A New Class of Organic Luminophores With a Stilbene Chromophore: 3-Phenylmethylene-1(3 H)-Isobenzofuranones

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

A new class of luminophores with a stilbene chromophore, 3-phenylmethylene-1(3 H)-isobenzofuranones (BPH's), has been investigated. The fluorescence occurs in the region 26000 – 16000 cm^{-1}, the maximal quantum yield being about 0.6. As a result of substitution or higher polarity of the solvent the $\pi\pi^*$ state of the BPH's separates from the fluorescently inactive $n\pi^*$ state.

The $S_0 - S_2$ absorption transition of the BPH's results from an excitation which is practically localized in the stilbene fragment. The good linear correlation of the fluorescence and absorption maxima and O – O transitions in ethanol with the σ_p-Hammett constants has been used for an interpretation of the changes in the potential hyperfaces of S_0 and S_1 states.

1. Introduction

On the basis of comparative studies of a number of organic molecules with conjugated π-electrons it was shown [1] that the degree of electron delocalization in the lowest excited state can be used as a criterion for their fluorescence ability. The quantum chemical calculations of stilbene [2] show that upon excitation to the S_1 state the length of its central double bond increases, while that of the neighbouring single bonds decreases, and that this leads to a considerable smoothing of bond alternation. Stilbene easily undergoes photoisomerization [3] because of the weakening of the double bond in the S_1 state, and this makes the radiation processes less probable.

In this paper investigations on the luminescence properties of a new class of organic luminophores with a stilbene chromophore, namely 3-phenylmethylene-1(3 H)-isobenzofuranones (also denoted as benzylidenephthalides – BPH) are presented. To our knowledge the fluorescence properties of BPH have not been studied before. The absorption spectra of some substituted BPH [4, 5, 6], and PPP calculations of the absorption transitions [6] are known but their characteristics have not yet been discussed in detail.

In BPH's the central double bond of the stilbene skeleton is fixed to a five membered ring, Figure 1. For that reason one would expect them to be more efficient and photostable than the stilbene derivates widely used as optical brighteners [7]. For completeness of the study, also a more detailed analysis of their absorption spectra was performed.

2. Experimental

All compounds investigated, except $X = N(CH_3)_2$, were synthesized by a standard procedure [8] and repeatedly recrystallized untill a constant melting point was obtained; their purity was controlled by chromatography. The presented spectral characteristics for $X = N(CH_3)_2$ refer to the product of photoisomerization of the $N(CH_3)_2$ substituted 2-phenyl-1,3-indandione. According to [4] it undergoes a photochemical conversion to the corresponding BPH. The photoisomerization products of the X = H and $X = OCH_3$ substituted indandiones turned out

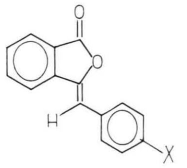

Fig. 1. 3-phenylmethylene-1(3H)-isobenzofuranones, denoted in the text as benzylidenephthalides (BPH). The substituents X are given in Table 1.

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to have identical spectral characteristics with those of the BPH synthesized by the standard method [8].

The corrected fluorescence and excitation spectra are recorded on a spectrofluorimeter Perkin Elmer MPF44 B. The absorbtion spectra are recorded on Specord M 40 (Carl Zeiss, Jena). The natural lifetime is measured on a nanosecond spectrofluorimeter PRA 2000. The solvents used are of fluorescence grade. The photostability is measured upon irradiation with a medium pressure Hg lamp Tungsram HGO 125 W.

