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Excited-State Proton Transfer Reaction in a New Benzofuryl 3-Hydroxychromone Derivative: The Influence of Low-Polar Solvents[*]

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Unique properties of a new 3-hydroxychromone derivative 2-(6-diethylamino-benzo[*b*]furan-2-yl)-3-hydroxychromone (FA) in its ability to exhibit excited-state intramolecular proton transfer (ESIPT) reaction are described. In contrast to all other chromone and flavone derivatives studied, in low-polar solvents it exhibits in emission, together with the tautomer (T*) band, an intensive band of the normal (N*) form. Previously the intensive N* form in emission was observed only in highly polar, mostly protic solvents. While its absorption spectra are sensitive to H-bond acceptor properties of the solvent, the fluorescence spectra are not. This suggests that intermolecular H-bonds with a solvent, if they exist in the ground state, are reorganized in the excited state in favor of intramolecular bond, which is the pathway for ESIPT reaction. The energy difference, $\nu_{N^*} - \nu_{T^*}$, between N* and T* emission maxima is in almost ideal correlation with the Reichardt solvatochromic parameter E_N^T. This suggests the use of FA as a highly sensitive polarity sensor. A good correlation between $\nu_{N^*} - \nu_{T^*}$, and the ratio of the N* and T* band intensities is observed. This allows to observe the solvent effects on a manifold increased level of sensitivity. The analysis based on Lippert and Bakhshiev equations and the quantum-chemical calculations suggest a substantial increase of the dipole moment on electronic excitation to the N* state. The appearance of the N* form in emission may be the result of its dielectric stabilization.

Key words: solvent effects, fluorescence probe, excited-state intramolecular proton transfer, dual emission, 3-hydroxychromones, hydrogen bond

The dynamics of excited-state intramolecular proton transfer (ESIPT) in H-bonded systems attracted considerable attention in many different fields, such as photochemistry and biochemistry. The biochemical proton transfer reactions are thought to be catalyzed in such a way that they occur along the low-activation-energy pathway connected by H-bond, and one of the roles of enzyme molecules is to eliminate the reaction site from perturbation by undesirable H-bonding partners [1]. The ESIPT reactions being of low activation energy may serve as models for biochemical reactions

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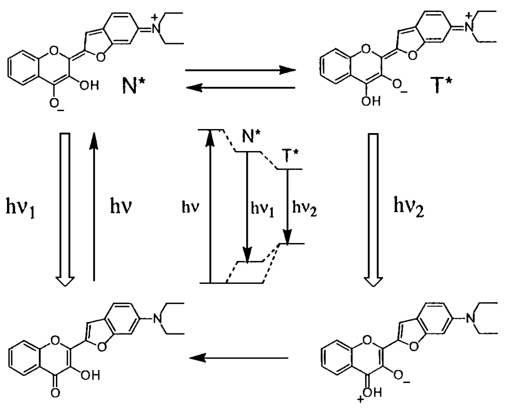
[2]. In photochemistry the ESIPT reactions are known to be among the fastest elementary events; they can occur on the time scale of femtoseconds [3,4]. These reactions are accompanied by a dramatic change in excited-state energies [5] and additional significant bathochromic shifts of emission wavelengths. The latter properties make their applications very promising in different fields, from laser dyes [6] to molecular ion sensors [7,8]. The most intensively studied chromophores exhibiting ESIPT are 3-hydroxyflavone [9] and its derivatives.

ESIPT is a reaction of tautomerization, occurring in the excited states of molecules, in which proton is transferred *via* intramolecular H-bond or a H-bonding bridge formed by solvent molecules [10]. The electronic excitation of the normal (N) form leads to the excited (N*) form, which in the course of photochemical reaction is transformed into a proton transferred tautomer (T*). This T* form relaxes radiatively or nonradiatively to the metastable ground state tautomer T, which reverts to N state *via* reverse proton transfer. Thus, in principle from light absorption and emission spectra we can obtain a number of independently measurable parameters, that are differentially sensitive to universal (dielectric) and specific (H-bonding) interactions with the environment. These are the position of N absorption band, the positions of N* and T* bands in emission, relative intensities of N* and T* bands (I_{N*}/I_{T*}) and the total fluorescence quantum yield Q of these bands [11]. 3-Hydroxyflavones are ideal for the analysis of these parameters, because their N* and T* bands are highly emissive and well-separated on energy scale. It was found that both the position of the N* form (which attains in some derivatives the strong CT properties) and the I_{N*}/I_{T*} ratio are very sensitive to different perturbations [12–14]. The latter can be mediated *via* the effect on intramolecularly H-bonded hydroxyl and carbonyl or result from the direct effect on the electronic system of chromophore.

