocyclic nitrogen

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ABSTRACT

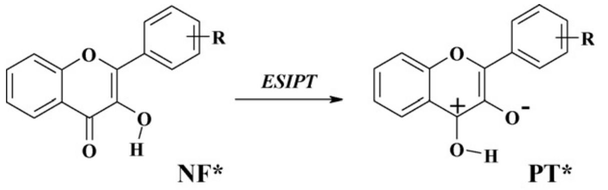
Two isomeric pyrazole derivatives of 3-hydroxychromone (3HC) with and without the possibility of the multiple intramolecular hydrogen bonds formation were compared theoretically and experimentally with the aim to find out whether the excited state intramolecular proton transfer (ESIPT) reaction follows the traditional to the most of 3HCs “flavonol-like” direction towards the C=O group oxygen or an “alternative” direction towards the heterocyclic nitrogen atom.

Quantum-chemical modeling and comparative study of the experimental spectral parameters of the title compounds indicated the preferential realization of “flavonol-like” ESIPT to oxygen channel.

The 3HC systems with the “alternative” intramolecular hydrogen bond to nitrogen were characterized as low fluorescent and practically unable to ESIPT with participation of the nitrogen containing heterocyclic unit.

1. Introduction

The excited state intramolecular proton transfer (ESIPT) reaction is in the focus of attention of science community during the last 60 years from the pioneer works of Weller [[1] and references therein]. The adiabatic excited state structural rebuilding followed by proton phototransfer results in appearance of the long-wavelength high Stokes shifted fluorescence band of the so-called phototautomer form (PT*), which relative intensity in respect to the initial normal form (NF*) is regulated significantly by the nature of the microenvironment of ESIPT molecule [2,3].



This remarkable property was utilized in the last decade for developing molecular sensors for chemical, environmental, biological and medical analysis [[4–6] and references therein]. The main advantage of such sensing systems is the possibility of ratiometric fluorescence detection [7], at which the intensity ratio of the two emission bands belonging to the NF* and PT* forms plays the role of analytical signal. This feature transforms the relative fluorescence intensity measurements into the absolute ones, making ratiometric sensors “auto-calibrated” and in many cases simultaneously increasing the selectivity and sensitivity of such analysis.

Derivatives of 3-hydroxychromone (3HC) seem to have become the most popular fluorescent sensing ESIPT molecules during the last years. Their moderate-to-high quantum yields, excellent response to variation of the microenvironment properties, possibility of ratiometric fluorescence detection, ease of chemical modification of their molecules favors appearance of great number of publications on this class of organic fluorescent dyes [8–11]. Let us mention only a few of the most important applications of 3-hydroxychromones: media polarity indicators [12–14], H-bonding/hydration probes [15–17], metal ions sensors [18,19], fluorescent probes for various biophysical applications, such as probes for proteins structure analysis [20–22], cell membranes studies [23–25] including investigation of membrane

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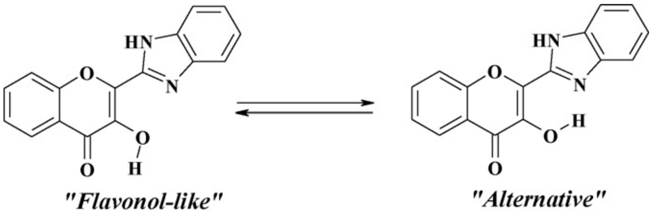
surface/transmembrane electric potential [26–28], fluorescence labeled nucleobases [29] and even fluorescence detection of apoptosis [30]. The above list does not pretend to be complete.

However, informational capacity of hydroxychromone-based sensors could be further increased by introducing in these molecules structural moieties able to undergo additional intra- and intermolecular interactions, which might be detected by the appearance of a new emission bands. For example, nitrogen containing heterocycle in position 2 of 3HC molecule should provide the new accepting center for intramolecular hydrogen bond and a new potential direction for the ESIPT reaction.

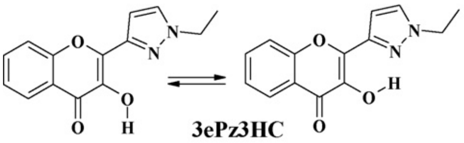
In our previous works [31,32], which seem to be the first publications focused on the possibility of the "alternative" intramolecular proton transfer reaction in 3-hydroxychromones, we investigated the nature of intramolecular hydrogen bonds in the molecule of 2-benzimidazolyl substituted 3HC.

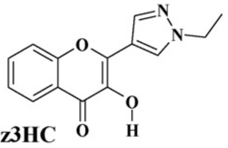


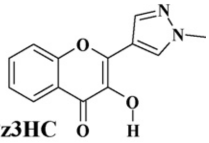
We found that the intramolecular H-bond of "flavonol-like" type to carbonyl group oxygen atom is realized in solutions, whereas in the crystalline state the benzimidazolic 3HC exist with the H-bond to heterocyclic nitrogen. Correspondingly, two alternative ESIPT pathways should be realized in this molecule for the transferring proton along each of the two possible intramolecular hydrogen bonds.

The intramolecular hydrogen bonding equilibria might be influenced by the probe microenvironment, thus for such class of organic molecules we would obtain the additional sensing instrument—switching between their two ESIPT directions resulting in formation of different photoproducts characterized by their individual optical parameters.

Our preliminary communication on the quinolynic 3HC [33] and the paper on the molecular structure and photophysics of the pyridinic 3HC [34] published recently indicated the appearing interest to the molecular systems with several possible ESIPT pathways.


3ePz3HC


4ePz3HC


4mPz3HC

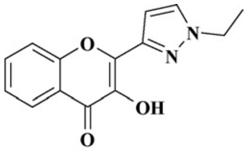
In this paper we examine two isomeric 3HCs carrying the pyrazole moiety in position 2 of the chromone bicycle. One of them, **3ePz3HC** with pyrazole unit connected to 3HC by its position 3, is able to form the alternative intramolecular hydrogen bonds. The other isomer, **4ePz3HC** is unable to form any intramolecular H-bonds except the traditional "flavonol-like" one between the hydroxy and carbonyl groups. Methyl analog of **4ePz3HC** was included in consideration as a model compound with the aim to elucidate if the alkyl chain length in position 1′ of the pyrazole moiety has any significant influence on the photophysics of the title compounds.