3. Results and Discussion

3.1. Absorption, fluorescence and excitation spectra

The absorption and fluorescence characteristics of trans-BPH and seven of its derivatives are presented in Table 1 a, b. 3-aminophthalimid with fluorescence quantum yield $Q_f = 0.6$ in ethanol and $Q_f = 0.36$ in heptane [9] is used as a standard for evaluation of the Q_f's. Figure 2 shows the absorption and the corrected fluorescence spectra of 3 representative compounds of the series: $X = -NH_2$, $-H$ and $-CN$. The excitation spectra are identical with the corresponding absorption spectra in the region 26000 – 40000 cm^{-1}, but the difference in the shape of the absorption and fluorescence spectra is obvious (Figure 2). While the fluorescence spectra are symmetrical, without a fine structure, the absorption in the region 24000 – 36000 cm^{-1} seems to result from the overlapping of a couple of spectral transitions. For X=H the data from [6], as well as our PPP-SCF-CI calculations with a standard parametrization [10] assign the longest wavelength absorption maximum (29580 cm^{-1}) to $S_0 - S_1$. In the region 31500 – 36000 cm^{-1} it is overlapped by another band, corresponding to $S_0 - S_2$.

We deconvoluted the complex spectral profile in the region 24000 – 36000 cm^{-1}, assuming the longest wavelength absorption band to be symmetrical – Fig. 2, X=H, dashed line. This assumption

Table 1 a, b. Experimental spectral characteristics. The frequencies ν of the maxima are given in cm^{-1}; ε in 10^4 l · mol^{-1} · cm^{-1}; τ_r in nsec; k_r, k_{nr} in nsec^{-1}; /: no fluorescence observed; +: very poor solubility; –: no measurement.

Table 1 a

N°	X	Ethanol							
		ν^{Abs}	ε	ν^{Fl}	Q_f	$\Delta\nu^{St}$	τ_r	k_r	k_{nr}
1	$N(CH_3)_2$	25 320	–	17 540	–	7780	–	–	–
2	NH_2	25 860	3.11	18 180	0.54	7680	2.74	0.36	0.31
3	OH	27 840	2.42	20 830	0.25	7010	2.45	0.41	1.22
4	OCH_3	28 040	2.65	21 460	0.14	6580	2.41	0.42	2.56
5	CH_3	28 920	2.22	21 880	0.03	7040	2.76	0.36	12.6
6	H	29 580	2.18	23 420	0.002	6160	2.39	0.42	249.6
7	CN	29 160	2.64	21 280	0.12	7880	17.5	0.06	0.41
8	NO_2	28 260	1.23	21 050	0.12	7110	60.9	0.02	0.12

Table 1 b

N°	X	Heptane			Cyclohexane		1,4 Dioxan	
		ν^{Abs}	ν^{Fl}	Q_f	ν^{Abs}	ν^{Fl}	ν^{Abs}	ν^{Fl}
1	$N(CH_3)_2$	25 480	21 740	0.1	25 450	21 650	26 320	19 230
2	NH_2	26 880	22 670	0.01	26 740	22 520	26 880	20 000
3	OH	29 520	/	/	+	+	28 200	22 030
4	OCH_3	28 240	23 250	0.001	28 010	23 260	28 120	22 470
5	CH_3	29 240	22 730	0.001	28 990	22 570	29 080	21 980
6	H	29 760	/	/	29 760	/	29 600	23 250
7	CN	29 600	/	/	29 410	/	29 000	22 730
8	NO_2	28 440	24 960	0.001	28 330	/	28 160	22 620

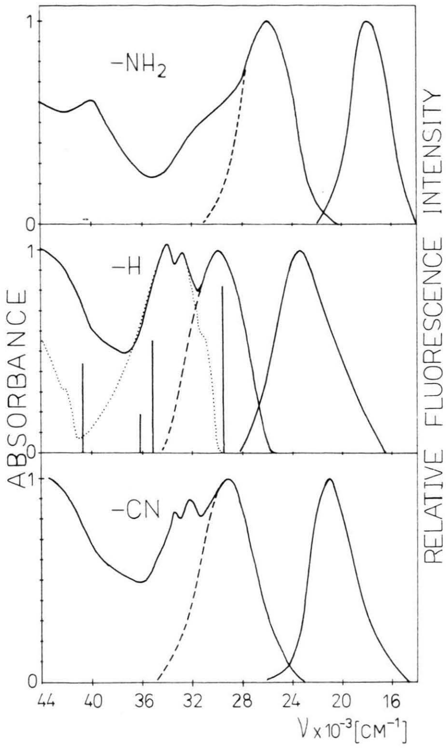

Fig. 2. Absorption and fluorescence spectra of some benzylidenephthalides ($X=NH_2$, H, CN) in ethanol at 20 °C. The vertical lines indicate calculated electron transitions ([7] and our results). Dashed line: S_0-S_1 absorption bands; dotted line: absorption spectra of unsubstitued stilbene in ethanol.

