A New Class of Organic Luminophores With a Stilbene Chromophore: 3-Phenylmethylene-1(3H)-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(3H)-isobenzofuranones (BPH), 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 πn* state of the BPH separates from the fluorescently inactive nπ* state.

The S₂ → S₁ 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 σp-Hammett constants has been used for an interpretation of the changes in the potential hyperfaces of S₀ and S₁ 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 de-localization 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 S₁ 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 S₁ 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(3H)-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 derivatives 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(CH₃)₂, were synthesized by a standard procedure [8] and repeatedly recrystallized until a constant melting point was obtained; their purity was controlled by chromatography. The presented spectral characteristics for X=N(CH₃)₂ refer to the product of photoisomerization of the N(CH₃)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=OCH₃ substituted indandiones turned out

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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 spectro fluorimeter Perkin Elmer MPF44 B. The absorption 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 1a,b. 3-aminophthalimid with fluorescence quantum yield $\Phi_f=0.6$ in ethanol and $\Phi_f=0.36$ 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: $X=-\text{NH}_2$, $-\text{H}$ and $-\text{CN}$. The excitation spectra are identical with the corresponding absorption spectra in the region $26000 - 40000 \text{ cm}^{-1}$, 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 $24000 - 36000 \text{ cm}^{-1}$ seems to result from the overlapping of a couple of spectral transitions. For $X=\text{H}$ the data from [6], as well as our PPP-SCF-CI calculations with a standard parameterization [10] assign the longest wavelength absorption maximum ($29580 \text{ cm}^{-1}$) to $S_0 - S_1$. In the region $31500 - 36000 \text{ cm}^{-1}$ it is overlapped by another band, corresponding to $S_0 - S_2$.

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

Table 1a, b. Experimental spectral characteristics. The frequencies $v$ of the maxima are given in cm$^{-1}$; $\varepsilon$ in $10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$; $\tau_r$ in nsec; $k_r$, $k_{nr}$ in nsec$^{-1}$; /: no fluorescence observed; +: very poor solubility; -: no measurement.

Table 1a

<table>
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<tr>
<th>N°</th>
<th>X</th>
<th>Ethanol</th>
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<tr>
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<td>$v_{\text{Abs}}$</td>
</tr>
<tr>
<td>1</td>
<td>N(CH$_3$)$_2$</td>
<td>25 320</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>4</td>
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<tr>
<td>5</td>
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<td>28 920</td>
</tr>
<tr>
<td>6</td>
<td>H</td>
<td>29 580</td>
</tr>
<tr>
<td>7</td>
<td>CN</td>
<td>29 160</td>
</tr>
<tr>
<td>8</td>
<td>NO$_2$</td>
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Table 1b

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<td>/</td>
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<td>6</td>
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<td>29 600</td>
<td>/</td>
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<td>NO$_2$</td>
<td>28 440</td>
<td>24 960</td>
<td>0.001</td>
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</table>
is reasonable, because 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 $\tau_r$ in Table 1a are computed according to [11] from the absorption 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 $\pi$-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 $\varepsilon$ of the longest wavelength absorption maxima in ethanol are high (over 20000 $l \cdot mol^{-1} \cdot cm^{-1}$) except $X=NO_2$ (Table 1a).

In the previous investigations of compounds 2, 4, 6, 8 in Table 1a very close $\varepsilon$-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 $\varepsilon$ 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 $Q_r = 0.25$. The value of $\tau_r$’ 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 $\tau_r$ and $Q_r$, 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 $\pi - \pi^*$ electron transitions $\nu^{(0)}(S_0 - S_1)$ can be determined quite correctly. For $X=H$, $\nu^{(0)}(S_0 - S_2) = 26500 \text{ cm}^{-1}$. Taking into account that $S_0 - S_2$ in BPH’s is localized in the stilbene fragment, $\nu^{(0)}(S_0 - S_2)$ should have the same value as $\nu^{(0)}(S_0 - S_1)$ for stilbene itself. Then, according to [14], $\nu^{(0)}(S_0 - S_2)$ ($X=H$) = 29 730 cm$^{-1}$. The small energy difference $\Delta E = E^{(0)} - E^{(0)} = 0.4$ eV points to a strong internal conversion $S_2 \rightarrow S_1$.

