Luminescence Properties of Some Coumarins with 3:4-Fused Ring System

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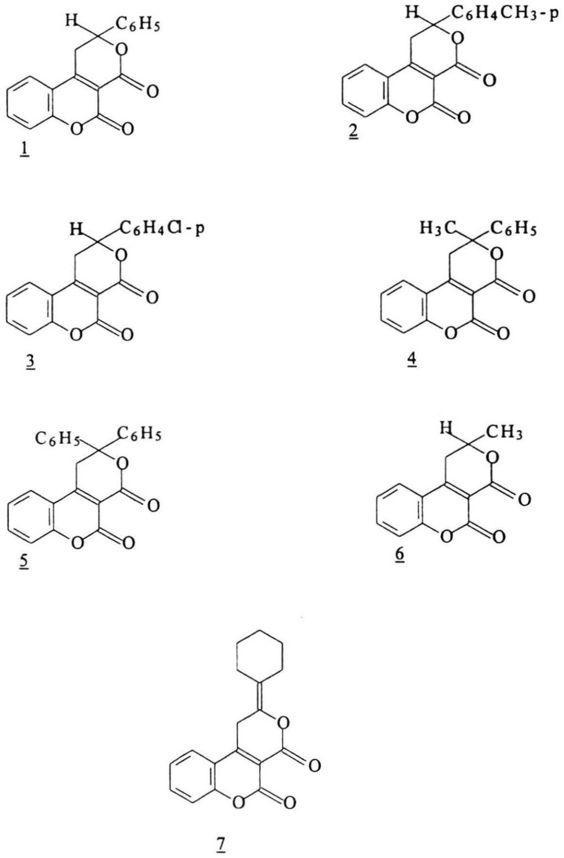
The photophysical characteristics of a group of coumarins with a 3:4-fused ring system (2-substituted-4,5-dioxo-1,2-dihydro-4H,5H-pyrano-[3:4-c][1]-benzopyrans) in solutions at room temperature, in frozen ethanol matrix at 77 K, in solid phase and in PVC films are reported. The low fluorescence quantum yield of the compounds investigated in solution is explained as a result of internal conversion from the fluorescent $S_2(\pi\pi^*)$ state to the lower lying $S_1(n\pi^*)$ state. The phosphorescence with a life time in the order of seconds is connected with intersystem crossing $S_1(n\pi^*) - T_1(\pi\pi^*)$. The absorption Franck Condon transitions in solid phase and in PVC matrix are only weekly batochromically shifted according to solution.

Key words: Electronic Spectra, Fluorescence; Coumarins with 3:4-Fused Ring System.

Introduction

Differently substituted coumarins are very useful as fluorescent dies [1–3], laser dyes [3–5], sun light transformers [3], and photosensitizers [6, 7]. On the other hand, compounds of this group have appropriate model structures for the investigation of non-radiative deactivation processes in carbonyl containing organic luminophores [8]. The aim of the present work is to study the effect of the presence of a 3:4 condensed ring system on the photophysical properties of a group of coumarins, namely 2-substituted-4,5-dioxo-1,2-dihydro-4H,5H-pyrano-[3:4-c][1]-benzopyrans in ethanol solution at 300 and 77 K, in solid phase and in a polymer PVC matrix.



Scheme 1. Structure of the investigated compounds.

1. Experimental

Scheme 1 shows the structure of the investigated compounds, the syntheses are described in [9]. All compounds are recrystallized until a constant melting point is 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) with equipment for solid state absorption measurements. The corrected excitation and fluorescence spectra are taken on a Perkin Elmer MPF 44B spectrofluorimeter with attachments for phosphorescence and

Table 1. Absorption and fluorescence maxima of the investigated compounds in ethanol, polymer PVC matrix and crystal phase at 300 K, and phosphorescence maxima in ethanol at 77 K. The absorption and luminescence maxima λ_{abs}, λ_{fl}, λ_{ph} are given in [nm], the molar extinction coefficients ε in $[l \cdot mol^{-1} \cdot cm^{-1}]$.