is reasonable, bacause the longwavelength slope of the S_0-S_1 absorption band possesses a mirror symmetry to the shortwavelength slope of the symmetrical fluorescence band. The radiation lifetimes τ_r in Table 1a are computed according to [11] from the absorptions curves, obtained as described above. The deconvoluted S_0-S_2 absorption band and the spectrum of the trans-stilbene, recorded at the same experimental conditions (Fig. 2, X=H, dotted line) are practically identical in position, intensity and vibronic structure.

Unlike the S_0-S_1 transition, the whole π-electronic conjugated system participates in the excitation of the molecule to the S_1 state.

The quantum chemical indices I [12] and A [13] reflect the uniformity in the electron distribution upon atoms and bonds. The calculated values for X=H indicate a higher electron delocalization in the $S_1(\pi\pi^*)$ state regarding S_0: $I(S_0)=0.0978$, $I(S_1)=0.0571$ and $A(S_0)=0.107$, $A(S_1)=0.165$. The molar extinction coefficients ε of the longest wavelength absorption maxima in ethanol are high (over 20000 l · mol^{-1} · cm^{-1}) except $X=NO_2$ (Table 1a). In the previous investigations of compounds 2, 4, 6, 8 in Table 1a very close ε-values are reported [4, 5, 6]. Most of the studied BPH's have a poor solubility in nonpolar solvents, so we have not presented data for ε in Table 1b. The high extinction coefficients in ethanol determine the short radiation lifetimes, computed from the absorption spectra according [11]. We calculated the reliable radiation lifetime $\tau_r' = 6.35$ nsec for X=OH, using its measured natural lifetime $\tau = 1.54$ nsec and $Q_f = 0.25$. The value of τ_r' is in fair agreement with $\tau_r = 2.45$ nsec, determined from its absorption spectrum, and hence we consider the k_r and k_{nr} values (Table 1a), calculated from τ_r and Q_f, to be reasonable for qualitative estimations.

3.2 *Energy levels and fluorescence ability of BPH's*

Because of the mirror symmetry between the S_0-S_1 absorption and fluorescence spectra, the position of the O–O $\pi\pi^*$ electron transitions $\nu^{00}(S_0-S_1)$ can be determined quite correctly. For X=H, $\nu^{00}(S_0-S_2) = 26500$ cm^{-1}. Taking into account that S_0-S_2 in BPH's is localized in the stilbene fragment, $\nu^{00}(S_0-S_2)$ should have the same value as $\nu^{00}(S_0-S_1)$ for stilbene itself. Then, according to [14], $\nu^{00}(S_0-S_2)$ (X = H) = 29730 cm^{-1}. The small energy difference $\Delta E = E^{00}_{S_2} - E^{00}_{S_1} = 0.4$ eV points to a strong internal conversion $S_2 \rightarrow S_1$.

The lowest $n\pi^*$ electron transition, due to the presence of C=O group in the BPH molecule, can not be observed experimentally because it is strongly overlapped by the intensive S_0-S_1 and S_1-S_2 $\pi\pi^*$ electron transitions. Having in mind that the position of the $n\pi^*$ transition, localized in the C=O group, is almost independent of the length of the conjugated system [15], the energy of the O–O $n\pi^*$ transition in the BPH's can be determined by analogy with aromatic aldehydes and ketones, where $\nu^{00}_{n\pi^*}$ is about 27000 cm^{-1} [16]. So one could expect a neglegible (about 0.06 eV) difference between the zero vibrational levels of the lowest $\pi\pi^*$ and $n\pi^*$ singlet electron states in the unsubstituted BPH. Moreover, the minima of the hypersurfaces $S_1(\pi\pi^*)$ and $S_1(n\pi^*)$ are displaced, because the excitation to $S_1(\pi\pi^*)$ causes a change in the geometry of the whole molecule (delocalized transition), while in the second case mainly the geometry of the C=O group is affected (localized transition). The insignificant energy difference and the displacement of the $S_1(\pi\pi^*)$ and $S_1(n\pi^*)$ minima means that they intersect near the minimum of the $S_1(\pi\pi^*)$ [17]. This will result in a strong nonradiative deactivation of the fluorescent $S_1(\pi\pi^*)$ state through the $S_1(n\pi^*)$ state. We consider this to be the reason for the extremely weak fluorescence from the unsubstituted BPH in nonpolar solvents. All factors, causing bathochromic shift of the $\pi\pi^*$ band, will increase the fluorescence quantum yield.

