

Photophysical properties of some derivatives of 3-arylmethylene-1(3H)-isobenzofuranone Indication of intermolecular hydrogen-bond formation in the singlet excited state

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Received 25 May 1999; received in revised form 23 November 1999; accepted 25 November 1999

Abstract

The fluorescence behavior of some derivatives of 3-phenylmethylene-1(3H)-isobenzofuranone and 5-amino-3-phenylmethylene-1(3H)-isobenzofuranone in different media at room temperature and in frozen matrix at 77 K are reported. It is found, that in the cases of the amino substituted compounds at 293 K the dependencies of the fluorescence Franck–Condon transition energy and the fluorescence quantum yield on the ET(30) constant of the solvent, as well as the fluorescence decay curves, are strongly influenced by the proton donating ability of the solvent. These experimental results indicate formation of intermolecular hydrogen bonded solute–solvent complexes in the fluorescent excited state at room temperature in protic solvents. The effect of the substituents in the p-position of the phenyl ring in the investigated isobenzofuranones on the deactivation processes of their singlet excited state is discussed. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Electronic spectra; Fluorescence; Intermolecular hydrogen bonds; 3-arylmethylene-1(3H)-isobenzofuranones

1. Introduction

The radiationless deactivation of the excited states of organic luminophores as a result of specific intra- or intermolecular interactions (intramolecular charge transfer; formation of excimers and exciplexes; formation of hydrogen bonds) has been studied by many authors, see for instance [1–14]. Some of these investigations are devoted to the possibility for formation of intermolecular hydrogen bonds in excited state between the molecules of the substance and the protic solvents [6,8–14]. The conclusions are made on the basis of the analysis of the specific photophysical properties of the studied compounds in solvents of different polarity and proton donating ability.

In this paper are presented the results of our investigations on the deactivation processes of the excited states of some derivatives of 3-phenylmethylene-1(3H)-isobenzofuranone (benzylidene-phthalide, BPH) and 5-amino-3-phenylmethylene 1(3H)-isobenzofuranone (amino-benzylidene-phthalide, ABPH). These compounds are characterized by the pres-

ence of both a carbonyl group and an electron donating substituent in their conjugated system.

The conclusions for the possible formation of intermolecular hydrogen bonds in the singlet excited state of the investigated BPH and ABPH in protic solvents at room temperature are based on the interpretation of the dependencies of the energy of the fluorescence Franck–Condon transitions and the fluorescence quantum yield on the ET(30) constants of the solvents [15], as well as on the analysis of the fluorescence decay curves.

2. Experimental details

The investigated compounds are synthesized by a standard procedure [16]. They are recrystallized until a constant melting point was obtained and are characterized by elemental analysis, NMR, IR, absorption and fluorescence spectra. The absorption spectra are recorded on a SPECORD M40 (Carl Zeiss, Jena). The corrected fluorescence spectra are taken on a Perkin Elmer MPF44 spectrofluorimeter. The fluorescence quantum yields (Q_F) are measured relative to 3-p-methoxyphenylmethylene-1(3H)-isobenzofuranone

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($Q_F=0.12$) [17]. The fluorescence lifetimes are measured on a nanosecond spectrofluorimeter PRA 2000 at room temperature. The low temperature luminescence measurements are performed at 77 K using the standard phosphorescence accessory of MPF 44 equipment and quartz tube of 4 mm diameter. The solvents used are of fluorescence grade.

3. Results and discussion

In our previous papers [12,13] it was shown that 5-amino-indan-1,3-diones (AID) and their structural analogues 5-amino-3-hetarylmethylene-1(3H)-isobenzofuranones (heterocyclic analogues of benzylidene-phthalides, HAB) form intermolecular hydrogen bonds of the type C=O...H–O with protic solvents in excited state. It has been established that the probability for formation of hydrogen bonds via the carbonyl group depends decisively on the presence of a strong electron donating substituent in the phthaloyl fragment.

These investigations have been recently extended on two groups differently substituted 3-phenylmethylene-1(3H)-isobenzofuranones (benzylidenephthalides, BPH). The first group of the studied compounds includes BPH, substituted in the p-position of the phenyl ring with electron donating substituents, compounds N 1 and N 2 (Table 1). The second group is BPH containing an amino-group in position 5 of the phthaloyl fragment and simultaneously electron donating or electron withdrawing substituents in the p-position of the phenyl ring (compounds N 3–N 7, Table 1). In all these structures the phthaloyl fragment and the substituents in the p-position phenyl ring are in common conjugated system, which gives the possibility to follow the influence not only of the substituents in the phthaloyl fragment (as in the case of AID and HAB) but also of the substituents in the p-position of the phenyl ring on their photophysical properties.