Comp.	Absorption				Fluorescence			Phosphorescence
	Ethanol, 300 K		PVC	Solid phase	Ethanol 300 K	PVC	Solid phase	Ethanol 77 K
	λ_{abs}	$\varepsilon . 10^{-3}$	λ_{abs}	λ_{abs}	λfl	λfl	λfl	λph
1	334	19.2	345	337	420	405	425	490
2	345	14.7	342	340	430	410	450	500
3	333	12.4	346	336	420	420	–	495
4	334	19.8	347	330	415	405	415	495
5	332	17.9	346	337	412	403	420	505
6	338	18.4	340	345	413	405	–	485
7	335	15.8	342	340	410	410	–	495

solid phase fluorescence measurements. The phosphorescence lifetimes are calculated from the decay curves in the phosphorescence maximum at 77 K. The fluorescence quantum yields Q_f are evaluated relatively to p-OCH_3-benzylidenephthalide with $Q_f = 0.14$ in ethanol [10]. The solvents used are of fluorescence grade.

2. Results and Discussion

In Table 1 the experimental data for the UV-VIS absorption and luminescence characteristics of compounds **1–7** are presented. The phosphorescence lifetimes in frozen ethanol solutions at 77 K, the relative fluorescence/phosphorescence intensity at 77 K and the ratio of the fluorescence intensities at 77 K/300 K are presented in Table 2. The absorption and luminescence spectra of compound **1** in ETOH solutions at 300 and 77 K and in polymer PVC matrix are shown in Figure 1.

2. A. *Absorption*

The analysis of the experimental data for the investigated compounds in ethanol solution at 300 K (Table 1) show that the presence of the 3:4 fused ring system in the investigated compounds leads to a decrease in the energy of the longest wavelength absorption band in comparison to the unsubstituted coumarin [8] with about 20 nm, the molar extinction coefficients remaining the same order of magnitude as in other 3-substituted coumarins [11]. The introduction of electron donating substituents in the 3:4 fused ring system, p-CH_3-phenyl (compound **2**) or methyl group (compound **6**), additionally shifts the absorption maximum to the red by about 10 nm, respectively 4 nm in comparison with compound **1**, while the electron accepting p-Cl-Phenyl substitution (compound **3**) has no influence on the absorption spectrum, Table 1. A similar effect of substituents on the absorption maxima in a structure with a saturated carbon atom is observed in some substituted indan-1,3-diones in fixed diketo form [12].

Table 2. Spectral characteristics of the investigated compounds in ethanol solutions at 77 K. τ_{ph}: phosphorescence life time, I_{ph}/I_{fl} (77 K): ratio between the phosphorescence and fluorescence intensity at 77 K, I_{fl} (77 K)/I_{fl} (300 K): ratio between the fluorescence intensity at 77 K and 300 K.

Compound	τ_{ph} [s]	I_{ph}/I_{fl} (77 K)	I_{fl} (77 K)/ I_{fl} (300 K)
1	3.7	1.0	1.5
2	1.2	0.2	3.0
3	1.8	0.2	6.1
4	2.2	0.3	1.7
5	4.8	4.0	5.2
6	6.2	4.5	4.0
7	5.1	5.3	2.5

Both in solid phase and polymer PVC film the energies of the absorption maxima are only weakly shifted to the red against ethanol solutions, Table 1. In solid phase the Frank Condon absorption transitions for compounds **2** and **6** are batochromically shifted against compound **1**, like in ethanol solutions.

2. B. *Fluorescence*

The compounds **1–7** fluoresce in solution at 300 K. In all cases the fluorescence quantum yields are low, less than 0.01. The Stokes shifts are large, about 6000 cm^{-1}, but the fluorescence band shows mirror symmetry to the longest wavelength absorption band, and the excitation spectrum is identical to the absorption in the whole spectral region 250 – 400 nm. Therefore there is no reason to attribute the relatively large Stokes shifts to structural changes in the fluorescent state. This conclusion is supported by the high photostability of the investigated com-