Upon freezing of the ethanol solutions, the fluorescence becomes more intensive and bathochromic shifts of the maxima ("frozen Frank Condon transitions") are observed. The PPP-SCF-CI calculations show that $\nu_{T_1}^{00}(\mathrm{H}) = 19640\ \mathrm{cm}^{-1}$, corresponding to a singlet-triplet splitting of about 2.44 eV.

3.3. *Effect of substituents*

The dependencies of the fluorescence and absorption maxima and the O−O transitions in ethanol upon the σ_P Hammett substituent constants are shown in Figure 3. Similar linear correlations are observed in dioxan also (see Table 1b and [18]). For all solvents used, both acceptors and donors cause a bathochromic shift of the spectral maxima

$$\Delta\nu^{\mathrm{Abs}} = \nu^{\mathrm{Abs}}(\mathrm{X}) - \nu^{\mathrm{Abs}}(\mathrm{H}) < 0,$$

$$\Delta\nu^{\mathrm{Fl}} = \nu^{\mathrm{Fl}}(\mathrm{X}) - \nu^{\mathrm{Fl}}(\mathrm{H}) < 0.$$

That phenomenon can be analysed using the approach proposed in [19]. From the experimental data, using (9) in [19], for donor substituents $\sigma_x < 0$, $\sigma_x = -1$ in ethanol,

$$\Delta\nu^{\mathrm{Abs}} = -5383\ \mathrm{cm}^{-1}$$
$$= (\varrho_{00} + \varkappa_1)\cdot(-1) = -6310 + 927,$$

while for acceptors $\sigma_x > 0$, $\sigma_x = 1$,

$$\Delta\nu^{\mathrm{Abs}} = -1442\ \mathrm{cm}^{-1}$$
$$= (\varrho_{00} + \varkappa_1)\cdot(+1) = -2270 + 828\,.$$

$\varkappa_0$ and $\varkappa_1$ are the steepnesses of the potential hypersurfaces S_0 and S_1, respectively; ϱ_{00} accounts for the influence of substitution on the $S_0 - S_1$ energy gap. The calculated values of $\varkappa_1$ and ϱ_{00} for $\sigma_x \lessgtr 0$ show that the bathochromic shifts of the absorption maxima for both donor and acceptor subbstituents are due to to the decrease of the $S_0 - S_1$ energy gap upon substitution ($\varrho_{00} < 0$), while the increase of the steepness of $S_1(\varkappa_1 > 0)$ weakly compensates this effect. Quantitatively, the influence of the donor substituents on the $S_0 - S_1$ O−O transition is stronger, $\varrho_{00}(\sigma_x < 0) = -6310\ \mathrm{cm}^{-1}$, $\varrho_{00}(\sigma_x > 0) = -2270\ \mathrm{cm}^{-1}$, and this causes a larger bathochromic shift. Probably, this difference is due to the presence of the electron accepting C=O group (A) in the BPH's. When X is a donor substituent (X=D′), the molecule behaves as a donor-acceptor conjugated system D′ − A, more easily polarized than the acceptor substitued molecule A′ − A. PPP-SCF-CI calculations show, that in comparison with the unsubstituted molecule (H − A), the energy of the S_1 state for the D′ − A system decreases more than the energy of its S_0 state; in the A′ − A system the opposite effect is observed [20]. Based on the experimental data, using equation (10) from [19], for the fluorescence maxima shifts $\updownarrow \Delta\nu^{\mathrm{Fl}}$ in ethanol we obtain

$$\Delta\nu^{\mathrm{Fl}} = -7256\ \mathrm{cm}^{-1}$$
$$= (\varrho_{00} - \varkappa_0)\cdot(-1) = -6310 - 954,$$