We hope comparison of the photophysical and photochemical properties of the above mentioned isomeric molecules could help us to answer the question how the alternative intramolecular H-bonding and possible realization of the alternative ESIPT pathway influences the optical parameters of the molecules belonging to 3HC series.

2. Experimental

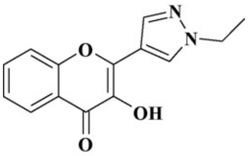
The investigated pyrazolic 3-hydroxychromones were synthesized by traditional Algar–Flinn–Oyamada scheme [35,36], purified by multiple crystallizations from MeOH–H_2O (**3ePz3HC**), MeOH (**4ePz3HC**) or EtOH (**4mPz3HC**) with TLC control. The main physico-chemical parameters for the synthesized pyrazolic 3-OH-chromones are listed below.

2.1. 3-Hydroxy-2-(1-ethyl-1H-pyrazol-3-yl)-4H-chromen-4-one


3ePz3HC:

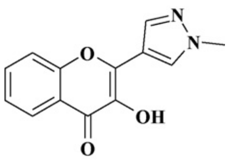
$C_{14}H_{12}N_2O_3$, MM 256.26, MP 118–121 °C, ^{1}H NMR, ppm: 1.54 (t, 3H, CH_3), 4.32 (q, 2H, CH_2), 6,99 (broadened s, 1H, pyrazolyl), 7.38 (t, 1H, C6), 7.62 (d, 1H, C8), 7.69 (t, 1H, C7), 7.78 (broadened s, 1H, pyrazolyl), 8.13 (d, 1H, C5), 8.45 (s, OH, exchangeable). ^{13}C NMR, ppm: 15.81, 47.60, 107.60, 118.88, 122.81, 125.00, 125.94, 131.44, 134.07, 138.98, 142.65, 143.48, 155.21, 172.94. MS, *m*/*z* (arbitrary intensity): 256 [M]+(100), 228 (30), 199 (73), 171 (31), 121 (35), 95 (24), 92 (22), 77 (31), 76 (42), 65 (23), 63 (24).

2.2. 3-Hydroxy-2-(1-ethyl-1H-pyrazol-4-yl)-4H-chromen-4-one


4ePz3HC:

$C_{14}H_{12}N_2O_3$, MM 256.26, MP 161–163 °C, ^{1}H NMR, ppm: 1.43 (t, 3H, CH_3), 4.25 (q, 2H, CH_2), 7.44 (td, 1H, C6), 7.67 (d, 1H, C8), 7.77 (td, 1H, C7), 8.09 (dd, 1H, C5), 8.11 (s, 1H, pyrazolyl), 8.42 (s, 1H, pyrazolyl), 9.38 (s, OH, exchangeable). ^{13}C NMR, ppm: 15.86, 47.34, 113.97, 118.63, 122.67, 124.94, 125.39, 130.26, 133.67, 136.90, 138.38, 144.36, 154.99, 172.27. MS, *m*/*z* (arbitrary intensity): 256 [M]+(11), 228 (4), 199 (7), 149 (22), 138 (27), 121 (24), 112 (36), 93 (24), 92 (19), 85 (52), 83 (40), 71 (46), 65 (30), 55 (100).

2.3. 3-Hydroxy-2-(1-methyl-1H-pyrazol-4-yl)-4H-chromen-4-one


4mPz3HC:

$C_{13}H_{10}N_2O_3$, MM 242.23, MP 211–214 °C, ^{1}H NMR, ppm: 3.98 (s, 3H, CH_3), 7.37 (t, 1H C6), 7.55 (d, 1H, C8), 7.66 (t, 1H, C7), 8.00 (s, 1H, pyrazolyl), 8.11 (d, 1H, C5), 8.30 (s, 1H, pyrazolyl), 9.18

(s, OH, exchangeable). MS, m/z (arbitrary intensity): 242 [M] + (9), 121 (25), 109 (47), 104 (29), 93 (26), 92 (70), 89 (24), 77 (52), 76 (100), 75 (35), 74 (46), 67 (31), 66 (50), 65 (69), 64 (65), 63 (95), 62 (38).

The commercially available solvents (Merck): *n*-octane, dichloromethane, acetonitrile and ethyl alcohol were additionally dried under zeolites (except ethyl alcohol) and distilled before use. Ultrasound treatment was applied to dissolve the investigated compounds in the above listed solvents to "spectrophotometric" concentrations.

NMR spectra were measured in DMSO-d_6 on Brucker AM-300, mass-spectra—on Kratos MS 30 (EI, 70 eV) instruments. Low solubility in carbon tetrachloride did not allow us to take IR spectra of appropriate quality in solutions.

The electronic absorption spectra were recorded on Hitachi U3210 spectrophotometer, whereas fluorescence spectra and quantum yields [37] were measured on Hitachi F4010 spectrofluorimeter. Quinine sulfate in 0.5 M sulfuric acid was served as quantum yield reference standard [38]. Fluorescence lifetimes were determined on the home-made nanosecond device described elsewhere [39]. Fluorescence spectra deconvolution onto individual bands was conducted using own software based on Siano and Metzler approximation of the individual emission band shape by the log-normal function [40].

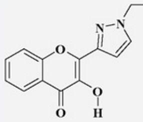
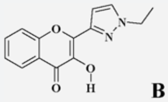
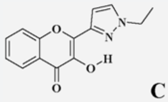
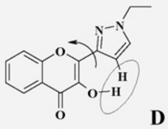
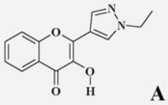
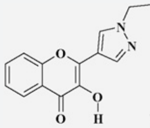
Quantum-chemical calculations were made by the following program packages: **Gaussian-03**, release E.01 [41] (for ground state molecular structure optimization), **Gamess US** [42] version R1 (for excited state optimization) and **NWChem** version 5.1 [43] (equipped with special module for ESS-analysis [44] "excited state structural analysis"—for electronic spectra calculation).