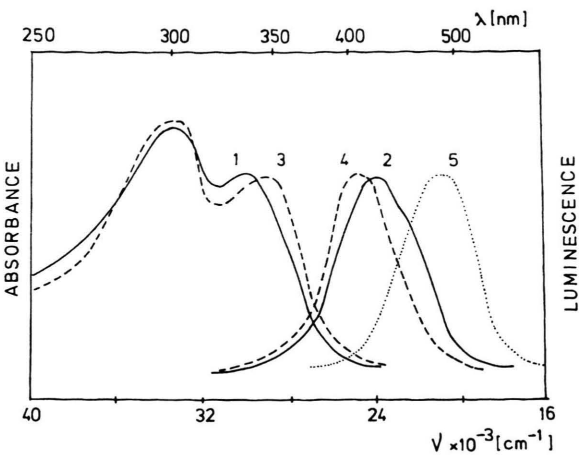


Figure 1. Absorption and luminescence spectra of compound **1**. Curves 1 and 2 (——): absorption and fluorescence in ethanol, 300 K; curves 3 and 4 (- - -): absorption and fluorescence in PVC matrix; curve 5 (· · ·): phosphorescence in ethanol, 77 K.

pounds: after irradiation of the ethanol solutions (10 mm cell, OD in maximum about 0.5) with a high pressure 450 W Hg lamp Narwa from 50 cm distance, the changes in the intensity of the absorption maximum are less than 5%.

The low fluorescence quantum yields of compounds **1–5** in all solutions at 300 K could be attributed to the intramolecular librations of the phenyl substituent in the 3:4 fused ring system in these structures (Scheme 1). But the results of the low temperature experiments in frozen matrix at 77 K do not support this hypothesis. As it is seen from the data in Table 2, the fluorescence intensity increases only slightly, less than one order of magnitude, after freezing the solutions of compounds **1–5** at 77 K. On the other hand, the compounds with similar structure but without the phenyl substituent in the 3:4 fused fragment (compounds **6** and **7**) have the same fluorescence properties: their Q_f values in solutions at room temperature ar also less than 0.01, and in frozen matrix Q_f increases in the same way as in compounds **1–5**.

Similarly to the unsubstituted coumarin and other coumarin derivatives [8, 13], the most reasonable explanation for the low fluorescence quantum yields of all the investigated compounds is connected with the nonradiative deactivation of the fluorescent $S_2(\pi\pi^*)$ state through the lower lying $S_1(n\pi^*)$ state. The position of the $S_1(n\pi^*)$ level in the investigated compounds can not be determinate experimentally because the S_0–$S_1(n\pi^*)$ transition is overlapped by the much more intensive $\pi\pi^*$ transitions. According to many theoretical and experimental studies (see for instance [14, 15] the energy of the transition localized on the carbonyl group C=O singlet $n\pi^*$ is only slightly affected by the changes in the π-electronic system of the main chromophore. That is why the energy of the $S_1(n\pi^*)$ level in the investigated compounds could be evaluated similarly to the unsubstituted courmarin [8] to be about 340 nm. This means that the $S_1(n\pi^*)$ level in the studied compounds is very closed to the fluorescent $S_2(\pi\pi^*)$ level, Table 1. Consequently one should expect a high efficiency of the internal conversion $S_2(\pi\pi^*) - S_1(n\pi^*)$ in the investigated coumarins with a 3:4 fused ring system, and this explains the observed low fluorescent quantum yields in all investigated coumarins **1–7**.

The unsubstituted coumarin fluoresces in solid phase [1]; we also observed fluorescence from the solid phase of compounds **1**, **2**, **4**, and **5**, Table 1.

Like the effect of the substituents on the absorption maxima in solution, the fluorescence characteristics in solid phase depends on the substituents in the 3:4 fused ring system: for example the fluorescence maximum of compound **2** is bathochromically shifted by 25 nm against compound **1**, while compound **6** has no fluorescence, Table 1.

