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1,4-*bis*-(3-hydroxy-4-oxo-4H-chromen-2-yl)-benzene (*bis*-flavonol): synthesis, spectral properties and principle possibility of the excited state double proton transfer reaction

Research Article

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Abstract: Synthesis and systematic investigation of the spectral-luminescent properties of “*bis*-flavonol” {1,4-*bis*-(3-hydroxy-4-oxo-4H-chromen-2-yl)-benzene} were performed. Hypothetical possibility for the double excited-state proton transfer reaction in *bis*-flavonol is discussed based on both quantum-chemical modeling and experimental data. Consecutive S_1*-state transfer of the two protons of the title molecule is shown to be energetically unfavorable, however, still preserving a possibility for the concerted double proton transfer in the excited dienol form.

Keywords: *3-hydroxychromones • ESIPT • Double proton transfer • Multi-banded fluorescence • Multiparametric fluorescent probes*

1. Introduction

Compounds exhibiting excited-state proton transfer processes (ESIPT) have been a subject of extensive scientific interest over the years [1-3]. Due to the formation of several light-emitting species in the excited states of such molecules, they possess a unique feature: at least two well-resolved bands in their fluorescence spectra [4]. Numerous investigations revealed that fluorescent properties of the ESIPT compounds are in most cases highly sensitive to a variety of characteristics of the fluorophore’s local environment on the molecular level. The spectral response of such compounds is rather complicated: while the excited-state proton transfer process is influenced by the dye molecule’s surroundings, intermolecular interactions affect not only the individual emission bands’ positions and intensities (intensometric approach, see Fig. 1), but their intensity ratio as well. This gave rise to a novel and prospective approach in fluorescence-based analytical methods – the so-called ratiometric fluorescent monitoring [5] (Fig. 1), where the analytical signal is “absolute”, “self-calibrated” [6] and does not depend on the fluorophore concentration, excitation light intensity, etc. This opens new horizons in the analysis of environmental and biological objects, where control of these parameters becomes challenging or even impossible.

From the number of different classes of organic compounds for which the ESIPT process is characteristic, 3-hydroxychromones (3HC) – a large family of natural and artificial dyes – attract particular attention. Due to their dual-banded fluorescence being very sensitive to various characteristics of the surrounding media, 3HC derivatives have been successfully proposed for their practical application as probes for solvent polarity [7,8], hydrogen bonding ability [9,10], metal ion content [11-13], as well as for a number of biologically-oriented investigations, such as those centered on proteins [14,15], nucleic acids and individual nucleotides [16,17], or cell membranes [18-21], *etc.*

Beside the fact that the dual-banded fluorescence opens the possibility for ratiometric fluorescence probing, it also allows the use of an increased number of data-collecting channels as compared to traditional intensometric measurements [23]. Thus, not only the fluorescence intensity ratio depends on the microenvironment characteristics, but also the emission bands’ positions, and – together with the absorption data

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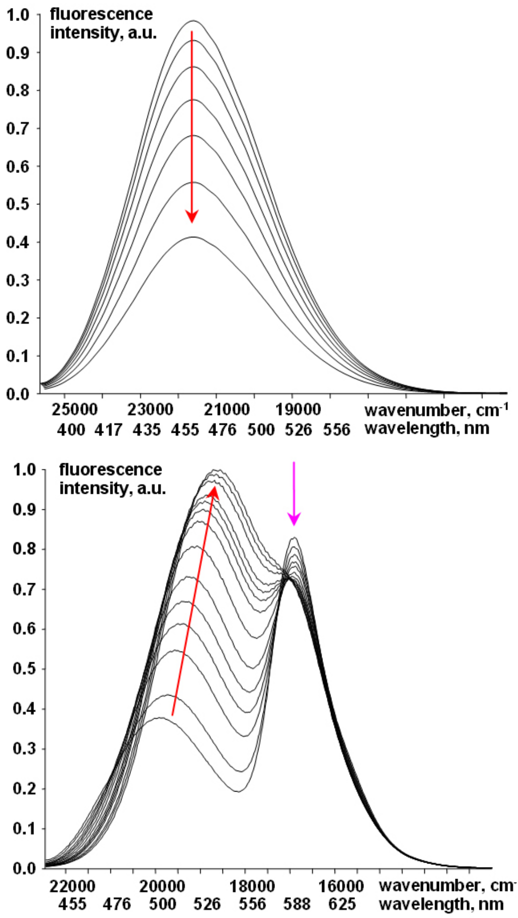


Figure 1. Schematic illustration of the principles of intensometric (top, simulated spectra) and ratiometric (bottom, our own data [22] fluorescence probing.

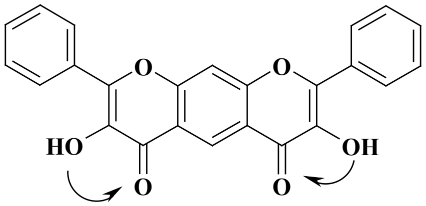


Figure 2. Considering the excited state double proton transfer in diflavonol molecule.