In order to increase the sensitivity to the solvent effects, a series of new 3-hydroxyflavone (3-HF) and 3-hydroxychromone (3-HC) molecules with extended π electronic system and variation of electron-donor substituent were synthesized [15,16]. Due to substantial modification of π electronic system, which also resulted in the change of H-bonding abilities of hydroxyl and carbonyl groups, these molecules attained new spectroscopic properties. One of them is the presence of intensive N* band in toluene [15], which is a very unusual fact that was never observed before with any 3-HF or 3-HC derivative. Moreover, a common belief persists, that for the appearance of this band in emission a strong perturbation by forming intermolecular H-bonding complexes is necessary [9,17]. An alternative point of view also exists, suggesting a strong dielectric stabilization of the N* state and the occurrence of dynamic equilibrium between the N* and T* forms [12,13].

The present report is the first in a series that are focused on detailed investigation of photophysical properties of these new fluorescent molecules and their testing as molecular sensors in different systems. Here, we perform the studies of benzofuran 3-HC, FA, in which we are focused on the answers to the following questions: What is the origin of N* emission observed for FA in low-polar solvents? Is it the result of dielectric stabilization of this state and its charge-transfer (CT) character? Then, is it the result of the redistribution of emission probabilities between the N* and T* states at equilibrium or of the existence of a kinetic barrier for ESIPT reaction? What is the role of intramolecular H-bond? Can it be perturbed by intermolecular bonds with the solvent as a result of changes in electronic spectra? Does the relative intensity of the N* and T* bands correlate with solvent polarity? Does the energy difference between the N* and T* bands correlate with the ratio of N* and T* band intensities? And if it is so, can the intensity ratio I_{N*}/I_{T*} provide a highly sensitive measure of solvent polarity? And finally, what is the dielectric nature of the N* and T* states, expressed in the distribution of charge densities and the dipole moments? In finding the answers to these questions an attempt is made to provide a consistent picture of solvent-dependent spectroscopic and photophysical behavior of FA.



Scheme 1. 2-(6-Diethylaminobenzo[*b*]furan-2-yl)-3-hydroxychromone (FA) and its excited-state transformation.

EXPERIMENTAL

The sample of FA, 2-(6-diethylaminobenzo[*b*]furan-2-yl)-3-hydroxychromone, was synthesized as described elsewhere [15] and purified by crystallization from ethanol, m.p. 226°C; ^{1}H NMR (200 MHz, CDCl$_3$) 1.23 (6H, t, 7.1 Hz), 3.45 (4H, q, 7.1 Hz), 6.76 (1H, dd, J 8.8, 2.2 Hz), 6.87 (1H, d, 2.2 Hz), 7.38–7.46 (1H, m), 7.48 (d, J 8.8 Hz), 7.64 (1H, s), 7.64–7.75 (2H, m), 8.25 (1H, dd, J 8.2); EI *m/z* 349.2 (M^+), 334.1, 305.1, 276.1, 248.1, 167.0. All solvents were of analytical grade (Aldrich, Fluka or Merck). Solvents with polarity of thiophen or higher were additionally purified by drying over sodium or sodium sulfate with subsequent distillation.

Fluorescence emission spectra were obtained on Quanta Master spectrofluorometer PTI (Photon Technology International, Canada) operating in quanta counting mode. Excitation and emission slits were 1 and 4 nm, respectively. Excitation wavelength was 430 nm. The measurements were made in cell holders at 22°C if other values are not indicated.

Fluorescence quantum yield was calculated using solution of 4′-diethylamino-3-hydroxyflavone (FE), (a gift of Dr. V.G. Pivovarenko from the Kiev Schevchenko University) in ethanol as a reference with quantum yield Q = 0.52 [13]. The common method was used, consisting in calculating the ratio of the area under fluorescence spectra of probe FA in a solvent and of the reference [19,20]. The correction of the difference of refraction indexes between the solvents has been accounted. The absorption values for FA and FE were about 0.1 at 430 nm. All the light absorption measurements were made on a Cary 3 BIO spectrophotometer (Varian, Australia).

Deconvolution of fluorescence spectra of probe FA, in the cases when two bands are overlapped, was made by a program kindly provided by Dr. A.O. Doroshenko from the Karazin University, Kharkiv. The program uses the iteration non-linear least-square method based on Fletcher-Powell algorithm. The shapes of individual emission bands were approximated by log-normal function [21] which accounts for the asymmetry of spectral bands.

Quantum-chemical calculations of the dipole moments were performed using AM1 method [22] and the program MOPAC 6.0.