2. C. *Phosphorescence*

All investigated compounds phosphoresce in frozen ethanol solutions at 77 K, Table 2. In case of the compounds **5**, **6**, and **7** the phosphorescence band dominates the luminescence spectrum, being more intensive than the fluorescence band. The fluorescence maxima in frozen solution are hypsochromically shifted by no more than 10 nm against the corresponding values at room temperature. The singlet–triplet splitting is in the order of 10,000 cm^{-1}, and this corresponds fairly to the calculated values for the $S_2(\pi\pi^*) - T_1(\pi\pi^*)$ gap in unsubstituted coumarin [8]. The phosphorescence lifetimes for all samples are relatively long, in the order of seconds, and these values are similar to the phosphorescence lifetime of the unsubstituted coumarin [13]. Bearing in mind the indirect population of the triplet excited states through intersystem conversion from the singlet $\pi\pi^*$ excited states, as well as El-Sayed's rules for the intersystem conversion efficiency [14], i.e. forbidden $S(\pi\pi^*) - T_1(\pi\pi^*)$ but allowed $S(n\pi^*) - T(\pi\pi^*)$ transitions, the observed intensive phosphorescence from the investigated courmarin derivatives could be seen as an indirect prove for effective internal conversion of the type $S_2(\pi\pi^*) - S_1(n\pi^*)$. There are two reasons for such a statement. First, the internal conversion of this type will strongly compete with the fluorescence processes, and this explains why the Q_f in solution is so low and does not increase in a frozen matrix at 77 K. Secondly, the large radiative lifetime of the $S_1(n\pi^*)$ level, which appears to be the lowest singlet excited state in the investigated compounds, makes possible the effective population of the phosphorescence $T_1(\pi\pi^*)$ level via $S_1(n\pi^*) - T_1(\pi\pi^*)$ internal conversion, and this is in line with the intensive phosphorescence observed at 77 K.

The presented experimental data give reason to propose the following scheme for describing the radiative and nonradiative processes through the electronically excited states in the investigated compounds:

$$S_2(\pi\pi^*) \xrightarrow{K_{IC}} S_1(n\pi^*)\,, \tag{1}$$

$$S_2(\pi\pi^*) \xrightarrow{K_{FL}} S_0 + h\nu^{FL}\,, \tag{2}$$

$$S_1(n\pi^*) \xrightarrow{K_{ISC}} T_1(\pi\pi^*)\,, \tag{3}$$

$$T_1(\pi\pi^*) \xrightarrow{K_{PH}} S_0 + h\nu^{PH}\,, \tag{4}$$

where the rate constants K indicate, respectively, K_{IC} internal conversion, K_{FL} fluorescence, K_{ISC} intersystem conversion, K_{PH} phosphorescence. The low values of the fluorescence quantum yield Q_f indicate that $K_{IC} \gg K_{FL}$, and from the experimental data at 77 K follows, that K_{ISC} is in the same order as K_{IC}.

All investigated compounds have a very poor solubility in the nonpolar solvents cyclohexane and dioxane, and this prevents a detailed analysis of their photophysical characteristics. We followed the effect of the solvent polarity on the Stokes shift only in the case of compound **1**. Increasing the solvent polarity (cyclohexane, dioxane, dicloroethane, ethanol, acetonitrile) leads to only a small enlargement in the Stokes shift; for cyclohexane – acetonitrile the difference is about 1000 cm^{-1}, and according to the Lippert's model [16] this corresponds to an increasing of the dipole moment in the fluorescence exited state of about 2D; this value is in the same order as the data for other 3-substituted coumarins [11].

3. Conclusions

The experimental data for the absorption and luminescence characteristics of the investigated compounds allow to conclude that the presence of a 3:4-fused ring system in coumarin diminishes the energy of the $S_2(\pi\pi^*)$ level in comparison to the unsubstituted coumarin, but does not give rise to inversion in the relative position of the $S_2(\pi\pi^*)$ and $S_1(n\pi^*)$ levels. The lowest lying singlet excited state in the compounds **1–7** is $S_1(n\pi^*)$, and the internal conversion $S_2(\pi\pi^*) - S_1(n\pi^*)$ determines the low fluorescence quantum yields both in solutions at 300 K and in frozen matrix at 77 K. The observed intensive phosphorescence in frozen ethanol solutions at 77 K is due to effective $S_1(n\pi^*) - T_1(\pi\pi^*)$ internal conversion.

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