– fluorescence Stokes shifts. This gives researchers an opportunity to build multiparametric correlations, and thus increase the reliability of obtained results, as well as to perform simultaneous and mutually independent analysis of two or more parameters of the probe microenvironment [24].

In the framework of the application of novel ESIPT compounds for multiparametric probing, design and synthesis of multi-banded fluorescent dyes exhibiting yet more complex emission spectra becomes highly promising. For example, compounds with several proton transfer sites could demonstrate single- and double- (dESIPT) excited state proton transfer reactions giving rise to the appearance of additional emission bands [25,26]. The double proton transfer is a very important process in biologically relevant systems, thus, understanding its photophysics is crucial for development of both fundamental and applied science [27]. For the last decade, the possibility of the transfer of two protons has been widely discussed for molecular dimers and ensembles [28-30] and symmetrical molecules [31,32] with two (inter/intra)molecular hydrogen bonds. Also, the question of the mechanism of such a double proton transfer has been discussed for various systems, discriminating between concerted and consequent ones [33].

The first thoroughly investigated molecule among the 3HC derivatives with a possibility of excited state double proton transfer was diflavonol (Fig. 2). However, only the single proton transfer was shown to be particularly favorable for this molecule [34]. The interplay between intramolecular and intermolecular proton transfer reactions has been discussed for diflavonol as well [35]. At the same time, excited state double proton transfer was reported for a *bis*-diethylamino substituted diflavonol [36].

Another representative of 3HC family having the potential to undergo excited state double proton transfer – 1,4-*bis*-(3-hydroxy-4-oxo-4H-chromen-2-yl)-benzene, *bis*-flavonol – was recently synthesized as described in [37]. This molecule contains two 3-hydroxychromone bicycles bound to *para*-positions of the same benzene

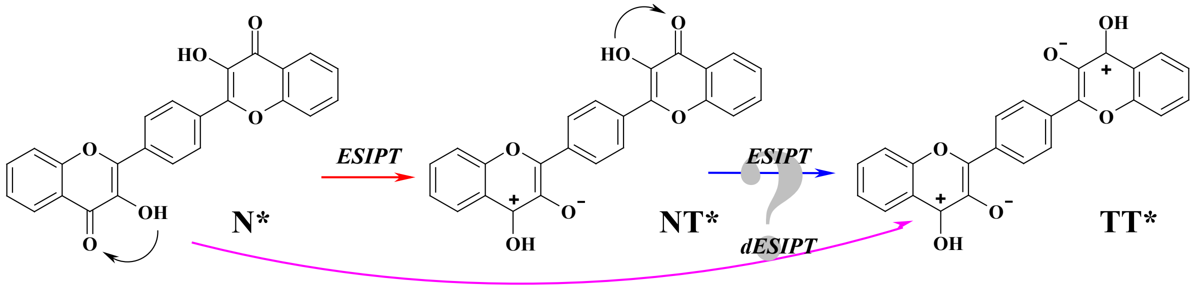


Figure 3. Possible excited state single and double proton transfer in the *bis*-flavonol molecule.

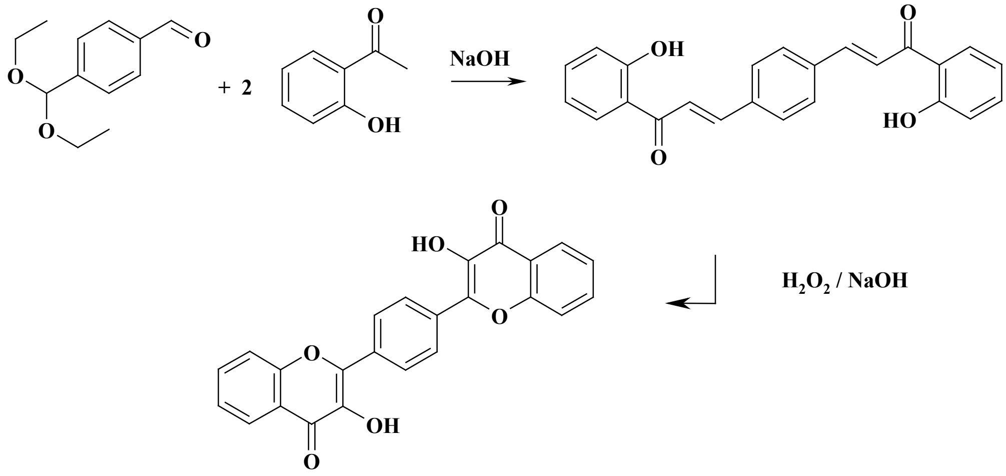


Figure 4. Synthesis of 1,4-bis-(3-hydroxy-4-oxo-4H-chromen-2-yl)-benzene.

ring, and thus possesses two intramolecular hydrogen bonds formed by the corresponding hydroxy- and carbonyl groups. To our knowledge, no further spectroscopic and physico-chemical studies, particularly of the ESIPT process, have been reported for the discussed molecule.