3. Results and discussion

Heterocyclic 3HCs with asymmetric moiety in position 2 could exist in several molecular conformations, some of which are characterized by the presence of the "alternative" intramolecular H-bond to nitrogen. Thus, the conformational analysis and elucidation of the most energetically favorable rotamers was our first task at establishing correlations between the molecular structure and photophysics of the investigated compounds. The results of quantum-chemical modeling are presented in Table 1.

First let us focus attention on the **3ePz3HC** conformer **D** without an intramolecular hydrogen bond. Owing to the repulsion between the OH group proton and the hydrogen atom in position 3 of the pyrazole cycle this molecular structure looses planarity and thus characterized by significantly increased energy (~10 kcal/mol). This and analogous highly energetically unfavorable conformations

Table 1
Theoretical (DFT) conformational analysis for the molecules of pyrazolyc 3-hydroxychromones in the ground state.

Rotamers	*b3lyp/cc-PVDZ* ΔΔH, kcal/mol	Equilibrium fraction	*b3lyp/6-31G*** ΔΔH, kcal/mol	Equilibrium fraction	*b3lyp/6-31++G(d)* ΔΔH, kcal/mol	Equilibrium fraction
3ePz3HC						
 **A**	0	85%	0	90%	0	95%
$TS_{A\leftrightarrow B}$	6.25		–		–	
 **B**	1.61	5%	1.78	4%	2.01	3%
$TS_{B\leftrightarrow C}$	11.02		–		–	
 **C**	1.27	10%	1.63	6%	2.20	2%
 **D**	10.4	0%	–	–	–	–
4ePz3HC						
 **A**	0	80%	0	82%	0	84%
$TS_{A\leftrightarrow B}$	7.54		–		–	
 **B**	0.80	20%	0.87	18%	0.96	16%

Here TS denotes transition states, equilibrium fractions of rotamers were estimated by the equation: $\exp(-\Delta\Delta H_i/RT)/\Sigma\exp(-\Delta\Delta H_i/RT)$ (20 °C).

with the extremely low abundance were further excluded from our consideration.

All the theoretical methods applied give quite good coincidence for **4ePZ3HC** conformation, whereas for its isomer, **3ePz3HC**, the mutual correspondence of the energetic parameters of its three main conformers were much poorer. Probably, this could be because of the difference in the accounting of the intramolecular H-bonds energy by various calculation schemes.

In all cases the most energetically favorable conformer of **3ePz3HC** was **A**, in which the intramolecular H-bond was additionally stabilized by the weak H-bond of the O···H–C type (otherwise this weak interaction might be considered as purely electrostatic). The similar case with the stabilization of one of the conformers by the additional hydrogen bond was described by us in [31,32] for the benzimidazolic 3HC.

Transition state energies for the pyrazole cycle and OH group rotation (transformations of **A** ↔ **B** and **B** ↔ **C** correspondingly) were calculated only in *b3lyp/cc-PVDZ* scheme, however, this could not affect the final conclusion: the most probable conformation for **3ePz3HC** is **A** with intramolecular H-bond of “flavonol-like” type. Its transformation into the structure **C** with the “alternative” hydrogen bond to heterocycle was additionally complicated by the high energetic barriers (see transition states energies, Table 1), which could not be overcome easily at room temperature.

In any case, up to 5–10% of the lesser energetically favorable conformation **C** could be present in the **3ePz3HC** equilibrium mixture. The discussed rotamer **C** with intramolecular hydrogen bond to nitrogen lies in the deep potential well (near 11 kcal/mol) and thus it should be kinetically stabilized at room temperature. As it was discussed earlier [31,32] the ground state conformation determines the excited state behavior of ESIPT molecules to a significant extent, because the already existed hydrogen bonds become stronger at electronic excitation. Thus no conformational equilibria shifting are expected at these conditions. According to the last statement we have to analyze the principle possibility for ESIPT reaction for all three conformations for **3ePz3HC** and two conformations for **4ePz3HC**.

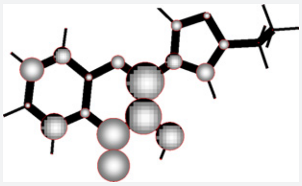
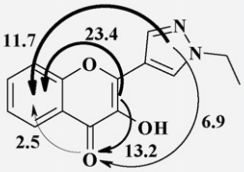
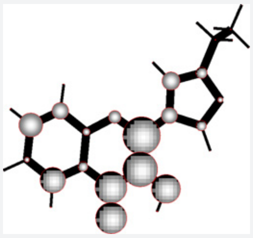
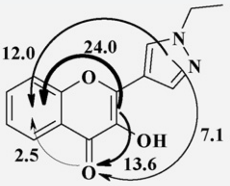
The main driving force of the ESIPT reaction is the excited state electron density redistribution [4,45,46], owing to which the OH group becomes more acidic in S_1, simultaneously the proton accepting centers increase their basicity, making possible intramolecular proton transfer reaction. It was also shown, that the proton donor group acidity increasing plays the key role in the realization of ESIPT [46,47].

In the present paper we are analyzing the nature of the lowest electronic transitions with the newly redeveloped ESSA method [44], which is the extension of the previously proposed approach [48] to the modern *ab initio* and DFT calculation schemes (Tables 2 and 3).