RESULTS AND DISCUSSION

Fig. 1 presents the fluorescence spectra of FA in a range of low-polar solvents. In all cases the presence of the N* form emitting at higher energies (shorter wavelengths) is found. Its relative magnitude compared to T* band exhibits a strong solvent-dependent variation, and this variation is coupled with the spectral positions of the bands. These properties can be easily correlated with the solvent polarity, expressed by empirical polarity scale E_T^N [23] and by Lippert equation [24] (see Table 1). With the increase of polarity, we observe a gradual transformation of fluorescence spectra from a highly emissive band, at lower energy (longer wavelengths), to the other, at higher energy (shorter wavelengths). This transformation is accompanied by shifts of both bands to longer wavelengths (Fig. 1). Thus, in the range of low-polar solvents, none of which can be a proton donor in intermolecular H-bonding and most of which cannot be proton acceptors, we observe the two forms in fluorescence emission. These forms can be assigned to emissions from the N* and T* excited states, the latter originating from ESIPT reaction N* ↔ T* (Scheme 1).

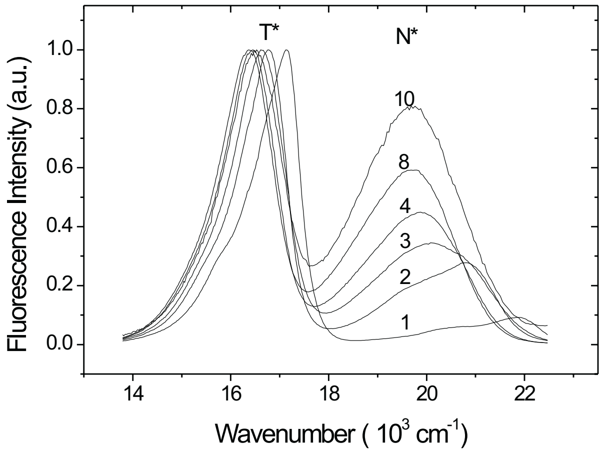


Figure 1. Fluorescence emission spectra of probe FA in hexane (1), CCl_4 (2), dibutyl ether (3), 1,4-dimethylbenzene (4), toluene (8) and diethyl ether (10). The spectra are normalized at T* maxima. For convenience, here and thereafter the solvents are numbered in sequence according to solvent polarity index E_T^N presented in Table 1.

In all studied solvents the excitation spectra obtained at N* and T* emission bands were identical and matched closely the absorption spectra, which is the direct proof for their origination as a result of ESIPT reaction. This corresponds to earlier results on other similar chromophores – 3-hydroxyflavone [9] and its derivatives [12–14], the two N* and T* bands, in which they were well characterized. For FA in hexane (1), which is the solvent of lowest polarity, we observe that the long-wavelength emission band, belonging to T* form, predominates with only a small contribution of short-wavelength N* component. With the increase of polarity the short-wavelength N* band increases in relative magnitude in a very regular way.

The solvent-dependent changes, if they are revealed in fluorescence and involve the ground state interactions, must be reflected in absorption spectra. This is actually observed (Table 1). The general effect is clear: with the increase of polarity, the absorption spectra shift to longer wavelengths, exhibiting positive solvatochromism (Fig. 2, line 1). This is typical for chromophores with the increase of the dipole moment on electronic excitation [23]. Meantime, there is a range of solvents, in which the positions of absorption spectra deviate systematically from this regularity and are located at shorter wavelengths (Fig. 2, line 2). Common for these solvents is the presence of oxygen in their structure, which allows them to be the proton acceptor in H-bond with hydroxyl group of FA. If it is so, then we can explain the shorter wavelength position of absorption bands by an additional stabilization via intermolecular H-bonding, which may be in the ground state stronger than the intramolecular H-bonding. The latter closes the 5-membered ring in the 3-HC structure, and due to this fact cannot attain the optimal geometry. In the excited state, due to redistribution of the electronic density, the intramolecular H-bonds have to become stronger, and if they are formed, these solvents start to fit the general regularity dependent on their polarity. This can explain the difference in behavior of absorption and fluorescence spectra. Fig. 3 illustrates the comparison of absorption and fluorescence spectra for two solvents that are very close in polarity – benzene (does not contain oxygen) and diethyl ether (containing oxygen). While the difference in band positions is essential in absorption spectra, it is very small for both fluorescence emission bands. Thus, we can conclude that the solute-solvent H-bonding effects are present in absorption spectra, but not in fluorescence spectra, and that reorganization of intermolecular H-bond into intramolecular one may occur for the excited-state species.

It is clearly observed that the magnitudes of solvent-dependent shifts in fluorescence spectra are much stronger for the N* band than for the T* band (Fig. 1). This is also in line with the results reported in studies of other 3-hydroxyflavone derivatives [9,10]. As a characteristic parameter of these shifts, we chose the difference in positions of these maxima on the wavenumber scale, $\nu_{N^*} - \nu_{T^*}$. The correlation between this parameter and the polarity scale is presented in Fig. 4, A.