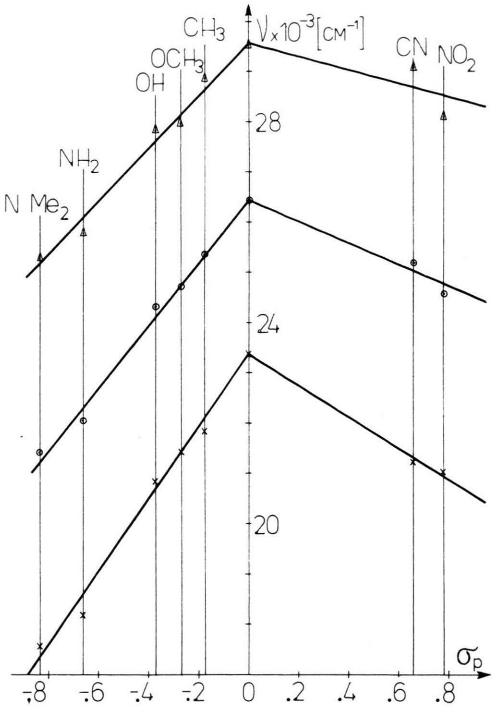

Fig. 3. Dependency of the spectral maxima in ethanol upon the σ_P-Hammett constants. △: absorption; ⊙: O−O transition; ×: fluorescence.

$$\Delta\nu^{\mathrm{Fl}} = -\,3113\ \mathrm{cm}^{-1}$$
$$= (\varrho_{00} - \varkappa_0)\cdot(+\,1) = -\,2270 - 834,$$

for donor and acceptor substituents, respectively. The simultaneous decrease of the $S_0 - S_1$ energy gap and the increase the steepness of the potential hypersurface S_0 as a result of substitution, both with donor and acceptor substituents, determine the stronger bathochromic shift of the fluorescence maxima compared to the absorption maxima.

According to [19], the change of the Stokes shift upon substitution depends only on the slopes of S_0 and S_1,

$$\Delta(\Delta\nu^{\mathrm{St}}) = \Delta\nu^{\mathrm{St}}(\mathrm{X}) - \Delta\nu^{\mathrm{St}}(\mathrm{H})$$
$$= \Delta\nu^{\mathrm{Abs}} - \Delta\nu^{\mathrm{Fl}} = (\varkappa_1 + \varkappa_0).$$

From the experimental data in ethanol we obtain

$\Delta(\Delta\nu^{\mathrm{St}}) = 1881\ \mathrm{cm}^{-1} = 954 + 927$ for $\sigma_x = -\,1$,

$\Delta(\Delta\nu^{\mathrm{St}}) = 1671\ \mathrm{cm}^{-1} = 843 + 828$ for $\sigma_x = +\,1$,

for all substituents $\Delta(\Delta\nu^{\mathrm{St}}) > 0$, $\Delta\nu^{\mathrm{St}}(\mathrm{H}) < \Delta\nu^{\mathrm{St}}(\mathrm{X})$, i.e. substitution leads to an increase the steepness of the two hyper-surfaces S_0 and S_1 and, hence, to larger Stokes losses. While ε and the rate constants of the radiation transitions k_r in ethanol are slightly dependent upon the substituents, the increase of $|\sigma_x|$ causes a monotonic increase of Q_f over 2 orders and a monotonic decrease of the corresponding nonradiative rate constants k_{nr} (Table 1 a).

We think the explanation of these dependencies is connected with the effect of substituents on the relative position of the $n\pi^*$ and $\pi\pi^*$ levels. Donor and acceptor substitution decreases the energy of both $n\pi^*$ and $\pi\pi^*$ states, but the influence on the $\pi\pi^*$ state is much stronger [21]. This enlarges the energy difference between the two states and decreases the nonradiative deactivation via the $n\pi^*$ state.