The ESS-analysis includes the calculation of the special quantum-chemical indices—localization numbers (L_i, $\Sigma L_i = 1$) and charge transfer numbers between atoms and assigned more complicated molecular fragments (l_{ij}, % of the electron charge being transferred). The localization numbers help to elucidate the participation of definite atoms and structural moieties of the whole molecule in the electronic excitation, whereas charge transfer indices give the total picture of electron density movement between the definite atoms and molecular fragments: showing the directions of electron density redistribution l_{ij} are much more informative than the net charge differences calculated by the most of quantum-chemical software. The analysis presented in Tables 2 and 3 was conducted for the ground state optimized molecular geometries in *b3lyp/cc-PVDZ* scheme recommended by the authors of [44] as providing the most accurate prediction of the electronic spectra of organic molecules (according to our own findings, the inclusion of the diffuse functions or enlargement of calculation basis to “triple zeta” *cc-PVTZ* does not improve principally the results, but significantly increases the calculation cost).

Table 2

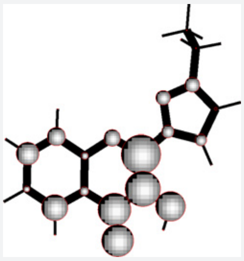
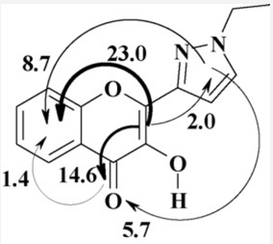
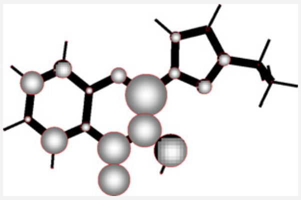
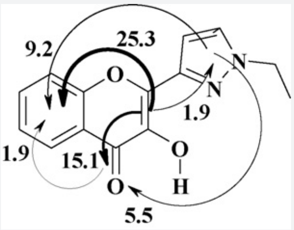
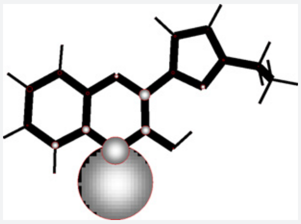
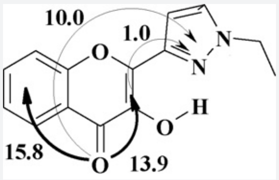
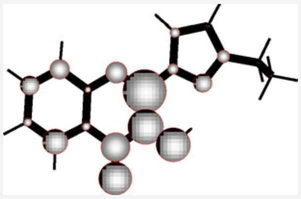
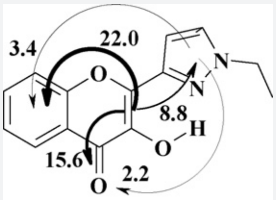
The nature of the long-wavelength electronic transitions in the absorption spectra of the most abundant conformers of **4ePz3HC** (*TD/B3LYP/cc-PVDZ*).

Transition	Energy, wavelength, oscillator strength	Electronic transition localization[a]	Charge transfer numbers[a]	$\Delta q_{=O}$ Δq_{OH}
Conformer **A**				
S_0–S_1	$29020\,cm^{-1}$ 345 nm 0.340 (ππ*)			−0.056 +0.168
S_0–S_2	$32790\,cm^{-1}$ 305 nm ~0 (nπ*)	–	–	–
Conformer **B**				
S_0–S_1	$28720\,cm^{-1}$ 348 nm 0.343 (ππ*)			−0.063 +0.176
S_0–S_2	$32630\,cm^{-1}$ 306 nm ~0 (nπ*)	–	–	–

Arrows width is proportional to the % of the electron charge transferred (see numbers at the arrows) between the definite structural fragments of the molecule.

[a] Circles radii are proportional to atomic localization numbers.

Table 3
The nature of the long-wavelength electronic transitions in the absorption spectra of the most abundant conformers of **3ePz3HC** (*TD/B3LYP/cc-PVDZ*).

Transition	Energy, wavelength, intensity	Electronic transition localization	Charge transfer numbers	$\Delta q_{=O}\,\Delta q_{OH}$
Conformer **A**				
S_0–S_1	29210 cm^{-1} 342 nm 0.324 ($\pi\pi^*$)			−0.062 +0.178
S_0–S_2	32730 cm^{-1} 306 nm ~0 ($n\pi^*$)	–	–	–
Conformer **B**				
S_0–S_1	28640 cm^{-1} 349 nm 0.302 ($\pi\pi^*$)			−0.063 +0.195
S_0–S_2	32500 cm^{-1} 308 nm ~0 ($n\pi^*$)	–	–	–
Conformer **C**				
S_0–S_1	28440 cm^{-1} 352 nm ~0 ($n\pi^*$)			−0.050 (=N–) −0.004
S_0–S_2	29740 cm^{-1} 336 nm 0.240 ($\pi\pi^*$)			−0.039 (=N–) +0.187

The ESSA approach applied to **4ePz3HC** (Table 2) have shown that the main electron density redistribution at transition to the lowest excited singlet state occurs from the enolic moiety (C=C–OH) and pyrazole cycle towards the carbonyl group with its neighboring chromonic benzene ring. This causes slight increase of negative charge of the carbonyl group oxygen atom and nearly three times more significant increase of the positive charge on the OH group, favoring ESIPT in S_1 state.

According to the calculated localization indices the chromone bicycle makes the most important contribution into the formation of the lowest electronically excited state, whereas pyrazole cycle plays a second-order role. The next excited state, S_2, is of $n\pi^*$ type and lies on ~3000 cm^{-1} over the S_1 $\pi\pi^*$ state. Both electron transition energy and electron density redistribution were quite similar to the two conformers of **4ePz3HC** thus we will be unable to distinguish their contributions into the experimentally observed spectra.

According to our calculations and the classical El-Sayed rule [49], **4ePz3HC** should be highly fluorescent compound, because their triplet $n\pi^*$ levels (~338 nm in "spectroscopic" wavelength scale) lie higher in energy then the lowest singlet excited state. As for the most ESIPT molecules, proton transfer should be the dominating radiationless deactivation pathway for the S_1 state of **4ePz3HC** normal form.