In the present paper, we report the investigation of spectral and fluorescent properties of *bis*-flavonol, as well as its suitability for ratiometric probing of various characteristics of the liquid phase. The possibility of the realization of the excited state double proton transfer (Fig. 3) is discussed as well, based on both spectral data and results of our quantum-chemical calculations.

2. Experimental procedure

2.1. Synthesis

The compound, 1,4-bis-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-benzene, referred in this paper as ***bis*-flavonol**, was synthesized according to the Algar-Flynn-Oyamada procedure (see Fig. 4) [38,39]. Purity of the obtained compound was tested by TLC (silica gel, methanol/chlorophorm 1:9) and further - by HPLC. *Bis*-flavonol structure was confirmed by elemental analysis and NMR ^{1}H spectroscopy in DMSO-d$_6$.

In the first stage, a corresponding chalcone was obtained by condensation of 0.5 g (2.42 mmol) of terephtalaldehyde monodiethylacetal with 0.66 g (4.83 mmol) of *o*-hydroxyacetophenone in 10 mL of methanol with 5 mL of 50% aqueous NaOH solution. A night after, the formed chalcone salt was neutralized to pH = 6-7 with 5% HCl. The precipitate was filtered, washed with methanol and dried.

The second stage consisted of an oxidative cyclization of the previously obtained chalcone into a corresponding chromone. Thus, 0.5 g of the chalcone was dissolved in 5 mL of 96% ethanol with 2 mL of 50% aqueous NaOH solution. Then 4.5 mL of 35% H_2O_2 solution was added dropwise, observing an intensive release of oxygen. Upon addition of the full amount of peroxide, the reaction medium was heated to boiling for 3-5 minutes, then cooled, diluted with cold water and neutralized to pH = 6-7 with 5% HCl. The precipitated chromone was filtered off, washed with methanol and then recrystallized from $CHCl_3$ giving 0.18 g of the product (33% yield).

Bis-flavonol, $C_{24}H_{14}O_6$, m.p. > 300°C (decomp.), MM 398.36, molecular ion in MS: m/z 398. Elemental analysis C(%): 72.36 (calc.), 73.0 (found); H(%): 3.54 (calc.), 3.3 (found). NMR ^{1}H data: 7.35-7.50 (m, 4H), 7.75 (s, 4H), 7.90-8.05 (t, 2H), 8.10-8.20 (d, 2H). Signal of the OH proton was not located because of H-D exchange at continuous heating of the sample needed to dissolve this poorly soluble compound in slightly humid DMSO.

2.2. Procedures and apparatus

Nuclear magnetic resonance spectra were measured on Varian VX-200 spectrometer, and the mass-spectra were recorded on Varian 1200L spectrometer (electron impact, 70 eV) (SSI “Institute for Single Crystals” NAS of Ukraine, Kharkov).

Measurement of steady-state absorption and fluorescence spectra was conducted using Hitachi U-3210 spectrophotometer and Hitachi F-4010 spectrofluorimeter, respectively, in quartz cells with dye solution layer thickness of 10 mm. Quinine bisulfate in 0.5 M aqueous sulfuric acid was used as reference standard to measure quantum yields [40].

Deconvolution of the emission spectra into elementary bands (necessary to calculate the normal-to-phototautomer integral fluorescence intensity ratios) was effectuated using special computer software developed in our group. The software synthesizes a nonlinear least-squares method with the iterative Fletcher-Powell algorithm and the individual emission band shape approximation by the asymmetric log-normal function proposed by Siano and Metzler [41]. In several cases, this procedure was applied to the spectra in the semi-logarithmic representation.

The normalized Reichardt solvent polarity index E_T^N [42], which is widely used for estimation of media polarity in numerous investigations of chemical and biological systems, was applied for characterization of the polarity-dependent properties of *bis*-flavonol.

Theoretical modeling was performed in DFT/TD-DFT schemes using the *b3lyp* hybrid potential [43] with the *cc-pvdz* basis [44]. Calculations of the molecular geometry and electron density redistribution upon electronic excitation of *bis*-flavonol were made with Gaussian-09 (release B.01 [45] – for ground state molecular structure optimization) and NWChem (version 5.1 [46] equipped with special module for ESS-analysis [47] “excited state structural analysis” – for electronic spectra calculation) program packages.

3. Results and discussion

3.1. Considering double proton transfer: a theoretical discussion

In the ground state, the molecule of *bis*-flavonol can exist in two conformations: *syn*-, a polar one with a dipole moment of 5.4 D according to our calculations, and a non-polar *anti*- (see Fig. 5).