Since the solvent-dependent spectral shifts are accompanied by very strong redistribution of intensity between N* and T* emission bands, we decided to investigate the correlation between these two effects in more detail. In the range of studied low-polar solvents, the intensity ratios at the band maxima I_{N^*}/I_{T^*} display a very good correlation with polarity and cross-correlation with $\nu_{N*} - \nu_{T*}$. The latter dependence can be almost ideally approximated by an exponential function, that can be linearized in coordinates $\log(I_{N*}/I_{T*})$ *vs.* $\nu_{N*} - \nu_{T*}$ (Fig. 4, B). These results suggest the use of FA as a probe for solvents of the low-polar range. For this purpose both $\log(I_{N*}/I_{T*})$ and $\nu_{N*} - \nu_{T*}$ can be equally applied. In the range of lowest polarities the spectral shifts are most precisely and easily detected. At higher polarities these shifts become smaller, and the most dramatic solvent-dependent changes are found for the ratio of intensities of the two bands (see Fig. 1).

Table 1. The fluorescence spectroscopic properties of probe FA in different solvents of low polarity.

No	Solvent	E_T^N	L	λ_{abs}^{max} ($\times10^{-3}$ cm^{-1})	$\lambda_{max}^{N^*}$ ($\times10^{-3}$ cm^{-1})	$\lambda_{max}^{T^*}$ ($\times10^{-3}$ cm^{-1})	I_{N^*}/I_{T^*}	Q
1	Hexane	0.009	0	22.6	21.8	17.1	0.093	0.20
2	CCl_4	0.052	0.0110	22.2	20.8	16.8	0.277	0.31
3	Dibutyl ether	0.071	0.0993	22.8	20.1	16.6	0.341	0.29
4	1,4-Dimethylbenzene	0.074	0.0040	22.4	19.9	16.4	0.447	0.34
5	1,3-Dimethylbenzene	–	0.0134	22.6	19.9	16.4	0.463	0.27
6	1,2-Dimethylbenzene	–	0.0274	22.3	19.7	16.4	0.539	0.29
7	Tetralin	0.086	0.0311	22.2	19.6	16.3	0.529	0.27
8	Toluene	0.099	0.0350	22.3	19.6	16.4	0.592	0.26
9	Benzene	0.111	0.0026	23.3	19.6	16.3	0.708	0.27
10	Diethyl ether	0.117	0.1667	22.1	19.7	16.5	0.847	0.02
11	Thiophene	0.145	–	22.2	19.1	16.1	1.133	0.32
12	Dioxan	0.164	0.0202	22.8	19.5	16.3	1.094	0.29
13	1,2,4-Trichlorobenzene	0.17	–	21.8	19.1	16.1	1.247	0.52
14	Bromobenzene	0.182	0.1279	21.9	18.6	15.9	2.21	0.41
15	Tetrahydrofuran	0.207	0.2097	22.8	18.5	16.0	2.276	0.23
16	Ethyl acetate	0.228	0.1997	22.9	18.6	16.2	2.629	0.26
17	Trichloromethane	0.259	0.1459	21.9	18.3	16.0	4.246	0.46

E_T^N is an empirical polarity scale [23]. L is the Lippert parameter of solvents studied here. λ_{abs}^{max} is the absorption maximum, Q is the real quantum yield, $\lambda_{max}^{N^*}$ and $\lambda_{max}^{T^*}$ are the fluorescence emission maxima of normal (N*) and tautomer (T*) band respectively, and $I_{N}*/I_{T}*$ is the fluorescence intensity ratio of N* and T* bands. For solvents numbered between 10 and 17, $\lambda_{max}^{N^*}$, $\lambda_{max}^{T^*}$, and $I_{N}*/I_{T}*$ were obtained after deconvolution of emission spectra into two separate bands.

It is commonly observed that in the range of solvents with low polarities the role of specific solute-solvent interactions is much less important than that of the universal interactions, which are determined by nuclear and electronic polarizabilities of the solvent. The latter are described within the frame of Onsager cavity model by different functions that involve the continuous solvent parameters – dielectric constant ε and refraction index n [23,24]. The equations suggested by Lippert [24] and Bakhshiev [25] allow not only to follow the polarity functions of solvents, but also to evaluate the change of the chromophore dipole moment on electronic excitation.

