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Deactivation processes of the excited states of 3-hetarylmethylene-1(3H)-isobenzofuranones in solution: possibility of the formation of intermolecular hydrogen bonds

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Abstract

The absorption and fluorescence characteristics of some heterocyclic analogues of benzylidene phthalides in solvents of different polarity and hydrogen bonding ability are reported. It is shown that the replacement of the phenyl ring of benzylidene phthalides by heteroaromatic five-membered cycle does not have a remarkable influence on the photophysical properties. The observed dependence of the fluorescence Franck–Condon transition energies and the fluorescence quantum yields of the compounds with the amino substituted in the phthaloyl fragment on the ET(30) constants of the solvents indicates that the nature of the emitting state in protic and non-protic solvents is different, probably owing to the formation of intermolecular hydrogen bonds in the excited state between the substance and the protic solvent.

Keywords: Heterocycles; Electronic spectra; Intermolecular hydrogen bonds; 3-Hetarylmethylene-1(3H)-isobenzofuranones

1. Introduction

The derivatives of 3-phenylmethylene-1(3H)-isobenzofuranone (benzylidene-phthalide, BPH) are organic luminophores with high photostability and fluorescence quantum yield in solution [1]. A transition localized on the *trans*-stilbene fragment is observed in the absorption spectra of benzylidene-phthalide and its derivatives substituted in the p-position of the phenyl ring. The presence of an amino group in the phthaloyl fragment of benzylidene-phthalides, however, leads to significant changes in the shape and position of the absorption bands of the benzylidene-phthalides [2].

The aim of the present study is to follow the effect of the replacement of the phenyl ring with a heteroaromatic five-membered cycle in benzylidene-phthalides and 5-amino-benzylidene-phthalides on the photophysical characteristics of this class of organic compounds.

The compounds investigated are a new group of 3-arylmethylene-1(3H)-isobenzofuranones in which the aryl substituent is pyrrole, furane, thiophene or indole (Table 1). They could have interesting applications because their main fragment diarylethylene, containing a heterocycle, has a potential biological activity, connected with its molecular geometry [3,4].

2. Experimental details

Table 1 shows the structures of the investigated compounds and the corresponding substituents. Compounds **1–5** and **7** were newly synthesized [5]; the synthesis of compound **6** is described in [6].

The compounds with no substituent in the phthaloyl fragment were synthesized according to [6] on heating a mixture of phthalic anhydride and the corresponding hetaryl-acetic acid in the presence of dry potassium acetate. The compounds in which Y ≡ NH_2 were obtained on reduction of 6-nitro-(2-hetarylidene)-phthalides, synthesized according to [7], with $SnCl_2$ in acetic acid medium under bubbling of dry HCl. All compounds were recrystallized until a constant melting point was obtained. They were characterized by elemental analysis, NMR, IR, absorption and fluorescence spectra. The absorption spectra were recorded on a SPECORD UV–visible spectrometer (Carl Zeiss, Jena). The corrected fluorescence spectra were recorded on a Perkin Elmer MPF 44 spectrofluorimeter. The fluorescence quantum yields Q_f were meas-

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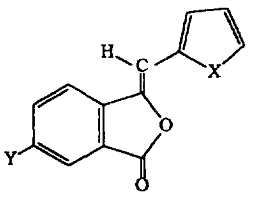
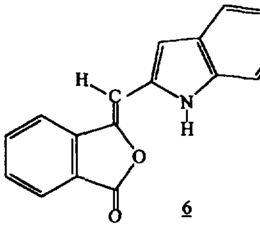
Table 1
Compounds investigated

Number	X	Y
1	S	H
2	S	NH_2
3	O	$HNCOCH_3$
4	O	NH_2
5	NH	NH_2

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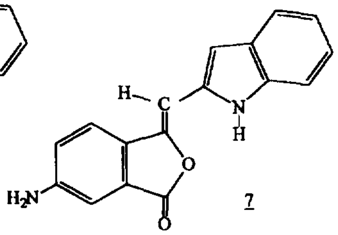
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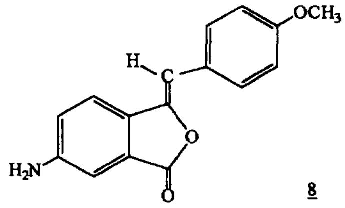
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ured relative to 3-*p*-methoxyphenylmethylene-1(3H)-isobenzofuranone ($Q_f = 0.12$ in ethanol) [1]. The solvents used were of fluorescence grade. The natural lifetimes were measured on a nanosecond spectrofluorimeter PRA 2000 at room temperature.