Increasing the solvent polarity, passing from diethylether through acetonitrile to ethanol, smoothly shifts to the red

the longest wavelength absorption bands maximum of the studied compounds. The dependence between the energy of the longest wavelength absorption maxima and the Δf constant of the solvent could be described by one linear correlation only, regardless of whether the solvent is protic or non-protic. Hence, there are no indications for specific interaction between the substance and the proton-donating solvents in the ground state.

3.1. Effect of the amino group in the p-position of the phenyl ring on the photophysical properties

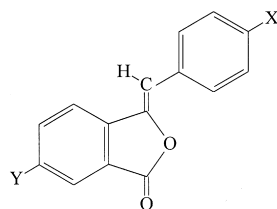
The energy of the fluorescence maximum of the *p*-OCH₃ substituted in the phenyl ring BPH (compound N 1, Table 1) decreases monotonously going from non-polar to polar solvents despite their proton donating properties (Table 2). Both the dependencies of the fluorescence transitions energy ν_F and the fluorescence quantum yield Q_F on the ET(30) constants of the solvent are on one line respectively. Consequently, having in mind the interpretation of the experimental data in [8–10] it could be concluded, that in the case of *p*-OCH₃, phenyl benzylidene-phthalide, there is no indication for the presence of emitting states with different nature in protic and non-protic solvents. Similar dependencies are observed also for the unsubstituted in the phenyl ring BPH.

The presence of an amino group in the p-position of the phenyl ring of BPH (compound N 2, Table 1) leads to significant changes in the interactions with protic solvents in the singlet excited state compared to BPH where X=H and OCH₃. Two different linear correlations are obtained for the dependencies $\nu_F/ET(30)$ and $Q_F/ET(30)$ in protic and non-protic solvents (Table 2). Consequently similar to AID and HAB [12,13] in the case of the amino-substituted in the phenyl ring BPH the nature of the emitting states in protic and non-protic solvents is different owing to the formation of intermolecular hydrogen bonds in the singlet excited state. The differences in the spectral behavior of *p*-methoxy- and *p*-amino substituted in the phenyl ring BPH could be explained by the significantly stronger electron donating properties of the amino group ($\sigma_p=-0.66$) in comparison to these of the methoxy group ($\sigma_p=-0.27$) [18]. As a result the partial negative charge on the carbonyl oxygen in the singlet excited state will be stronger in the case of *p*-NH₂ substituted BPH compared to the *p*-OCH₃-substituted one. As it was shown in [13] the negative charge value on the carbonyl oxygen in excited state is unambiguously connected with the probability for specific interactions with protic solvents via the carbonyl group which explains the absence of spectroscopic data for intermolecular hydrogen bonds formation in the case of compound N 1.

3.2. Effect of the amino group in the phthaloyl fragment on the photophysical properties

The other type of BPH in which a formation of intermolecular hydrogen bonds with protic solvents in the fluorescent

Table 1
Investigated 3-arylmethylene-1(3H)-isobenzofuranones



Number	X	Y
1	OCH ₃	H
2	NH ₂	H
3	N(CH ₃) ₂	NH ₂
4	CN	NH ₂
5	OCH ₃	NH ₂
6	Cl	NH ₂
7	NHCOCH ₃	NH ₂

Table 2

Fluorescence characteristics of the investigated compounds: ν_F is the energy of the fluorescence maximum in cm^{-1} ; Q_F is the fluorescence quantum yield; the numbers of the compounds correspond to these given in Table 1