3.4 *Solvent effects and dipole moments*

Solvents with different Δf values [22] were used. The quantum yields of all BPH's investigated become greater with increasing polarity of the solvents (in cyclohexane and heptane some of BPH's do not fluoresce, Q_f of the others is very weak). Like the substituent effect, this experimental result can be explained with the separation of the $n\pi^*$ and $\pi\pi^*$ states in polar solvents [21].

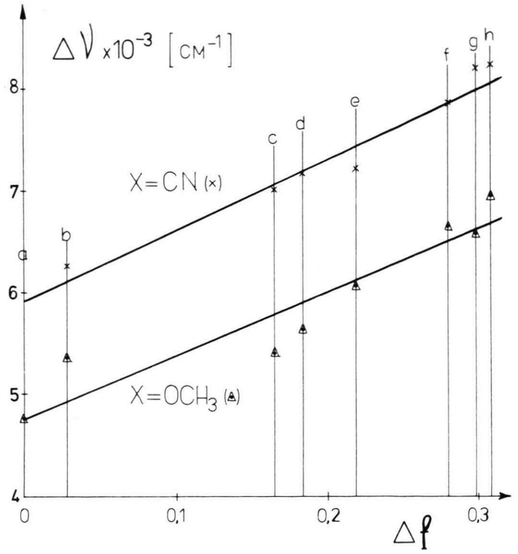

Fig. 4. Dependency of $\Delta\nu = \nu^{\mathrm{Abs}} - \nu^{\mathrm{Fl}}$ upon the Δf constants of the solvents. a: cyclohexane, b: dioxan, c: diethylether, d: chloroform, e: dichlormethane, f: n-propanol, g: ethanol, h: methanol. Correlation coefficients of the linear dependencies: $r^2 = 0.87$ for $\mathrm{X{=}OCH_3}$ and $r^2 = 0.95$ for X=CN.

From the observed absorption and fluorescence maxima shift in different solvents we calculated, according to [22], the dipole moment change $\Delta\mu$ upon excitation. The results for 2 typical representatives of donors ($\mathrm{X{=}OCH_3}$) and acceptors (X=CN) are shown in Figure 4. As pointed out in [22], the deviations from the linear correlation are greater in solvents with smaller Δf. The correlation coefficients r^2 for both cases are comparatively high for the experimental dependencies of this type. Assuming the Onsager radius of the molecule to be 5 Å (approximately half of the geometric distance between the two most outlying atoms), we calculated $\Delta\mu = \pm\,6.75$ D for $\mathrm{X{=}OCH_3}$ and $\pm\,7.31$ D for X=CN. The $\Delta\mu$ values for donor and acceptor substituted BPH's are close and of the same order as those quoted in [22], for molecules with similar structure.

3.5. *Photostability*

The BPH's investigated exhibit a considerably higher photostability than stilbene itself. We irradiated (Hg lamp) ethanol solutions of trans-stilbene and $\mathrm{X{=}OCH_3}$ substituted BPH with equal optical density in their absorption maxima (0.6).

After 30 min the optical density of trans-stilbene was 46% of the initial level, while that of the BPH was 95%.

4. Conclusion

A new class of efficient luminophores with a stilbene chromophore (3-phenylmethylene-1(3H)-isobenzofuranones) has been found. They fluoresce in the region 26000 − 16000 cm^{-1} with a maximal quantum yield of about 0.6. Due to the double bond, fixed to the five-membered ring, the BPH's are much more photostabile than stilbene. It is shown that as result of substitution or higher polarity of the solvent the $\pi\pi^*$ state of the BPH's separates from its nπ^* state. Coupled with the stronger conjugation in the excited $S_1(\pi\pi^*)$ state, this causes a rise of Q_f. The higher electron delocalization in the excited molecule hinders the intramolecular movements, and this reduces the nonradiative deactivation [1].

It must be mentioned that the $S_0 - S_2$ absorption transition of the BPH's results from an excitation which is practically localized in the stilbene fragment.

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