3. Results and discussion

3.1. Absorption spectra

All the investigated heterocyclic analogues of benzylidene-phthalide (HAB), described in Table 1, have two absorption bands in ethanol at room temperature in the region 33 000–20 000 cm^{-1}. The shape of their absorption spectra is practically identical with that of the corresponding benzylidene phthalides; a slight bathochromic shift for the HAB is observed. The longest wavelength band of HAB has maxima between 27 000 and 24 000 cm^{-1}, the molar absorptivity is 20 000–25 000. The maxima of the second band lie between 31 000 and 29 000 cm^{-1} and their molar absorptivity is 14 000–18 000 (Fig. 1, Table 2).

The bands in the absorption spectra of the compound **1** unsubstituted in the phthaloyl fragment (X ≡ S, Y ≡ H) (Table 1, Fig. 1) in ethanol were identified on the basis of comparison with the spectra of benzylidene-phthalide, as well as with literature data for the spectrum of the heterocyclic analogue of stilbene, 2-styryl-thiophene [8,9]. The longest wavelength absorption band with maximum at 27 550 cm^{-1} (Fig. 1), similar to BPH [1], could be assigned to an S_0–S_1 $\pi\pi^*$ transition, delocalized on the whole molecule. The position and the shape of the second band which has a clearly expressed vibronic structure is identical with the longest wavelength S_1 $\pi\pi^*$ absorption transition of *trans*-2-styryl-thiophene [8,9]. Therefore it could be concluded that the second absorption band in the spectrum of compound **1**, similar to BPH, is localized on its *trans*-2-styryl-thiophene fragment.

In the absorption spectrum of compound **3** (X ≡ O, Y ≡ $HNCOCH_3$ with $\sigma_p = 0$) the band with maxima in the region 31 250–29 400 cm^{-1} also has a vibronic structure; its shape and position coincide with those of the longest wavelength absorption maximum of *trans*–2-styryl-furane described in [10].

The HAB compounds with amino substituted in the phthaloyl fragment (compounds **2**, **4**, **5** in Table 1) have two absorption bands in ethanol with maxima in the region 31 200–29 400 cm^{-1} and 27 000–25 600 cm^{-1} respectively (Table 2). Their longest wavelength absorption transition is shifted bathochromically by approximately 1000 cm^{-1} relative to that of the parent compound **1** (Y ≡ H). No transition localized on the *trans*-2-styryl-heteroaromatic fragment is observed in their absorption spectra, as in the case of amino-benzylidene-phthalides [2], which testifies to the strong influence of the substituent in the phthaloyl fragment on the electron delocalization (Fig. 2, Table 2).

The absorption spectrum in ethanol of compound **6** (X ≡ NH, Y ≡ H), which is a longer conjugated system as a result of replacing pyrrole with indole, is similar to that of compound **1**; its two absorption maxima are shifted bathochromically relative to the corresponding maxima of compound **1** by 1200 and 2000 cm^{-1} respectively. An amino group in the phthaloyl fragment (compound **7**) also leads to a decrease

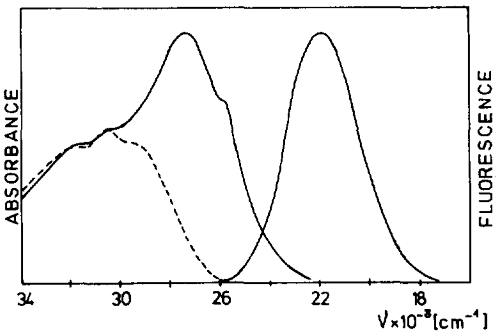

Fig. 1. Absorption and fluorescence spectra of compound 1 in ethanol at 293 K; – – –, absorption spectrum of 2-styryl-thiophene in ethanol according to [9].

in the energy of the S_0–S_1 transition by approximately 1000 cm^{-1} (Table 2).

The heteroaryles thiophene, furane and pyrrole are electron-donating systems with an average value of σ_a^+ constants of −0.8, −0.9 and −1.2 respectively [11]. No distinct dependence of the position of the S_0–S_1 transition on the nature of the heteroaromatic cycle is observed in the frames of the investigated compounds (Table 2). At the same time, however, the replacement of the phenyl group with a heterocycle leads to a bathochromic shift of the longest wavelength absorption maxima of the heteroanalogues relative to those of benzylidene-phthalides, unsubstituted in the phenyl ring, by approximately 2000 cm^{-1} [1,2].