The two conformations have very similar energies (the estimated difference is only about 0.06 kcal mol^{-1}), thus the equilibrium mixture should contain ~47% of *syn*- and ~53% of *anti*-conformer.

The energies of the intramolecular hydrogen bonds in both conformations, estimated within Bader’s AIM (atoms in molecule) theory [48-51] on the basis of the calculated characteristics of the critical point (3, -1) of the H-bond OH···O= according to recommendations of [52,53] were equal to 8.41 kcal mol^{-1} for the *syn*-conformer and 8.47 kcal mol^{-1} for the *anti*-conformer.

The calculated characteristics of the long-wavelength electronic transitions for both conformers also turned out to be very close (due to the symmetry of both conformers, electronic excitation localization, as well as electronic density redistribution dynamics estimated within the ESSA approach [47] are shown only for one part of each structure in the Tables 1-3). To make the ESS analysis more illustrative, the following structural fragments were defined in the molecule under study: benzene rings of the chromone bicycles, carbonyl groups, enolic fragments together with pyrone oxygen atoms, and the central benzene ring.

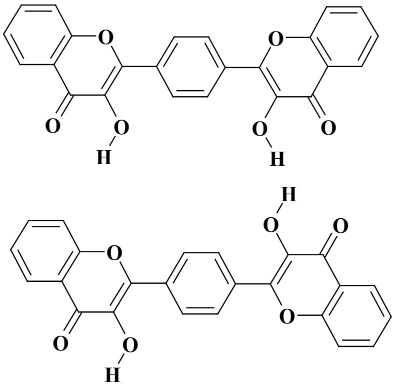


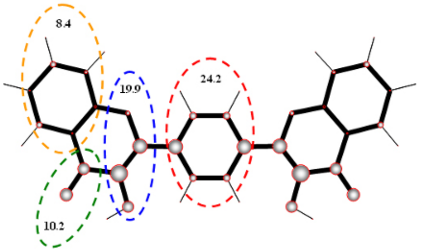
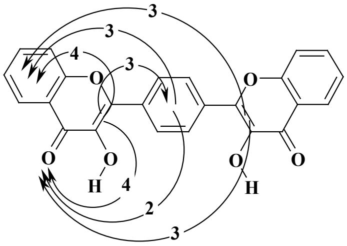
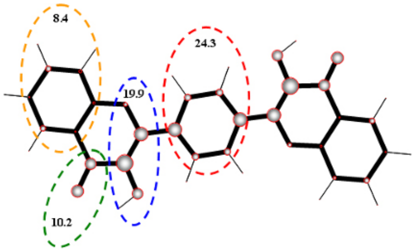
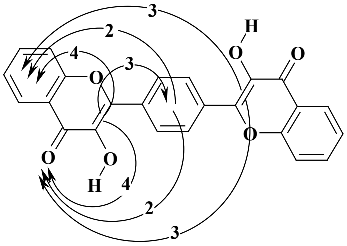
Figure 5. *Syn*- (top) and *anti*- (bottom) conformations of bis-flavonol molecule.

For both conformers of *bis*-flavonol, prevailing localization of the electronic excitation S_0-S_1 on the central part of their molecules is characteristic, while a considerably lesser contribution is observed from the peripheral benzene rings of the chromone bicycles. The calculated charge transfer indices at the electronic transition to the lowest singlet excited state for the symmetrical *bis*-flavonol molecule are relatively low. However, the tendency towards electronic density redistribution from the center to the periphery of the discussed molecules – to the terminal chromone benzene rings and carbonyl groups – is observed clearly on the corresponding diagrams. In this case, the enolic fragments act as electron-donor centers, while the carbonyl groups play the role of electron-acceptor centers. Such a redistribution of the electron density in the excited molecules should lead to an increase of the hydroxyl groups’ acidity, as well as an increase of the carbonyl groups’ basicity, thus strengthening the intramolecular hydrogen bonds between them. As a result, these simultaneous processes (with the first one considered to play the crucial role [54]) become the driving force of the intramolecular proton phototransfer reaction, which is characteristic for the entire class of 3-hydroxychromone derivatives.

Taking into account the significant similarity between the spectral characteristics of both conformers, all further resource-intensive calculations, including the excited state molecular geometry optimization, were performed only for the *anti*-conformer as a model structure.

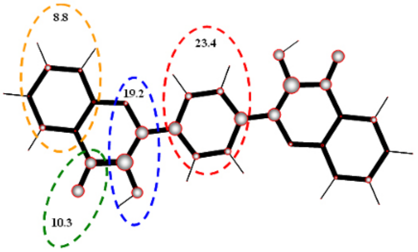
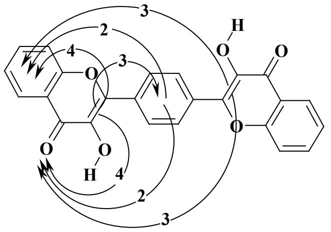
Geometry optimization for the excited *anti*-conformer of *bis*-flavonol and further calculation of its spectral characteristics is a common approach for fluorescence spectrum estimation. It is interesting to note that the character of the electronic excitation localization and

Table 1. Characteristics of the long-wavelength electronic transitions in the molecules of *syn-* and *anti-* conformers of *bis*-flavonol.