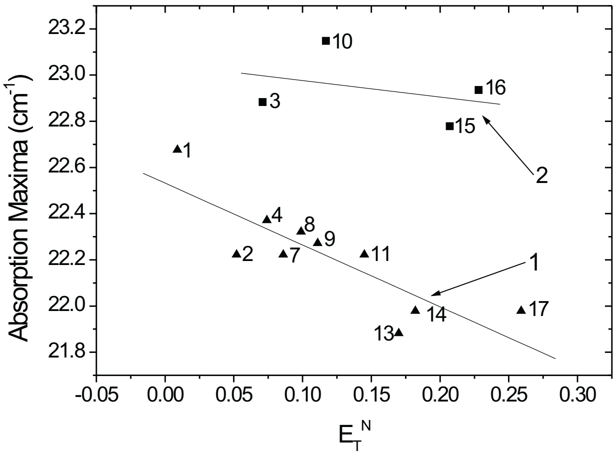


Figure 2. The solvent-dependent behavior of absorption spectra of FA in the range of low polar solvents. The positions of absorption maxima are plotted as a function of solvent polarity index E_T^N [23]. Curve 1 is the linear fit of triangle marks, which belong to solvents which do not contain oxygen atoms: hexane (1), CCl_4 (2), 1,4-dimethylbenzene (4), 1,3-dimethylbenzene (5), 1,2-dimethylbenzene (6), tetralin (7), toluene (8), benzene (9), thiophene (11), 1,2,4-trichlorobenzene (13), bromobenzene (14), trichloromethane (17). Curve 2 is the result of linear fitting of square marks, which are for oxygen-containing solvents: dibutyl ether (3), diethyl ether (10), tetrahydrofuran (15), ethyl acetate (16).

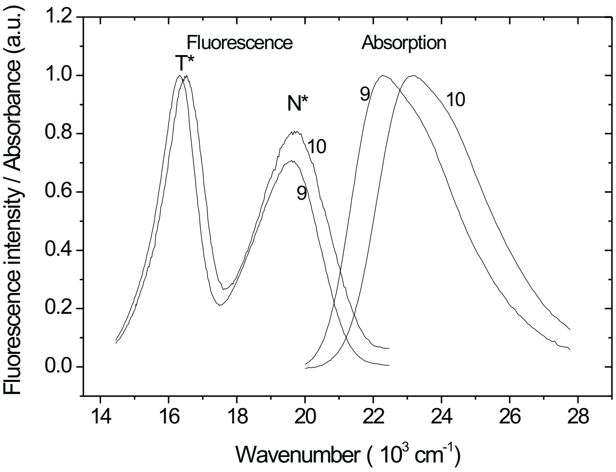


Figure 3. Comparison of absorption and fluorescence spectra for benzene (9) and diethyl ether (10).

The Lippert equation relates the spectral shifts to the solvent properties (dielectric constant, ε, and refraction index, n) as:

$$\tilde{\nu}_a - \tilde{\nu}_f = \frac{2}{hc}\cdot\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)\cdot\frac{(\mu_1 - \mu_0)^2}{a^3} + \text{const} \tag{1}$$

where $\tilde{\nu}_a$ is the position of absorption band maximum, $\tilde{\nu}_f$ the position of emission band maximum, h – the Planck constant, c – the velocity of light in vacuum, a – the Onsager radius (the radius of cavity occupied by solute molecule, in our case we used a = 4 Å). μ_0 and μ_1 are the dipole moments of the solute molecule in the ground and excited states.

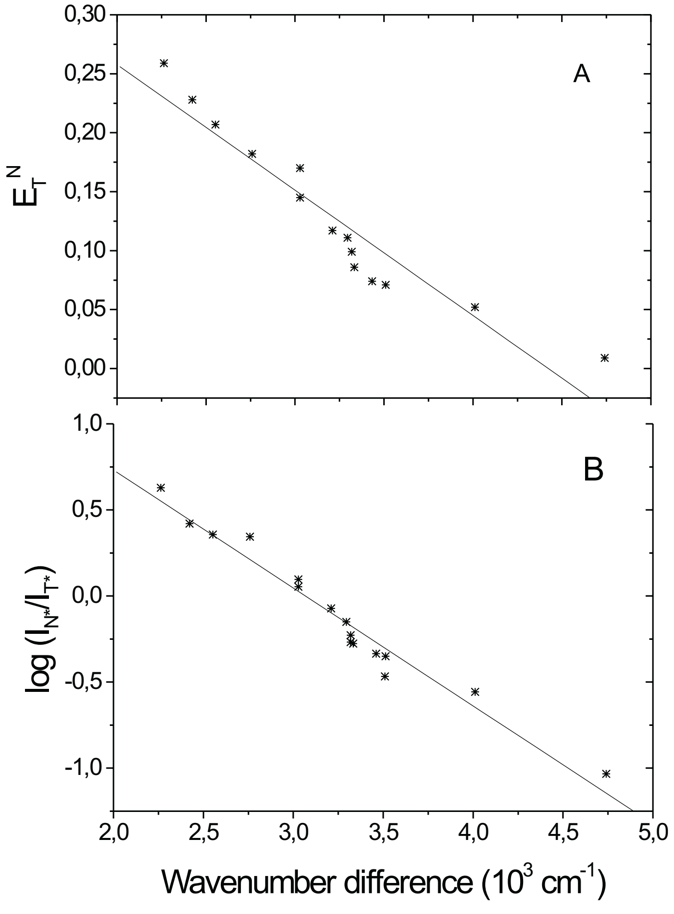


Figure 4. The correlation of solvent polarity index E_T^N (A) and $\log(I_{N^*}/I_{T^*})$ (B) with wavenumber difference $\nu_{N^*} - \nu_{T^*}$ for fluorescence spectra of FA

Lippert equation allowed us to evaluate the change of the FA molecule dipole moment upon excitation. This value, equal to scalar difference of dipole moments in the excited and ground states ($\Delta\mu = \mu_1 - \mu_0$), was estimated as 3.3 D. Fig. 5 represents the linear fit of the Stokes' shift *versus* Lippert parameter of solvent polarity.