Two conformations of **3ePz3HC** (**A** and **B**, Table 3) should behave quite similarly to those of **4ePz3HC**, thus we expect for them very close spectra and photophysics. The principal discrepancy was predicted for the conformation **C** of **3ePz3HC** with the intramolecular H-bond to the pyrazole cycle nitrogen. The latter circumstance caused the inversion of the lowest singlet excited states of rotamer

C in comparison to **A** and **B** ones: the singlet nπ* state of **C** became the lowest-energy one (352 nm), whereas the ππ* state significantly increases its energy (to 336 nm). We could explain this fact on the basis of the hydrogen bond influence on the excited states of different orbital origin: H-bonding with the unshared electronic pairs of carbonyl group oxygen increases the energy of nπ* transitions for the **A** and **B** conformers of **3ePz3HC** and **4ePz3HC**, thus they are located at 305–308 nm in the calculated spectra. The discussed intramolecular hydrogen bond had effect onto the electronic transitions of ππ* type as well: increasing of the electron accepting properties of carbonyl group at H-bonding shifts the S(ππ*) transition to the longer-wavelength region of 342–349 nm.

We expect also principal changing of **3ePz3HC** photophysical/photochemical behavior in its conformation **C**. First of all, the latter should not be able to undergo ESIPT: its lowest singlet excited state is of nπ* type, in which the electron density of the unshared electron pair of the carbonyl group oxygen delocalizes over the rest of the molecule, thus significant decrease of its nucleophilicity should take place with OH group acidity remaining the same as in the ground state. In this case the electronic excitation is strongly localized on the C═O moiety, all the other atoms insignificantly participate in the S_0–S_1 electronic transition (Table 3). The second excited singlet state is of the same nature as the lowest ones for another conformations of **3ePz3HC** and **4ePz3HC**, though it should be very rapidly depopulated owing to the fast internal conversion (IC) towards the S_1(nπ*). The calculated energy gap between S_2 and S_1 levels of **3ePz3HC** conformation **C** is near 1300 cm^{-1}, this roughly gives the IC rate of the order of $8.7 \times 10^{13}\ s^{-1}$ according to the empirical Robinson and Frosch equation [50]. The S_2 ESIPT rate should be on several orders of magnitude slower than this $S_2 \rightarrow S_1$ IC, thus could not concur with it.

Second conclusion, which should be made on the background of the data of Table 3: we do not expect any detectable fluorescence for the **C** conformer of **3ePz3HC**: the rapid intersystem crossing (ISC) S_1(nπ*, 352 nm) → T_2(ππ*, 401 nm) should dominate over the low-intense fluorescence emission originating from the S_1(nπ*) state.

Basing on the above findings we have to consider alternatively hydrogen bonded conformation **C** of **3ePz3HC** as non-emissive and unable to ESIPT on the contrary to the two other ones, **A** and **B**. Any conformation of **4ePz3HC** should demonstrate ESIPT and two-banded fluorescence emission of their possible protolytic forms: normal and phototautomer, the relative intensity of which is regulated by the ESIPT reaction rate. The outlined circumstances would determine the main difference in photophysics of the two title compounds.

The spectral parameters of phototautomer forms of the investigated compounds were modeled on the basis of their excited state geometry optimized in *TDDFT* scheme followed by the calculation of their electronic spectra and ESS-analysis. Despite of our conclusion concerning the low probability of the ESIPT reaction in the conformation **C** of **3ePz3HC**, its phototautomer form was also included into consideration. As it follows from the data of Table 4, the lowest singlet excited states of phototautomer forms of the investigated compounds with ESIPT to oxygen are quite close to each other with slightly more bathochromic PT* emission of 3-isomer. The electronic transitions in the emission spectra of PT* forms were strongly localized on the molecular fragments, in which the proton transfer takes place: 3-hydroxychromone bicycle in the case of ESIPT to oxygen; pyrone and pyrazole cycles in the case of ESIPT to nitrogen. The phototautomer fluorescence at ESIPT to nitrogen should be observed in significantly lower-wavelength region (450–500 nm), thus these two alternative mechanisms of proton phototransfer might be easily distinguished by the position of their photoproducts emission bands, if both these alternative ESIPT pathways would be realized under experimental conditions.

Table 4
The nature of the long-wavelength electronic transitions in the fluorescence spectra of the most important phototautomer forms of **3ePz3HC** and **4ePz3HC** (*TD/b3lyp/cc-PVDZ*).

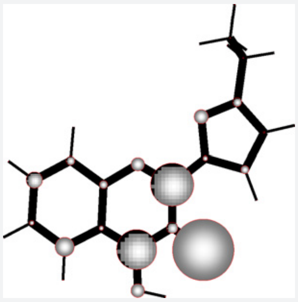
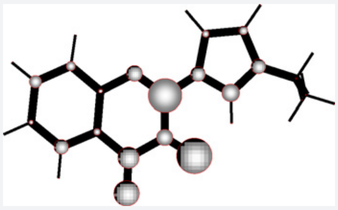
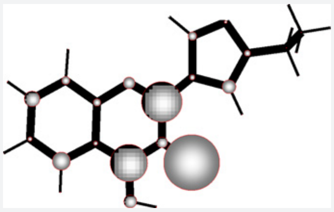
Transition	Energy, wavelength, intensity	Electronic transition localization
3ePz3HC, proton transferred to oxygen		
S_1–S_0	18310 cm^{-1} 546 nm 0.244 (ππ*)	
3ePz3HC, proton transferred to nitrogen		
S_1–S_0	21630 cm^{-1} 462 nm 0.232 (ππ*)	
4ePz3HC, proton transferred to oxygen		
S_1–S_0	18740 cm^{-1} 534 nm 0.270 (ππ*)	

Table 5
Electronic absorption and fluorescence spectral data and photophysics of **3ePz3HC**, **4ePz3HC** and **4mPz3HC** in solvents of different polarity.