Conformation	Transition S_0-S_1	Localization numbers	Excited state charge transfer indices
syn-	24240 cm^{-1} 413 nm f = 1.001		
anti-	24260 cm^{-1} 412 nm f = 1.006		

Due to the symmetry of the above molecules, electronic excitation localization and electron density redistribution dynamics estimated within the ESSA approach are shown only for one part of each structure

Table 2. Characteristics of the long-wavelength electronic transition in the molecule of the anti-conformer of bis-flavonol for the S_1 state optimized geometry.

Conformation	Transition S_0-S_1	Localization numbers	Excited state charge transfer indices
anti-	22070 cm^{-1} 453 nm f = 1.112		

See footnote for the Table 1.

the intramolecular electron density redistribution change only insignificantly when comparing the ground- and excited state optimized molecular structure. However, the energy of the S_1 electronic state is reduced by almost 2200 cm^{-1}. These data can be considered a theoretical estimation of the fluorescence Stokes shift for *bis*-flavonol in non-polar media, which is in good agreement with experiment (see Table 4 below). Regardless of the above-mentioned general similarity of the electronic density redistribution character in the discussed molecules in their S_0 and S_1 states, our calculations unambiguously show an increase of the energies of both intramolecular hydrogen bonds in the excited state up to 10.2 kcal mol^{-1} (AIM, [52]). This circumstance also favors higher probability of the excited state proton transfer reaction.

For the molecules bearing two moieties potentially able to provoke the proton phototransfer reaction, a question obviously arises about the number of protons that could be involved in such an intramolecular transformation. The performed calculations do not give us any reason to consider the asymmetrization of either geometry of the molecule under study nor its excited-state electronic density redistribution. Thus, one can assume a potential possibility for the double proton transfer to be observed in *bis*-flavonol. However, there are a number of examples in the earlier works, where the phototransfer of only one of the two protons was realized even in symmetrical molecules with two protolytic centers [34].

To model both single and double proton transfer scenarios, we have performed calculations of the

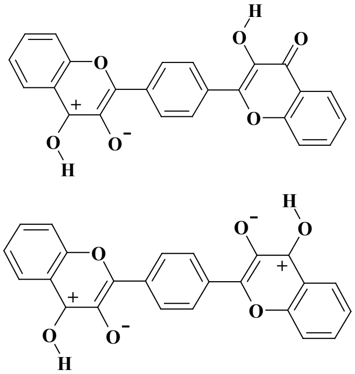


Figure 6. Structures of mono- (NT*, top) and di- (TT*, bottom) phototautomers of bis-flavonol.

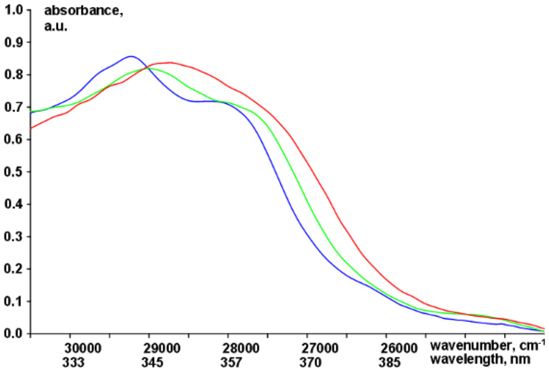


Figure 7. Absorption spectra of bis-flavonol in octane (blue), toluene (green) and ethanol (red); see colors in the online version of this paper.

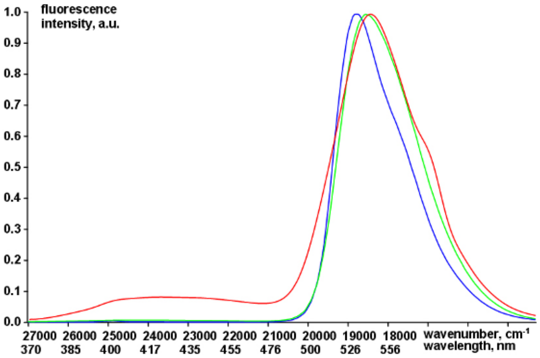


Figure 8. Fluorescence spectra of bis-flavonol in octane (blue), toluene (green) and ethanol (red); see colors in the online version of this paper

molecular geometry and spectral characteristics for the mono- and ditautomeric forms correspondingly, which might be formed in the excited state of *bis*-flavonol (Fig. 6).