The ground-state dipole moment μ_0 has been calculated using the semiempirical method AM1. We obtained $\mu_0 = 1.79$ D. Consequently, using the theoretical μ_0 and the $\Delta\mu$ one obtained in experiment, enabled us to estimate the FA dipole moment in the excited state – μ_1. The estimated value of this parameter is 5.09 D, which indicates a 2.8-fold increase of the dipole moment of FA molecule on excitation.

We also used Bakhshiev equations to determine the dipole moment change in the excited state. The Bakhshiev approach allowed to account for dipole orientation, induction and dispersive interactions between chromophore and the solvent and to make an estimate of the change in orientation of the dipole moment on electronic excitation.

$$\tilde{\nu}_a = C_1^a \frac{2n^2+1}{n^2+2} \cdot \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2-1}{n^2+2} \right) + C_1^a \cdot P_a \cdot \frac{n^2-1}{n^2+2} + \tilde{\nu}_a^0 \tag{2}$$

$$\tilde{\nu}_s = C_2 \frac{2n^2+1}{n^2+2} \cdot \frac{\varepsilon - 1}{\varepsilon + 2} + C_2 \cdot P_s \cdot \frac{n^2-1}{n^2+2} + \tilde{\nu}_s^0 \tag{3}$$

$$\Delta\tilde{\nu}_{af} = \Delta C_{af} \frac{2n^2+1}{n^2+2} \cdot \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2-1}{n^2+2} \right) + \Delta C_{af} \cdot P_{af} \cdot \frac{n^2-1}{n^2+2} + \tilde{\nu}_{af}^0 \tag{4}$$

$$\mu_1 = \sqrt{\mu_0^2 - C_2 \cdot hca^3} \quad (5); \qquad \Delta\mu_1 = \sqrt{0.5 \cdot \Delta C_{af} \cdot hca^3} \quad (6)$$

$$\mu_1 \cdot \cos\Theta = \mu_0 - \frac{C_1^a \cdot hca^3}{2\mu_0} \quad (7); \quad \cos\Theta = \frac{1}{2\mu_0\mu_1} \cdot \left[\left(\mu_0^2 + \mu_1^2 \right) - \frac{\Delta C_{af}}{2C_2} \cdot \left(\mu_0^2 + \mu_1^2 \right) \right] \quad (8)$$

Here $\tilde{\nu}_s$ is the half-sum of positions of absorption and emission maxima on wavenumber scale (in cm^{-1}), $\tilde{\nu}_{af}$ is the Stokes shift, $\tilde{\nu}_a - \tilde{\nu}_f$, $\Delta\mu$ is the scalar difference between μ_0 and μ_1, and Θ is the angle between dipole moment vectors of μ_0 and μ_1. C_a^1, P_a, C_2, P_s, ΔC_{af}, P_{af} are the coefficients that allow transition from (2), (3) and (4) to (5–7).

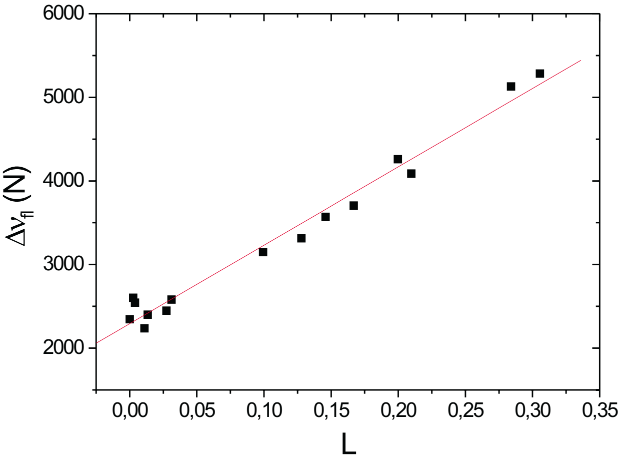


Figure 5. The dependence of Stokes shift on the Lippert parameter.

The analysis of experimental data, using Bakhshiev equations results in somewhat larger values of the dipole moments, than those obtained by Lippert equation (1), though the differences are not very significant. Thus, the scalar difference $\Delta\mu$ is 3.99 D. This allows us to obtain $\mu_1 = 5.78$ D (which is 3 times larger than in the ground state). The vector difference between dipole moments ($\Delta\vec{\mu}$) is 4.61 D, and the angle between absorbing and emitting dipole is 42°. Thus, we can prove that the dipole moment increases on electronic excitation approximately 3 times. Due to this reason, the ground-state and excited-state energies of FA are so sensitive to solvent polarities.