Solvent[a] (E_T^N)	Abs., cm^{-1}, nm	Fluor. (NF), cm^{-1}, nm	Fluor. (PT), cm^{-1}, nm	τ_{PT}, ns	φ_Σ	I_{PT}/I_{NF}	k_{ESIPT}, s^{-1}
3ePz3HC							
n-Octane (0.012)	29780 336	–[b]	19220 520	4.85	0.42	(~600)[b]	(3.1×10^{11})
CH_2Cl_2 (0.309)	29740 336	24600 406	19240 520	4.07	0.35	200	1.4×10^{11}
CH_3CN (0.460)	29900 334	24400 410	19060 525	2.18	0.16	70	1.0×10^{11}
C_2H_5OH (0.654)	29320 341	23250 430	18900 529	0.76	0.068	5	–
4ePz3HC							
n-Octane (0.012)	29500 339	–[b]	19260 519	4.64	0.53	(~360)[b]	(2.2×10^{11})
CH_2Cl_2 (0.309)	29120 343	25200 397	19400 515	2.96	0.37	160	1.5×10^{11}
CH_3CN (0.460)	29340 341	24600 407	19240 519	1.41	0.17	48	1.0×10^{11}
C_2H_5OH (0.654)	28920 346	23830 419	19220 520	1.26	0.14	7.5	–
4mPz3HC							
n-Octane (0.012)	29580 338	–[b]	19280 519	4.86	0.57	(~500)[b]	(3.0×10^{11})
CH_2Cl_2 (0.309)	29200 342	25130 398	19460 514	3.65	0.38	230	1.9×10^{11}
CH_3CN (0.460)	29420 340	24500 408	19260 519	1.72	0.20	60	1.0×10^{11}
C_2H_5OH (0.654)	28960 345	24000 417	19180 521	1.61	0.16	8	–

[a] The normalized Reichardt parameter E_T^N [53] was applied for qualitative characterization of the solvents polarity.
[b] Too low intensity to determine the emission maximum correctly. Values of lower precision are given in brackets.

The experimental photophysical data for **3ePz3HC**, **4ePz3HC** and **4mPz3HC** in several solvents of different polarity are presented in Table 5, electronic absorption and emission spectra of **3ePz3HC** and **4ePz3HC** are shown in Fig. 1.

In Table 5 the total quantum yields values (φ_Σ) refer to both normal form and phototautomer. PT* fluorescence decay data measured at phototautomer band fluorescence maximum were satisfactorily fitted by mono-exponential functions yielding the τ_{PT} values. The ESIPT reaction rate constants k_{ESIPT} were roughly estimated on the background of the photophysical data—fluorescence emission rate constants for both NF* and PT* forms ($k_f = 2f\nu^2/3$, where f is the oscillator strength, ν is the electronic transition energy in cm^{-1} taken from the calculation data, Tables 2–4), experimental relative integral intensity ratios of phototautomer to normal forms I_{PT}/I_{NF} (obtained by the deconvolution of the experimental emission spectra onto the individual fluorescence bands) and phototautomer lifetimes τ_{PT}: $k_{ESIPT} \sim (k_f^{NF}/k_f^{PT}) \cdot (I_{PT}/I_{NF})/\tau_{PT}$ [51,52].

Photophysical parameters of **4ePz3HC** and **4mPz3HC** appeared quite similar one to another, showing the generally low effect of the alkyl substituent in position 1′ of the pyrazole cycle. According to our quantum-chemical calculations, the difference in the electronic transitions wavelengths of the methyl and ethyl substituted pyrazolic 3-hydroxychromones should not exceed a few nanometers; the ESS-analysis demonstrates the very low participation of these alkyl groups in the electronic excitation.

We would like to emphasize here that our quantum-chemical modeling reproduces the spectra and photophysics of the investigated molecules *in vacuo*, they should be similar to that in the inert low polar solvents like octane. Solvent influence on the calculated electronic spectra and especially on the localization indices (ESS-analysis) deserves special independent investigation. All our data and discussion concerning the photophysics of pyrazolic 3HCs in polar and protic solvents are given here for comparison reasons: to show that our molecules of interest behave quite similarly in different environments. This means that their photophysics and photochemistry are regulated mainly by the intramolecular factors, whereas intermolecular interactions play the role of external perturbation.

Data for all the examined aprotic solvents indicate high ESIPT rate, which determines domination of the high Stokes shifted phototautomer fluorescence bands (Fig. 1, Table 5).

Fluorescence spectra shape and quantum yields of **3ePz3HC** and **4ePz3HC** in octane do not variate with excitation wavelength in the range of 280–380 nm. No expected red edge effect was observed in the case of **3ePz3HC**, for which we assumed coexistence of oxygen and nitrogen H-bonded species in equilibrium in the ground state. This could be only in the case when no fluorescence of the conformation with intramolecular H-bond to nitrogen was emitted, while as the spectral properties of the two conformers with H-bond to oxygen are quit similar to each other. Thus the presence of the “alternatively” intramolecular hydrogen bonded conformation **C** could be detected experimentally only at comparison of the total fluorescence quantum yields of the investigated 3- and 4-isomers of the pyrazolic 3HCs manifesting itself by the systematic decrease of the fluorescence efficiency of **3ePz3HC** in respect to that of **4ePz3HC** in all the examined solvents.

In ethyl alcohol the normal form emission was significantly more intensive than in the other cases (basing on the data of Table 5 one could obtain φ_{NF^*} values of the order of 0.002 for acetonitrile and 0.01–0.02 for ethanol). This fact is caused by the concurring of the intramolecular hydrogen bond in **3ePz3HC** and **4ePz3HC** with the intermolecular hydrogen bonds to the protic solvent molecules. Alcoholic solutions demonstrated significant dependence of the emission spectra shape upon the excitation wavelength reflecting the presence of several H-bonded species. That is why no estimation of the ESIPT reaction rate for ethyl alcohol solutions was presented in Table 5.