Presumably, both products of the intramolecular phototautomerization could be formed from the excited normal form N*. Thus, the first question to be answered was which one of the possible directions of this protolytic transformation is more energetically favorable. From another point, it was important to elucidate whether a synchronous transfer of two protons is possible, or the ditautomeric form could be the product of a consequential two-step process involving the intermediate monotautomeric form.

Further calculations showed that, taking into account the difference between the energies of corresponding ground states, the energy of the excited monotautomer is 3.7 kcal mol^{-1} lower than that for the excited normal form, while the ditautomer exceeds the excited normal form by ~1.0 kcal mol^{-1}. Thus, the energetic favorability of the di-tautomer turns out to be rather questionable, especially in the case in which it is formed through the intermediate stage of the monotautomer. Moreover, in the monotautomeric form, the energy of the remaining intramolecular hydrogen bond of –OH···O=C< type was shown to be lower than in the case of the excited normal form – 8.93 kcal mol^{-1} (AIM, [52]). This gives a reason to presume that the possibility for the second proton transferring in the excited monotautomer is low. Additionally, the electronic excitation in the monotautomer is significantly localized on the fragments which have already participated in the transfer of the first proton (see Table 3). Thus, there are no explicit prerequisites for the second stage of the consequent proton transfer to occur.

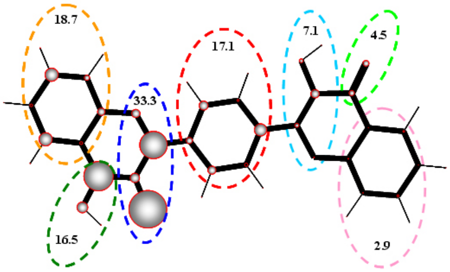
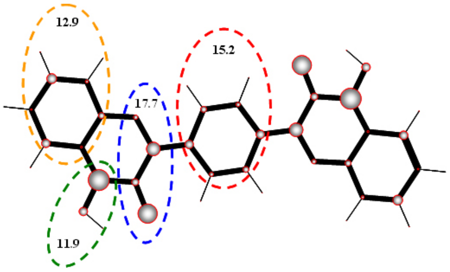
However, a hypothetical possibility for the synchronous double proton phototransfer could not be excluded from consideration completely, because the energy difference between the excited normal form and the di-tautomer is not particularly large.

3.2. Spectral properties of bis-flavonol

Absorption spectra of *bis*-flavonol in representative organic solvents are quite similar to those of the parent 3-hydroxychromone: the absorption maximum is located near 360-365 nm, while the long-wavelength peak is complex and should consist of two bands which correspond to S_0-S_1 and S_0-S_3 ππ*-transitions of the dye molecule [55,56] and – hidden below them – low-intensity nπ*-bands. Examples of absorption spectra of *bis*-flavonol are shown in Fig. 7, while the full spectral data set can be found in Table 4.

The electronic excitation of the *bis*-flavonol molecule leads to the simultaneous increase of the 3-OH group acidity as well as the 4-carbonyl group basicity, which results in intramolecular proton transfer along the hydrogen bond existing in the ground state. This gives rise to the second band in the fluorescence spectra of the compound under study – emission of the phototautomer (Fig. 8). Thus, *bis*-flavonol is characterized by two-banded fluorescence with the short-wavelength band located near 24000 cm^{-1} in solvents of various physico-chemical properties from the inert low-polar octane and

Table 3. Calculated spectral characteristics of the excited mono- and ditautomeric forms of *bis*-flavonol.

Excited species	Transition S_0-S_1	Localization numbers
Mono-tautomer	17050 cm^{-1} 587 nm f = 0.759	
Di-tautomer	15350 cm^{-1} 652 nm f = 1.080	

For the case of di-tautomer see footnote for the Table 1.

Table 4. Spectral data for *bis*-flavonol.

Solvent	E_T^N	ν_{abs}, cm^{-1}	ν_{fl}^N, cm^{-1}	$\Delta\nu_{ST}^N$, cm^{-1}	ν_{fl}^T, cm^{-1}	$\Delta\nu_{ST}^T$, cm^{-1}	φ
octane	0.012	27920	24930	2990	18705	9215	0.23
toluene	0.099	27780	23180	4600	18440	9340	0.23
1,4-dioxane	0.164	27720	22875	4845	17670	10050	0.11
dichloromethane	0.309	28700	23640	4160	18385	9415	0.21
acetone	0.355	27960	22245	5715	17695	10265	0.063
acetonitrile	0.460	28040	22520	5520	18065	9975	0.062
ethanol	0.654	27620	23175	4445	18410	9210	0.031
methanol	0.762	27580	23400	4180	18360	9220	0.026

ν_{abs}, ν_{fl}^N, ν_{fl}^T – *positions of absorption, normal and phototautomer forms fluorescence maxima respectively;*
$\Delta\nu_{ST}^N$, $\Delta\nu_{ST}^T$ – *normal and phototautomer forms fluorescence Stokes shifts;* **φ** – *total fluorescence quantum yield;*
E_T^N –*normalized Reichardt solvent polarity index.*

toluene to polar acetonitrile and alcohols. The discussed fluorescence band is normally attributed to the emission of the so-called normal form, whereas the long-wavelength band situated near 18000 cm^{-1} corresponds to the emission of the phototautomeric form. The latter is characterized by abnormally high fluorescence Stokes shift values of 9200-10300 cm^{-1}.