Increasing the polarity and proton-donating ability of the solvent (passing from hexane, through acetonitrile to ethanol) does not exert a substantial influence on the position and shape of the absorption bands in the spectra of HAB. Only a slight bathochromic shift of the absorption maxima of less than 300 cm^{-1} is observed (Table 2).

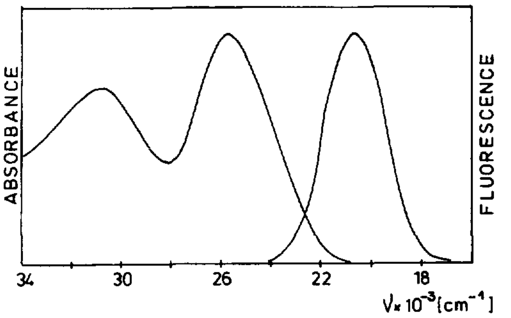

Fig. 2. Absorption and fluorescence spectra of compound **2** in ethanol at 293 K.

3.2. Fluorescence spectra

The fluorescence characteristics of HAB in hexane, acetonitrile and ethanol are given in Table 2. The corrected excitation spectra are identical with the absorption spectra.

All HAB, except compound **1**, fluoresce in hexane in the region 20 000–24 000 cm^{-1}. In ethanol, where compound **1**

Table 2

Experimental spectral characteristics of the investigated compounds; the numbering corresponds to that given in Table 1; the frequencies ν of the maxima are given in cm^{-1}; ϵ in 10^4 l mol^{-1} cm^{-1}; Q_f is the fluorescence quantum yield; / very pure solubility; — no fluorescence observed

Number	n-Hexane				Acetonitrile		
	ν^A	ϵ	ν^F	Q_f	ν^A	ν^F	Q_f
1	31250	11000			31060		
	27780	14100	—	—	27930	22260	0.003
2	30960	13760			30930		
	25970	17800	22520	0.003	25970	22200	0.16
3	30770	12430			30770		
	26670	14600	22550	0.001	26670	21520	0.05
4	30770	12300			30670		
	26530	16000	22360	0.003	26280	21770	0.13
5	30770	12080			30670		
	25970	16080	23970	0.004	26180	20530	0.07
6	29850	/			29850		
	26320	/	21000	/	25640	19880	0.28
7	29760	/			29760		
	25000	/	20800	/	24750	19900	0.40

Number	Ethanol			
	ν^A	ϵ	ν^F	Q_f
1	30680	14300		
	27550	20300	21940	0.012
2	30660	15200		
	25810	21000	20720	0.39
3	30490	14800		
	26470	20500	21490	0.08
4	30300	15800		
	26180	21200	20400	0.37
5	30300	15600		
	25890	21000	19760	0.15
6	29500	16320		
	25390	23030	19320	0.35
7	29400	17930		
	24350	24230	19190	0.55

Table 3
Fluorescence characteristics of the investigated compounds; the numbering corresponds to that given in Table 1; ν^F is the energy of the fluorescence maximum in cm^{-1}; Q_f is the fluorescence quantum yield

Solvent	1		2		3		4		5		6		7		8	
	ν^F	Q_f	ν^F	Q_f	ν^F	Q_f	ν^F	Q_f	ν^F	Q_f	ν^F	Q_f	ν^F	Q_f	ν^F	Q_f
1 *n*-Hexane	—	—	22520	0.003	22550	0.001	22360	0.003	23970	0.004	21000	/	20800	/	/	/
2 Diethylether	—	—	22470	0.12	21730	0.004	22000	0.08	22260	0.05	20820	0.28	20680	0.40	22560	0.11
3 Ethylacetate	22500	0.001	22390	0.13	21960	0.01	22100	0.08	21790	0.05	20540	0.45	20520	0.56	22470	0.20
4 Acetone	22240	0.002	22270	0.14	21540	0.02	21830	0.13	20810	0.05	19830	0.37	20370	0.40	22420	0.21
5 Acetonitrile	22260	0.003	22200	0.16	21520	0.05	21770	0.13	20530	0.07	19880	0.28	19900	0.40	22210	0.38
6 2-Butanol	21340	0.014	20850	0.34	21550	0.07	20610	0.21	19800	0.18	19690	0.24	19200	0.43	21060	0.44
7 2-Propanol	22390	0.014	20830	0.36	21510	0.08	20630	0.30	19940	0.18	19350	0.31	19280	0.57	20780	0.40
8 1-Propanol	21740	0.012	20850	0.40	21510	0.08	20630	0.40	20070	0.19	19250	0.32	19250	0.68	20720	0.46
9 Ethanol	21940	0.012	20720	0.39	21490	0.08	20400	0.37	19760	0.15	19320	0.35	19190	0.55	20600	0.34
10 Methanol	21850	0.014	20660	0.33	21430	0.09	20450	0.24	19840	0.13	19160	0.33	19050	0.47	20570	0.29
11 Water	21280	0.028	20100	0.02	20580	0.11	19880	0.08	18950	0.09	18080	/	18200	/	19800	0.10