Recently formation of 3HCs ground state anionic species was reported not only for such highly nucleophilic media as DMSO [54], but even for the pure alcohols [55,56]. We observed analogous behavior for our compounds as well: the anionic forms manifest themselves as low-intensive long-wavelength shoulders

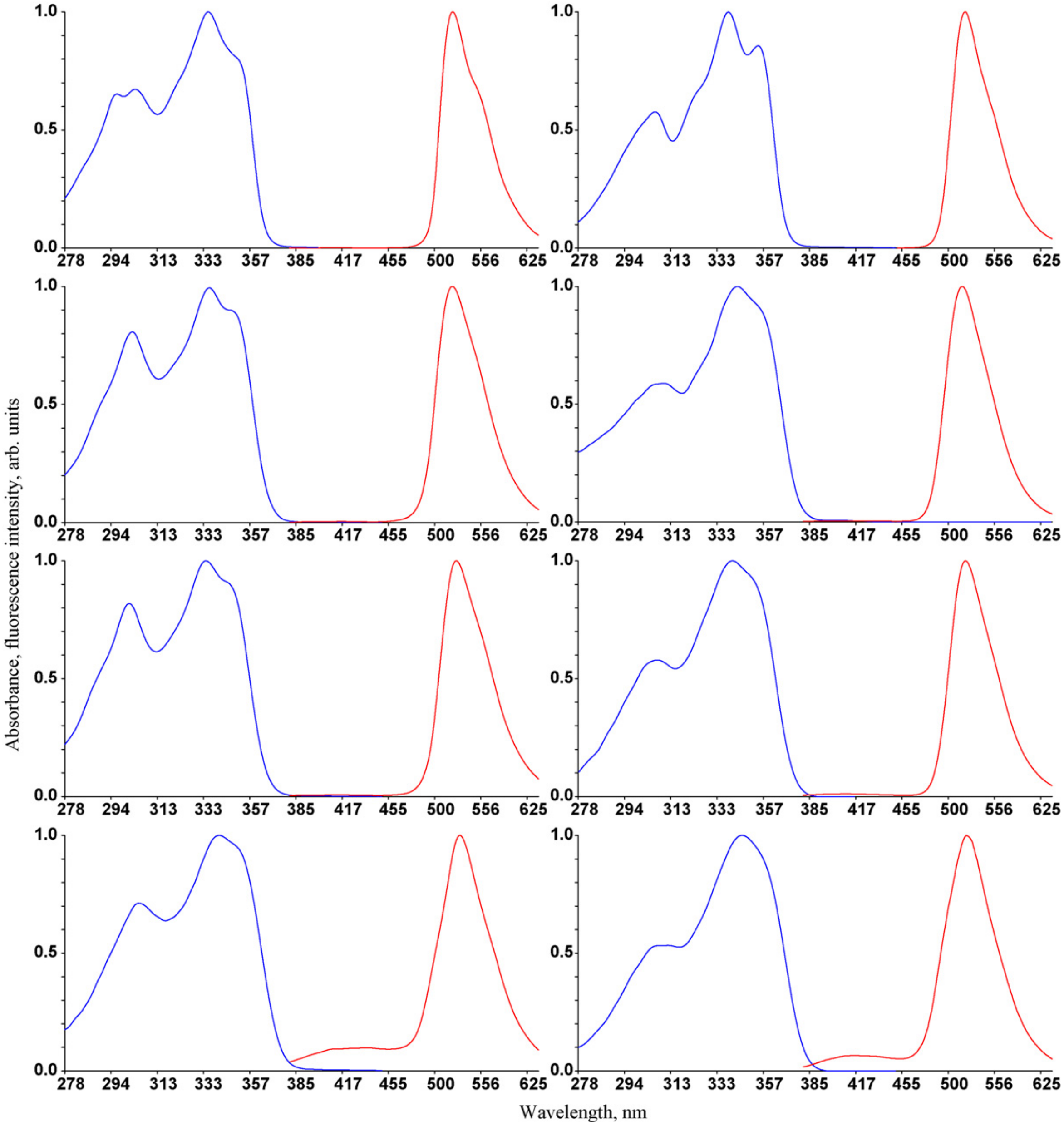


Fig. 1. Electronic absorption (blue) and fluorescence (red) spectra of **3ePz3HC** (left column) and **4ePz3HC** (right column) in four solvents of different polarity: *n*-octane (E_T^N 0.012, top), dichloromethane (E_T^N 0.309), acetonitrile (E_T^N 0.460) and ethyl alcohol (E_T^N 0.654, bottom). Excitation wavelength: 340 nm in all cases. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

in the absorption spectra of **3ePz3HC** and **4ePz3HC** alcoholic solutions (Fig. 2). Excitation at 420 nm resulted in the appearance of pure anion fluorescence band at 485–487 nm. Acidification of the ethanol solutions (one drop of concentrated aqueous *HCl* per 4 ml—the volume of the fluorimetric cell) resulted in the disappearance of the anion absorption and emission, the shape and intensity of fluorescence spectra at these conditions did not show any other variations in comparison to that of the neutral solutions.

Comparison of the absorption spectra of the basic (~0.3 g of solid *KOH* per 4 ml) and neutral ethyl alcohol solutions (Fig. 2) allowed concluding that at 340 nm irradiation the fraction of the excitable anionic species was negligible in respect to that of the neutral ones. Thus, presence of the traces of anionic forms could not influence substantially the experimentally detected emission of **3ePz3HC** and **4ePz3HC** in ethyl alcohol.

The phototautomer fluorescence band of **3ePz3HC** (Fig. 1, Table 5) was observed in slightly long-wavelength region in comparison to **4ePz3HC**, in correspondence with our theoretical findings. No detectable emission was registered for **3ePz3HC** in the range below 500 nm for all the solvents examined. This indicates the absence of the alternative phototautomer form with ESIPT to nitrogen for this compound in fluid solvents at room temperature.