N	Solvent	Compound N 1		Compound N 2		Compound N 3		Compound N 4		Compound N 5		Compound N 6		Compound N 7	
		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	Diethylether	23040	0.001	20580	0.23	22480	0.40	22480	0.031	22560	0.11	23410	0.12	23260	0.04
2	Ethylacetat	22800	0.008	19860	0.19	19200	0.37	21380	0.047	22470	0.20	21660	0.11	22540	0.023
3	Aceton	22100	0.01	25640	0.14	18620	0.26	20740	0.05	22420	0.21	22280	0.10	22060	0.02
4	Acetonitrile	21920	0.03	18250	0.08	17800	0.24	20600	0.062	22210	0.38	22080	0.08	21940	0.015
5	2-Butanol	22130	0.07	18260	0.18	18420	0.36	19910	0.17	21060	0.44	20700	0.20	20710	0.032
6	2-Propanol	21750	0.10	18240	0.16	18180	0.31	20160	0.16	20780	0.40	20620	0.18	20700	0.032
7	1-Propanol	21700	0.13	18190	0.12	17860	0.28	20070	0.14	20720	0.46	20640	0.18	20650	0.03
8	Ethanol	21770	0.14	18100	0.13	17600	0.22	19890	0.13	20600	0.34	20520	0.17	20580	0.028
9	Methanol	21770	0.14	18100	0.13	17600	0.22	19860	0.11	20570	0.29	20320	0.14	20400	0.02

excited state is found contains amino group in the phthaloyl fragment, ABPH. These compounds are structural analogues of 3- and 4-aminophthalimides [10], 5-aminoindan-diones [12] and 5-amino-3-hetarylmethylene-isobenzofuranones [13]. In the case of ABPH the substituents in the *p*-position of the phenyl ring are varied (Table 1). The experimental results indicate that independent of the nature of the substituent X in the phenyl ring of ABPH, electron donating ($\text{N}(\text{CH}_3)_2$ and OCH_3 — compounds N 3 and N 5, Table 1), or electron withdrawing (CN and Cl — compounds N 4 and N 6, Table 1), the linear correlations $\nu_F/\text{ET}(30)$ are different for protic and non-protic solvents (Table 2, Fig. 1). As it is already mentioned for the cases of the *p*-phenyl substituted BPH, see also [8–13], this spectral behavior is an evidence for formation of intermolecular hydrogen bonds in the singlet excited state. Hence, even the presence of strong electron withdrawing center in the molecule of ABPH, the cyano group in the *p*-position of the phenyl ring, does not lead to remarkable decreasing of the partial negative charge, localized on the carbonyl oxygen as a result of the presence of the amino group in the phthaloyl fragment and thus to diminishing the possibility for formation of complexes with protic solvents in excited state.

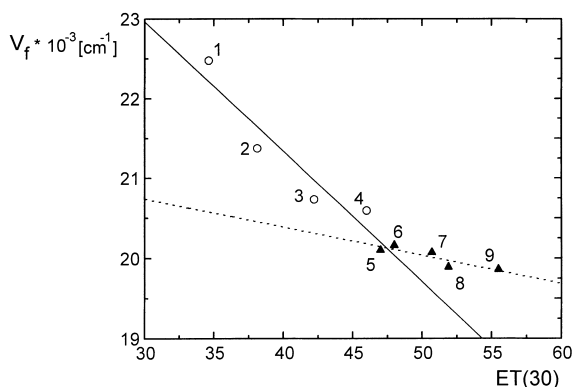


Fig. 1. Energy of the fluorescence maxima of compound 4 upon the solvent polarity parameter $\text{ET}(30)$. The numbers of the solvents correspond to these given in Table 2.

The different linear correlations $Q_F/\text{ET}(30)$ which are obtained in protic and non-protic solvents (Table 2, Fig. 2) also support the assumption for formation of intermolecular hydrogen bonds in the singlet excited state of the investigated BPH, containing amino group both in the phenyl ring and in the phthaloyl fragment.

The fact that the fluorescence quantum yield always decreases in protic solvents with increasing of $\text{ET}(30)$ constants shows, that the vibrations of the formed intermolecular hydrogen bonds of the type $\text{C}=\text{O} \dots \text{H}-\text{O}$ define a new possibility for radiationless deactivation of the singlet excited states of the studied amino-substituted compounds like in the cases described in [6,8,12,13].