also exhibits fluorescence, the emission is shifted bathochromically relative to that in hexane by 1500–2000 cm^{-1}; the fluorescence maxima are between 19 000 and 22 000 cm^{-1}.

The presence of an amino group in the phthaloyl fragment of HAB reduces the energy of the fluorescence Franck–Condon transition in ethanol by about 1000 cm^{-1} relative to the unsubstituted compound **1**. In hexane this effect is less pronounced — the difference between the position of the fluorescence maxima of compounds **3** and **4** is approximately 200 cm^{-1}.

The nature of the heteroatom in the five-membered cycle has a slight influence on the position of the fluorescence maxima. The compound in which X ≡ S fluoresces at shortest wavelength, followed by the compounds in which X ≡ O and X ≡ N; the difference between the first and the last is 700 cm^{-1} (Table 2).

As for the case of benzylidene-phthalides [1,2], the fluorescence quantum yield of HAB is about two orders of magnitude higher in ethanol than in hexane (Table 2).

The energy of the lowest lying singlet nπ^* state in aromatic aldehydes and ketones is between 26 000 and 30 000 cm^{-1} [12] and practically coincides with that of the longest wavelength absorption transition of the investigated HAB (Table 2). Hence their low fluorescence quantum yield in non-polar solvents could be explained by strong non-radiative deactivation of the fluorescent S_1 ($\pi\pi^*$) state through the singlet nπ^* level, and the increase in the Q_f value in polar solvents is due most probably to the greater energy difference between the lowest lying singlet nπ^* and $\pi\pi^*$ states.

The singlet lifetimes of compounds **1** and **2**, 0.71 ns and 4.28 ns respectively, and the corresponding constants of radiative K_f and non-radiative K_{nf} transitions 0.014 ns^{-1} and 1.39 ns^{-1} for **1**, 0.09 ns^{-1} and 0.14 ns^{-1} for **2**, were calculated from the fluorescence decay curves in ethanol at 300 K. Similar to benzylidene-phthalides [1], the presence of an amino group in the phthaloyl fragment leads to a significant (around one order of magnitude) increase in K_f and respective decrease in K_{nf}, which correlates with the observed enhancement (40 times) of the fluorescence quantum yield of compound **2** (Y ≡ NH_2), relative to that of compound **1** (Y ≡ H).

No phosphorescence was observed at 77 K in ethanol. The increase in the fluorescence intensity in frozen matrix is not very significant, from 3 to 10 times, indicating that the intramolecular motions of great amplitude do not determine the value of the fluorescence quantum yield.

3.3. Effects of solvent on the fluorescence properties

The energy of the fluorescence Franck–Condon transitions of compounds **1** and **3** (non-substituted with an amino group

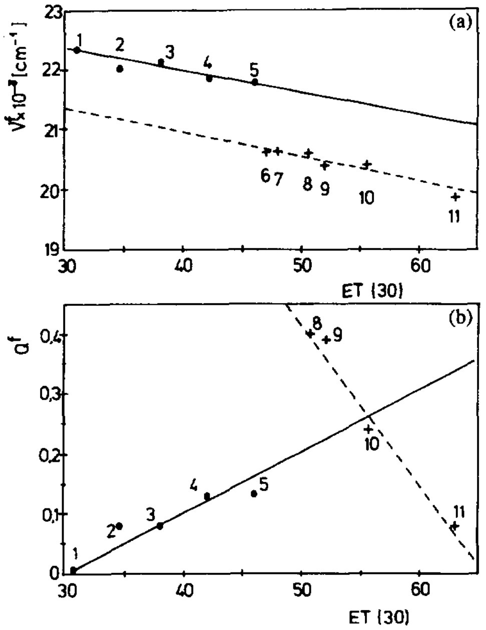

Fig. 3. (a) Energy of the fluorescence maxima of compound **4** vs. the solvent polarity parameter ET(30); (b) fluorescence quantum yield Q_f of compound **4** vs. the solvent polarity parameter ET(30). The numbers of the solvents correspond to those given in Table 3.

in the phthaloyl fragment) decreases monotonically with increasing polarity and proton-donating properties of the solvent (Table 3).