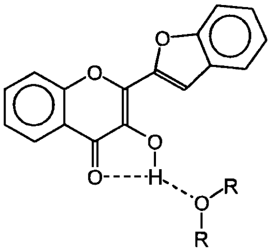
ESIPT commonly occurs in those molecules, whose proton donor acidity and proton acceptor basicity are enhanced upon electronic excitation. The donor and acceptor groups have to occupy proximate location, and commonly they should be connected by hydrogen bond(s). In this case, ESIPT is the ultra-rapid and solvent-independent process of proton tunneling between proximal groups connected by pre-existing H-bond. Such bond is usually stable, when it closes the six-member ring. In these cases, the PT emission is only observed in the steady-state spectra [10]. In 3-HC derivatives, the H-bond closes the five-member ring, which makes it unstable. But in particular conditions, in which the intramolecular H-bond is stabilized, the steady-state spectra demonstrate only the emission from the T* form. The direct or indirect measurements of reaction rates in this case provide the estimates of tens to hundreds of femtoseconds [3,4]. Thus, the appearance of the N* form in emission can be the result of a slower rate of practically irreversible $N^* \rightarrow T^*$ reaction, due to appearance of some solvent-dependent energy barrier or to the rapid establishment of $N^* \leftrightarrow T^*$ equilibrium with the subsequent emission from the two states. The distinction between these models can be made only based on careful picosecond time-resolved measurements, which for FA are presently lacking. But our steady-state studies provide some indirect evidence for excited-state equilibrium model. Since most of the studied solvents do not exhibit any specific interactions with FA, it is hard to conceive, what kinetic barriers they should produce, and why these barriers should correlate with solvent polarity. Meantime, the dielectric stabilization of the N* form, possessing higher dipole moment and interacting stronger with more polar dielectric medium, can be explained within the equilibrium model. Moreover, if we assume that the spectral shifts of the N* and T* bands display the solvent-dependent change of their excited-state energies and that the Boltzmann distribution of occupancies between the N* and T* states is established at times faster than the emission, then we can expect a logarithmic relationship between relative band intensities, I_{N*}/I_{T*}, and the bands separation, $\nu_{N*} - \nu_{T*}$. This is exactly observed in the experiment (Fig. 4, B).

The specific type of ESIPT reactions with the involvement of intermolecular H-bonding interactions is also known. It involves the formation of the bridge for proton transfer by protic solvent molecules or by formation of dimers [10]. This bridge or dimer can also be formed dynamically, and in this case the process can attain activational character and the rate can be retarded by several orders of magnitude. In these cases, the emission from the N* form can be observed at deficiency of the H-bond partners, forming the bridge and at very short observation times. This is not the present case, since all studied solvents are not able to form H-bonding bridges, and we did not observe any signs of association of FA molecules into dimers in any solvent.

Meantime, the excited-state equilibrium model is based on one condition, which is not apparent. The N* and T* states should be nearly degenerated (the energy gap between them should be small). This may occur because of strong CT character of the solvent-stabilized N* state. The strong charge separation in this state is supported by performed above estimations of the dipole moment, but it is not easy to understand, how this CT state can be stabilized by very small, mostly induced-dipole and dispersive interactions with low-polar solvents.

One important property of 3-HC – 3-HF systems is really unique. Instead of inducing larger charge separation by forming an electric dipole, ESIPT reaction occurs in the direction of reducing the charge-separation and compensation of initially large N*-state dipole. This property in the case of FA can be easily recognized by substantially smaller solvent-dependent shifts of fluorescence spectra of T* form in comparison to N* form (Fig. 1). Therefore, a dielectric stabilization of the N* form can occur as a result of which the emission from this form becomes possible. In the parent 3-HF in all cases when the interactions with the solvent are minimized (for instance, in Ar matrices [3,4]) the ESIPT reaction is ultra-rapid, and the emission of N* form is never observed. The presence of the N* form in emission in polar solvents was primarily explained by H-bonding perturbation [17,18]. Introduction of dialkylamino group into phenyl ring of 3-HF increased substantially the dipole moment and the CT character of the N* state. This allowed to observe the presence of the N* form in emission in solvents of medium and even low polarity [12,13]. The results of the present studies provide a clear evidence that the appearance of the N* form in emission cannot be related to intermolecular H-bonding effects.

It remains to be conceived, how the solvents effects arising from the H-bond acceptor ability can be observed in the shifts of absorption spectra, but not in redistribution of intensities between the N* and T* forms in emission. One of the possibilities to explain this fact may be the following: The weak intermolecular H-bond is formed in the ground state, but its formation does not result in the complete break of intramolecular bond, which can be depicted by the scheme presented below.