High sensitivity of the parent compound of the 3HC family, flavonol, to intermolecular hydrogen bonding was reported just in the early publications of Kasha on this class of compounds [9,57]. Later, intermolecular ground state proton transfer leading to the formation of anionic species was reported for several flavonols dissolved not only in such highly nucleophilic solvents as DMF [58,59] and DMSO [60], but in various neutral alcohols [61] as well. Presence of the intermolecularly H-bonded and anionic species results in the reported dependence of 3HC fluorescence spectra on the excitation wavelength [61,62].

To confirm our attribution of the ~24000 cm^{-1} fluorescence band to the emission of the normal form (not distinguishing between its intra- and intermoleculary bonded species having highly overlapped fluorescence spectra), we have performed a preliminary investigation aimed to estimate the position of the anionic fluorescence band of the title compound and outline the general influence of anionic species on the optical characteristics of *bis*-flavonol. Indeed, in protic solvents, such as alcohols, traces of the anion absorption were observed near 420 nm. Once the solution was slightly basified, we were able to detect either a mixture of neutral molecule and anion emissions (Fig. 9, purple line), or individual anion emission excited directly in its absorption maximum (red line).

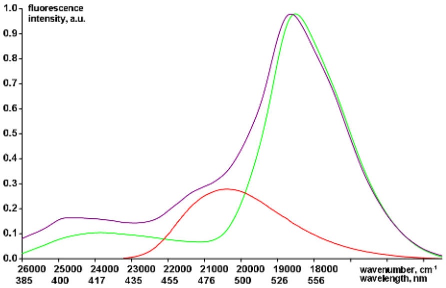


Figure 9. Fluorescence of bis-flavonol in methanol ($\lambda^* = 360$ nm, green) and methanol + $NaOH_{aq}$ ($\lambda^* = 360$ nm, magenta and $\lambda^* = 420$ nm, red); see colors in the online version of this paper.

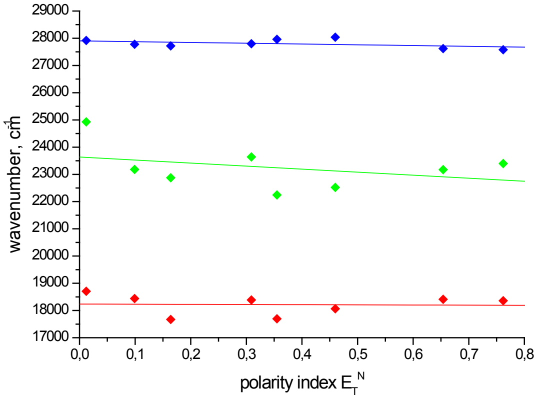


Figure 10. Solvatochromism of bis-flavonol: plots of positions of the absorption (top, blue), normal fluorescence (middle, green) and phototautomer fluorescence bands (bottom, red) versus Reichardt solvent polarity index E_T^N; see colors in the online version of this paper.

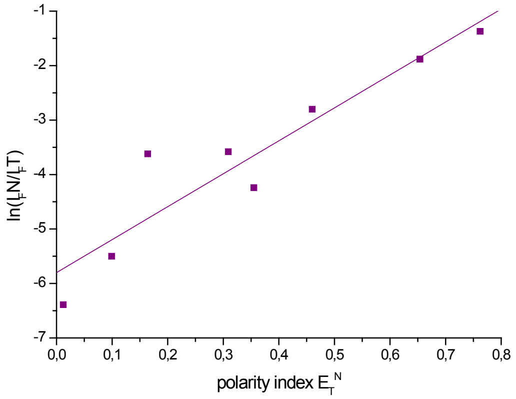


Figure 11. Normal-to-phototautomer emission intensity logarithm plot *versus* a solvent polarity.

However, when the fluorescence spectrum of an alcoholic solution was recorded with the excitation wavelength corresponding to the neutral molecule's absorption maximum ($\lambda^* = 360$ nm), no anionic emission was observed as the *bis*-flavonol anion absorption on this wavelength is negligible (Fig. 9, green line), analogously to the case reported by us earlier [63].

Fluorescence quantum yields of *bis*-flavonol are quite moderate, but still a bit higher than that of the parent 3HC molecule. As clearly seen from the Table 4, solvent polarity induced fluorescence quenching resulting in a significant decrease of fluorescence efficiency is typical to the title molecule.