The lowest $\pi\pi^*$ 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 $\nu^{(0)}$ is about 27000 cm$^{-1}$ [16]. So one could expect a negligible (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 $v^0_{F1}(H) = 19640 \text{ cm}^{-1}$, 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 $\sigma_p$ Hammett substituent constants are shown in Figure 3. Similar linear correlations are observed in dioxan also (see Table 1 b and [18]). For all solvents used, both acceptors and donors cause a bathochromic shift of the spectral maxima

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

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

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,

$$\Delta v^\text{Abs} = -5383 \text{ cm}^{-1}$$

$$= (\phi_0 + x_1) \cdot (-1) = -6310 + 927,$$

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

$$\Delta v^\text{Abs} = -1442 \text{ cm}^{-1}$$

$$= (\phi_0 + x_1) \cdot (+1) = -2270 + 828.$$

$x_0$ and $x_1$ are the steepnesses of the potential hypersurfaces $S_0$ and $S_1$, respectively; $\phi_0$ accounts for the influence of substitution on the $S_0$—$S_1$ energy gap. The calculated values of $x_1$ and $\phi_0$ for $\sigma_x \leq 0$ show that the bathochromic shifts of the absorption maxima for both donor and acceptor substituents are due to the decrease of the $S_0$—$S_1$ energy gap upon substitution ($\phi_0 < 0$), while the increase of the steepness of $S_1 (x_1 > 0)$ weakly compensates this effect. Quantitatively, the influence of the donor substituents on the $S_0$—$S_1$ O—O transition is stronger, $\phi_0 (\sigma_x < 0) = -6310 \text{ cm}^{-1}$, $\phi_0 (\sigma_x > 0) = -2270 \text{ cm}^{-1}$, 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 substituted 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 $\Delta v^{Fl}$ in ethanol we obtain

$$\Delta v^{Fl} = -7256 \text{ cm}^{-1}$$

$$= (\phi_0 - x_0) \cdot (-1) = -6310 - 954,$$
$\Delta v^{\text{Fl}} = -3113 \text{ cm}^{-1}$

$$= (q_{00} - x_0) \cdot (1) = -2270 - 834,$$

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 $S_1$,

$$\Delta(S^{\text{St}}) = \Delta v^{\text{St}}(X) - \Delta v^{\text{St}}(H) = \Delta v^{\text{Abs}} - \Delta v^{\text{Fl}} = (\sigma_i + x_0).$$

From the experimental data in ethanol we obtain

$\Delta(S^{\text{St}}) = 1881 \text{ cm}^{-1} = 954 + 927$ for $\sigma_i = -1$,

$\Delta(S^{\text{St}}) = 1671 \text{ cm}^{-1} = 843 + 828$ for $\sigma_i = +1$,

for all substituents $\Delta(S^{\text{St}}) > 0$, $\Delta v^{\text{St}}(H) < \Delta v^{\text{St}}(X)$, 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 $\varepsilon$ and the rate constants of the radiation transitions $k_r$ in ethanol are slightly dependent upon the substituents, the increase of $|\sigma_i|$ causes a monotonic increase of $Q_i$ 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 $n \pi^*$ 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 $\Delta f$ 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, $Q_i$ 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 $\Delta v = v^{\text{Abs}} - v^{\text{Fl}}$ upon the $\Delta f$ 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 $X = OCH_3$ and $r^2 = 0.95$ for $X = CN$.](image)

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 ($X = OCH_3$) 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 $\Delta f$. 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 $\Delta \mu = \pm 6.75 \text{ D}$ for $X = OCH_3$ and $\pm 7.31 \text{ D}$ 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 $X = OCH_3$ 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 photostable than stilbene. It is shown that as result of substitution or higher polarity of the solvent the ππ* state of the BPH’s separates from its nπ* state. Coupled with the stronger conjugation in the excited S₁(ππ*) state, this causes a rise of Qr. The higher electron delocalization in the excited molecule hinders the intramolecular movements, and this reduces the non-radiative deactivation [1].

It must be mentioned that the S₀ – S₂ absorption transition of the BPH’s results from an excitation which is practically localized in the stilbene fragment.

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