This scheme is similar to that presented earlier [26] to explain the behavior of 3-HF derivatives in H-bonding solvents. Similar to 3-HF in our case, the connected by intramolecular H-bond five-member ring can be formed with correct for ESIPT configuration of 3-OH group. If this case is realized, the intermolecular bond will be broken in the excited state, and the ESIPT reaction will normally occur. This is expected to happen, because the proton has to make a choice between binding to chromone carbonyl oxygen with the charge –0.348e and to oxygen atom of acetone or ether with the charges –0.292e and –0.276e correspondingly. It is natural that the proton will move along intramolecular pathway to carbonyl oxygen. If intramolecular H-bond is broken in the ground state with the change of configuration of the OH group, there should be a certain probability of proton transfer to the solvent molecule, which we do not observe.

In conclusion, it has to be noted that the values of fluorescence quantum yield of FA presented in Table 1 are relatively high (0.20–0.52) in all the solvents studied, except in diethyl ether (0.02). Together with relatively high molar coefficient of extinction (44800 ml·mol^{-1}·cm^{-1} in hexane [15]), the high quantum yield provides a promising possibility of routine work with FA in the nanomolar concentration range. This suggests the using FA as a very sensitive molecular sensor for solvent polarities in the low-polar range.

REFERENCES

1. Northrop D.B., *Acc. Chem. Res.*, **34**, 790 (2001).
2. Demchenko A.P., *Biochim. Biophys. Acta*, **1209**, 149 (1994).
3. Schwartz B.J., Pateanu L.A. and Harris C.B., *J. Phys. Chem.*, **96**, 3591 (1992).
4. Ameer-Beg S., Ormson S.M., Brown R.G., Matousek P., Towrie M., Nibbering E.T.J., Foggi P. and Neuwahl F.V.R., *J. Phys. Chem. A*, **105**, 3709 (2001).
5. Kasha M., *J. Chem. Soc. Farad. Trans. 2*, **82**, 2379 (1986).
6. Chou P.T., McMorrow T.J.A. and Kasha M., *J. Phys. Chem.*, **88**, 4596 (1984).
7. Roshal A.D., Grigorovich A.V., Doroshenko A.O., Pivovarenko V.G. and Demchenko A.P., *J. Phys. Chem. A,* **102**, 5907 (1998).
8. Rochal A.D., Grigorovich A.V., Doroshenko A.O., Pivovarenko V.G. and Demchenko A.P., *J. Photochem. Photobiol. A. Chem.*, **127**, 89 (1999).
9. Sengupta P.K. and Kasha M., *Chem. Phys. Lett.*, **68**, 382 (1979).
10. Formosinho S.J. and Arnaut L.G., *J. Photochem. Photobiol. A: Chem.*, **75**, 21 (1993).

11. Demchenko A.P., Klymchenko A.S., Pivovarenko V.G. and Ercelen S., in Fluorescence Spectroscopy, Imaging and Probes – New Tools in Chemical, Physical and Life Sciences (Kraayenhof R., Visser A.J.W.G., Gerritsen H.C., eds.) Springer Series on Fluorescence Methods and Applications, Vol. 2, Springer-Verlag, Heidelberg, Germany, 2002.
12. Swinney T.C. and Kelley D.F., *J. Chem. Phys*., **99**, 211 (1993).
13. Chou P.-T., Martinez M.L. and Clements J.H., *J. Phys. Chem*., **97**, 2618 (1993).
14. Ormson S.M., Brown R.G., Volmer F. and Rettig J., *J. Photochem. Photobiol. A: Chem*., **81** 65 (1994).
15. Klymchenko A.S., Ozturk T., Pivovarenko V.G. and Demchenko A.P., *Tetrahedron Lett*., **42** 7967 (2001).
16. Klymchenko A.S., Ozturk T., Pivovarenko V.G. and Demchenko A.P., *Can. J. Chem*., **79,** 358 (2001).
17. McMorrow D. and Kasha M., *J. Am. Chem. Soc*., **105**, 5133 (1983).
18. McMorrow D. and Kasha M., *J. Phys. Chem*., **88**, 2235 (1984).
19. Parker C.A. Photoluminescence of Solutions, Elsevier, Amsterdam, 1968.
20. Demas J.N. and Crosby G.A., *J. Phys. Chem*., **75**, 991 (1971).
21. Siano D.B. and Metzler D.E., *J. Chem. Phys*., **51**, 1856 (1969).
22. Stewart J.J.P*., J. Comp. Chem*., **10**, 209 (1989).
23. Reichardt C., *Chem. Rev*., **94**, 2319 (1994).
24. Liptay W., *Angew. Chem. Int. Ed*., **8**, 177 (1969).
25. Bakhshiev N.G., Spectroscopy of Intermolecular Interactions, Nauka, Leningrad, 1972.
26. Strandjord A.J.G., Smith D.E. and Barbara P.F., *J. Phys. Chem*., **89**, 2362 (1985).