Absorption spectra of the compound under study show very weak positive solvatochromic effects, as can be seen from the corresponding plot built versus the Reichardt solvent polarity index (Fig. 10). The complex nature of the E_T^N [42,64,65] notwithstanding, it was nevertheless used here owing to its suitability for qualitatively presenting the general solvent influence on the given photophysical property in two-dimensional plots. The above mentioned behavior of *bis*-flavonol is in good accordance with the results of theoretical modeling and can be explained by weak charge redistribution in this symmetric molecule at the electronic excitation (see Table 1).

The influence of the media polarity on the spectral properties of *bis*-flavonol has been studied in a series of seven organic solvents including both aprotic ones and alcohols. As it follows from the data presented in the Fig. 10, the fluorescence maximum of the normal form demonstrates a bathochromic shift on increase of polarity, showing distinct positive solvatofluorochromism connected with substantial increase of its dipole moment in the S_1* state. In contrast, the phototautomer emission band position is unaltered and practically independent of solvent polarity. This fact is usually explained by the difference in the dipole moments of the excited normal and phototautomer forms: polarity of the latter is close to that of the normal form in its ground state, thus, the difference between the dipole moments of N and N* forms is much more significant than that between the dipole moments of N and T*.

To elucidate the suitability of *bis*-flavonol for its application as a ratiometric sensor for various characteristics of a liquid phase, a correlation between the normal-to-phototautomer emission intensity ratio and the solvent polarity was examined. As it is shown in the Fig. 11, the logarithm of the above-mentioned function shows a good linearity *vs.* Reichardt's normalized polarity index. As solvent polarity increases, specific intermolecular solvent-solute interactions begin to concur with the intramolecular hydrogen bond, leading to a decrease of the observed phototautomer emission. The above mentioned difference in the dipole moments of the excited normal and phototautomer forms results in retardation of the ESIPT process in polar surroundings. The last factor worth mentioning is the already discussed fluorescence quenching induced by solvent polarity; it is

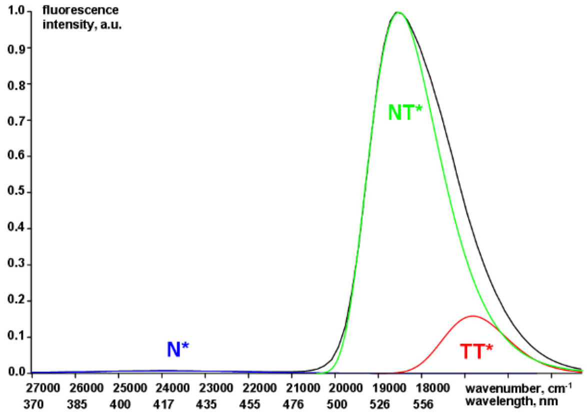


Figure 12. Possible deconvolution of bis-flavonol fluorescence spectrum in toluene onto three individual components.

especially important for the phototautomer form [66,67]. All these circumstances cause a shift of the normal-to-phototautomer emission bands intensity ratio by several orders of magnitude, making it a sensitive analytical signal suitable for practical application in chemical, biophysical and environmental sensing.

Despite the hypothetical probability of observing at least two fluorescence emission bands belonging to mono- and di-tautomeric species, only one band was detected in the long-wavelength spectral region. According to our quantum-chemical modeling, positions of the mono-and di-phototautomer bands should not differ significantly. In conditions of their substantial overlap, only band shape analysis should be applied to resolve the question of the realization of the excited state double proton transfer. Fluorescence excitation spectra recorded at different wavelengths within the phototautomer emission band demonstrate good coincidence with each other. This leads to the conclusion that all the observed fluorescence comes from the same parent molecule in its ground state.

The phototautomer fluorescence band shape of the title molecule is characterized by a slightly enlarged asymmetry, which allows us to try to seek the hidden ditautomer emission located under the long-wavelength wing of the experimental phototautomer band. The application of the mathematic deconvolution procedure to the *bis*-flavonol fluorescence spectrum in toluene is shown in the Fig. 12. According to the presented data, the experimental fluorescence spectrum for *bis*-flavonol could be interpreted as consisting of at least three emission bands corresponding to the excited normal, mono-tautomer and di-tautomer forms. However, this should not be considered as final proof and further investigations are needed to give a definite answer about the nature of the *bis*-flavonol long-wavelength emission.

4. Conclusions

A molecule with two intramolecular hydrogen bonds – *bis*-flavonol – was synthesized and its spectral and fluorescent properties were investigated. The title compound exhibits bathochromic shifts of the absorption and normal form fluorescence maxima upon increase of solvent polarity, and is characterized by moderate fluorescence quantum yields and abnormally high Stokes shifts of the phototautomer emission. Theoretical modeling was performed to elucidate the possibility of a double intramolecular proton transfer process to be realized. While the hypothetical probability of the ditautomer formation cannot be excluded, its consequential generation *via* the intermediate stage of monotautomer form is shown to be energetically unfavorable.

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