The fluorescence maxima of the HAB compounds with amino substituted in the phthaloyl fragment (compounds **2**, **4**, **5** and **7**) in aprotic solvents, like those of the compounds without an amino group, move monotonically to the red with increasing solvent polarity. A sharp drop in energy of the fluorescence Franck–Condon transition of about 1000 cm^{-1} is observed between acetonitrile and iso-butanol, despite their similar polarity. The results are analogous for the amino-benzylidene-phthalides (Table 3). No linear correlation between the fluorescence frequency of these compounds and the Δf constants for protic solvents is observed, while such a correlation is present for the aprotic solvents, including polar solvents. This fact shows that the significant red shift of the fluorescence maxima of amino-substituted HAB in protic solvents could not be due only to their higher polarity.

Two different linear correlations are obtained for the relation between the fluorescence frequency of the amino-substituted HAB and the ET(30) constants of the solvents [13], one for the protic and another for the aprotic solvents (Table 3, Fig. 3). The same dependence is observed also for the benzylidene-phthalides with amino substituted in the phthaloyl fragment (Table 3). The presence of two correlation lines shows that the nature of the emitting states in protic and aprotic solvents is different. Similar spectral behaviour is typical also for other organic compounds containing simultaneously amino and carbonyl groups, e.g. *p*-dimethylaminophenyl-indenone, 5-amino-indan-diones, dihydroquinolinones, 3- and 4-amino-phthalimides, and is explained in the literature [14–17] by the possible formation of intermolecular hydrogen bonds in the fluorescence excited state between the substance and the protic solvent.

The dependence of the fluorescence quantum yield of the amino-substituted HAB and benzylidene-phthalides on the ET(30) constants is similar to this, described in [15] and [16], and also supports the assumption of formation of intermolecular hydrogen bonds. In aprotic solvents with increasing ET(30) value, Q_f increases monotonically from hexane to acetonitrile. The opposite tendency is observed in alcohols, where on increasing ET(30) the Q_f value decreases. The fluorescence quantum yield is highest in *n*-propanol and diminishes in ethanol, methanol and water (Table 3, Fig. 3).

Intermolecular hydrogen bonds may be formed at room temperature between the nitrogen of the amino group or the oxygen of the carbonyl group in the molecule of HAB and the protic solvent, i.e. they could be of the type H–N···H–O or C=O···H–O. The quantum chemical PM3 calculations [18] show that in the first excited singlet state the negative charge is localized on the oxygen of the carbonyl group which increases its proton-accepting properties, while the nitrogen atom has a partial positive charge. The charges in the S_1 state of the nitrogen and oxygen atoms in compound **4** ($X \equiv O$, $Y \equiv NH_2$) are 0.1238 and −0.2418 and in compound **5** ($X \equiv NH$, $Y \equiv NH_2$) they are 0.1257 and −0.2944 respectively. That is why it could be assumed that in the case of the investigated HAB containing an amino group in the phthaloyl fragment, intermolecular hydrogen bonds of the type C=O···H–O are formed similar to the compounds described in [15] and [16]. The observed lowering of the Q_f in protic solvents with increasing ET(30) values is connected with the H–O vibrations of the solvent which play the role of an accepting mode in the radiationless deactivation of the excited states.

The dependence of the fluorescence frequency on the ET(30) value for the HAB without an amino group substituted in the phthaloyl fragment (compounds **1**, **3** and **6**, as well as BPH), is described by one linear correlation only. The Q_f/ET(30) dependence differs from that which is observed for compounds with $Y \equiv NH_2$ (Table 3). Consequently in this case no intermolecular hydrogen bonds are formed between the substance and the protic solvent.

4. Conclusions

On the basis of the described experimental data it could be concluded that replacing the phenyl ring of benzylidene-phthalides by a heteroaromatic five-membered cycle does not exert a remarkable influence on the photophysical properties. The presence of the amino group in the phthaloyl fragment, however, both in benzylidene-phthalides and HAB leads to significant changes in the charge distribution in their fluorescent S_1 ($\pi\pi^*$) state. The electronegativity of the oxygen atom in the carbonyl group increases strongly and this offers the opportunity for formation of intermolecular hydrogen bonds of the type C=O···H–O and for the presence of emitting states with a different nature in protic and aprotic solvents.

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