The ESIPT reaction demonstrates a tendency to retarding at the increase of solvent polarity (see k_{ESIPT} values, Table 5). The simultaneous decrease of the quantum yield and lifetime reflects the acceleration of radiationless decay of the excited phototautomer form regulated by the solvent polarity. This is the common behavior of the ESIPT molecules belonging to various classes of organic compounds [[45,57,58] and references therein].

The fluorescence quantum yields of **3ePz3HC** in aprotic solvents are lower to those of **4ePz3HC** by approximately 5–20% (Table 5). We consider this difference as a consequence of conformational composition of the investigated heterocyclic analogs of 3HC, the estimation of which by different quantum-chemical methods give

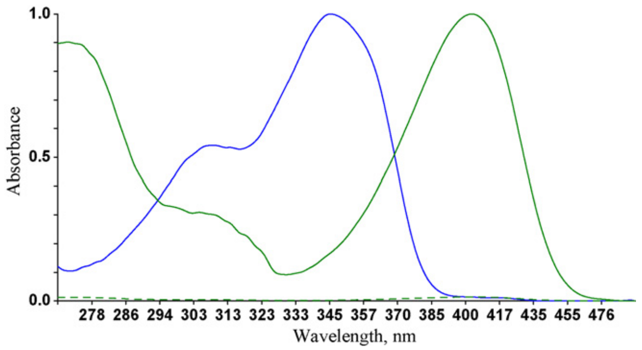
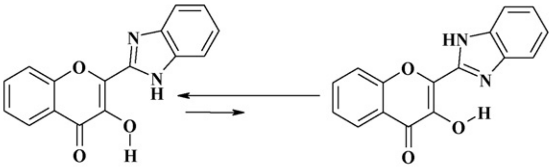


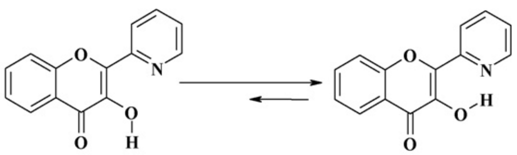
Fig. 2. Absorption spectra of **4ePz3HC** in the neutral (blue) and basified ethyl alcohol (green). The last spectrum was normalized on the long-wavelength shoulder at 400–420 nm of the first one to demonstrate the relative abundance of the anionic form in the neutral alcohol solution (green, dashed). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

results of nearly the same order (Table 1). Thus, the discussed quantum yields ratio **3ePz3HC**/**4ePz3HC** should reflect the presence of the definite fraction of photochemically and spectrally inactive **3ePz3HC** conformation **C** with the intramolecular hydrogen bond to pyrazole cycle nitrogen.

Significant decrease of the fluorescence ability was reported recently for several heterocyclic derivatives of 3HC with six-membered nitrogen containing substituents: 2-pyridyl [34] and 2-quinolyl [33], in which molecules the alternative H-bonding to the heterocyclic nitrogen is realized. On the contrary to the six-membered heterocycles, the five-membered ones still demonstrate effective ESIPT and moderate-to-high fluorescence quantum yields generally typical to the 3HC series [[31,32], present paper].

We could explain the above mentioned difference in photophysical properties between the 5- and 6-membered nitrogen heterocycle containing 3HCs by the fact, that the H-bond accepting center of the six-membered heterocyclic systems lies closer to the proton donor OH group of the corresponding 3HC derivatives. The reported distances between the hydroxy group proton and heterocyclic nitrogen atoms are the following: 1.73 Å for 2-pyridynic 3HC [34], 1.60 Å for 2-quinolynic 3HC [33] and 1.85 Å for the 2-benzimidazolic 3HC [31] (X-ray structural analysis data). Thus, the intramolecular hydrogen bond to the six-membered heterocycles nitrogen should be stronger and more energetically favorable than that of the five-membered ones: it is well-known that the H-bond length substantially correlates with its energy. This causes the higher fractions of the discussed heterocyclic 3HC molecules conformers with H-bond to nitrogen, which emission parameters and ability to ESIPT should be much poorer.





Summarizing the above considerations we could formulate a hypothesis, that alternative intramolecular hydrogen bond to nitrogen in the molecules of heterocyclic analogs of 3-hydroxychromone acts as the factor of fluorescence ability decreasing. From another side, any intermolecular interactions (H-bonding, protonation, coordination with cationic species, etc.), which could influence the intramolecular H-bonding equilibria in favor of the traditional flavonol-like hydrogen bond to the carbonyl group oxygen, should result in the increase of fluorescence intensity. Acidifying of the 2-pyridyl-3-hydroxychromone solution reported in [34] leads to significant ignition of its fluorescence; the same behavior demonstrates our quinolinic 3HC analog, but not the benzimidazolic and pyrazolic ones. This feature of the six-membered nitrogen containing heterocyclic systems could be utilized in the design of the novel molecular sensors on the base of 3HC unit with the possibility of the "alternative" intramolecular hydrogen bonding.

4. Conclusion

Several newly synthesized pyrazole substituted 3-hydroxychromones with and without the principal possibility of intramolecular hydrogen bonding to the heterocycle nitrogen atom were studied both theoretically and experimentally.

Quantum-chemical calculations demonstrated the preferential formation of the intramolecular hydrogen bond to carbonyl group oxygen for the investigated pyrazolic 3-hydroxychromones rather than the alternative H-bond to heterocyclic nitrogen atom. However, definite probability of hydrogen bonding to nitrogen was revealed by several calculation schemes to the compound, which pyrazole cycle is attached by its position 3 to the chromone unit.

Low fluorescence ability and absence of the excited state intramolecular proton transfer reaction was predicted theoretically for the pyrazolic 3-hydroxychromone conformation with intramolecular H-bond to nitrogen; systematically lower fluorescence quantum yields of **3ePz3HC** in solvents of different polarity in comparison to those of **4ePz3HC** supported our findings experimentally.

Peculiarities in preferences of the alternative intramolecular H-bonding to oxygen or to nitrogen were discussed for 5- and 6-membered nitrogen containing heterocyclic moieties introduced into 3-hydroxychromone system basing on the geometrical considerations.

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