The hypothesis for formation of intermolecular hydrogen bonds in excited state of the amino-substituted benzylidene-phthalides at room temperature is supported by the results obtained in frozen matrix at 77 K (Table 3). For compound N 1 which does not form hydrogen bonds with protic solvents in excited state there is practically coincidence of the fluorescence maxima in EtOH and methylcyclohexane (MCH) at 293 K, the corresponding values are 21770 and 21790 cm^{-1} . But as it is seen from the experimental data presented in Table 3 the difference between

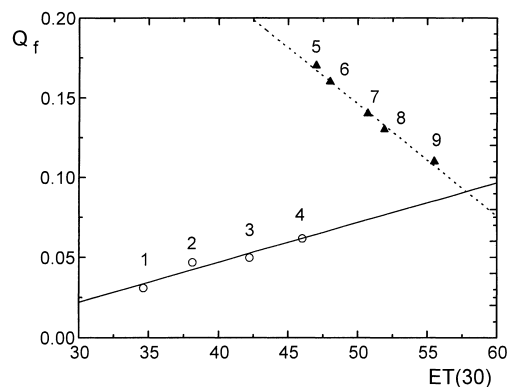


Fig. 2. Fluorescence quantum yield of compound 4 upon the solvent polarity parameter $\text{ET}(30)$. The numbers of the solvents correspond to these given in Table 2.

Table 3

Fluorescence maxima ν_F in cm^{-1} of compounds N 1, N 3 and N 4 in ethanol and methylcyclohexane at 293 and 77 K; the numbers of the compounds correspond to these given in Table 1

Compound N	293 K		77 K	
	ν_F (EtOH)	ν_F (MCH)	ν_F (EtOH)	ν_F (MCH)
1	21770	21790	23740	23700
3	17600	19460	20410	20430
4	19890	21500	21920	21960

the fluorescence maxima of compounds forming hydrogen bonds — for instance N 3 and N 4 in EtOH and MCH at 293 K is remarkable — is about 2000 cm^{-1} . Freezing the solutions shifts hypsochromically the fluorescence maxima of compound N 1 both in EtOH and MCH but keeps the difference between them practically the same as at room temperature. On the contrary, in frozen matrix at 77 K the difference between the fluorescence Franck–Condon transitions of compounds N 3 and N 4 strongly diminishes in comparison to 293 K and becomes less than 50 cm^{-1} , reaching the value for compound N 1 which does not form intermolecular hydrogen bonds (Table 3).

The experimental data in fixed matrix, mentioned above, indicate that the reorientation of the solvent's molecules has a significant influence on the possibility for formation of intermolecular hydrogen bonds in the singlet excited state of the studied compounds. Similar results in frozen solutions at 77 K have been obtained for 4- and 5-aminoindan-diones also [12].

In Table 4 are presented the experimental data for the fluorescence quantum yields, the fluorescence lifetimes τ and the calculated radiative K_r and non-radiative K_{nr} deactivation constants of compound N 4 in solvents of different polarity and proton donating ability. Both in the frames of the protic and non-protic solvents the K_{nr} have similar values. On the other hand in non-protic solvents the increasing of the solvent polarity (ethylacetat, acetone, acetonitrile) leads to a smooth enhancement of the radiative constant values. The opposite tendency is observed in the case of protic solvents

Table 4

Experimental values of fluorescence quantum yields Q_F and fluorescence lifetimes τ , as well as calculated from Q_F and τ constants of radiative K_r and nonradiative K_{nr} deactivation of compound N 4 (Table 1) in solvents of different polarity and proton donating ability

Solvent	Q_F	τ	K_r	K_{nr}
Ethylacetat	0.047	0.75	0.065	1.27
Acetone	0.05	0.54	0.093	1.76
Acetonitrile	0.062	0.51	0.12	1.84
2-Butanol	0.17	2.4	0.07	0.35
Ethanol	0.13	2.2	0.06	0.39
Methanol	0.11	2.67	0.04	0.33

(2-butanol, ethanol, methanol). The increasing of their polarity and proton donating ability causes diminishing of the radiative constant values and this effect on K_r could be attributed to the formation of intermolecular hydrogen bonds which leads to intensifying of the quenching processes.

4. Conclusions

The analysis of the photophysical characteristics of the investigated amino-substituted benzylidene-phthalides show that the character of the fluorescence emitting state strongly depends on the protic ability of the solvent. The presence of two different linear correlations $\nu_F/ET(30)$ for protic and non-protic solvents, as well as the decreasing of Q_F with increasing the proton donating ability of the solvents is referred to the presence of solute–solvent complexes as a result of formation of intermolecular hydrogen bonds in the fluorescence excited state. This conclusion is supported also by the data obtained in frozen matrix at 77 K. The experimental results indicate, that the nature of the electron-donating substituents in the p-position of the phenyl ring of the investigated structures are of decisive importance for the possibility for hydrogen bonds formation.

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