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Time-resolved fluorescence spectroscopy of helically distorted aromatic systems

H. Lanig [a], M. Hof [b,1], G. Bringmann [c], F.W. Schneider [b]

[a] *Computational Chemistry Center, University of Erlangen / Nürnberg, Nägels-bachstr. 25, D-91052 Erlangen, Germany*
[b] *Institute for Physical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany*
[c] *Institute for Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany*

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Abstract

The fluorescence deactivation of several lactones and phenanthrene derivatives has been investigated by stationary and time-resolved fluorescence spectroscopy. Due to steric repulsions, these molecules are helically twisted around a central axis. Surprisingly, they show a negative temperature dependence of the natural fluorescence constant $k_{fo} = \Phi_f k_f$. Considering both electronic and structural contributions we propose that the strain within the fluorescing molecules can be qualitatively described using the observed temperature dependence of k_{fo}. The larger this negative temperature dependence, the larger is the internal motion barrier in the molecules. © 1997 Published by Elsevier Science B.V.

1. Introduction

One of our main interests is to explore intramolecular dynamic properties such as barriers to internal rotation in twisted organic compounds using stationary and time-resolved fluorescence spectroscopy. We have previously shown that the intramolecular fluorescence deactivation of zwitterionic quinolinium dyes, where the quenching ion is attached to the chromophore via a flexible alkyl chain, can be interpreted in terms of an orbital overlap between the quenching sulfonato group and the aromatic quinolinium chromophore [1,2].

In the present work, we focus on a different type of intramolecular motion: the helimerization (or atrop-isomerization) of twisted aromatic systems. The biaryl axis is a common structural element in many naturally occurring compounds of different origin (e.g. naphthylisoquinoline alkaloids [3]). For the stereoselective synthesis of biaryls [4,5], benzo[b]naphtho[1,2-d]pyranones **1–3**, i.e. lactone-bridged biaryls (see Fig. 1) have been found to be useful precursors that can easily be built up by intramolecular aryl coupling [6,7]. Structurally, these compounds are not planar, but split up into helicene-like distorted atropisomers, as investigated by X-ray crystallography [6–8] and by semiempirical and ab initio calculations [5,9]. Compared with the ring-opened final target molecules, they are characterized by dramatically lower rotational barriers at the axes, which, dependent on the size of the substituent R, give rise to a more or less rapid atrop-isomerization process, as investigated by dynamic NMR and by

[1] Present address: Department of Physical Electronics, Technical University in Prague, CZ-18000 Praha 8, Czech Republic.

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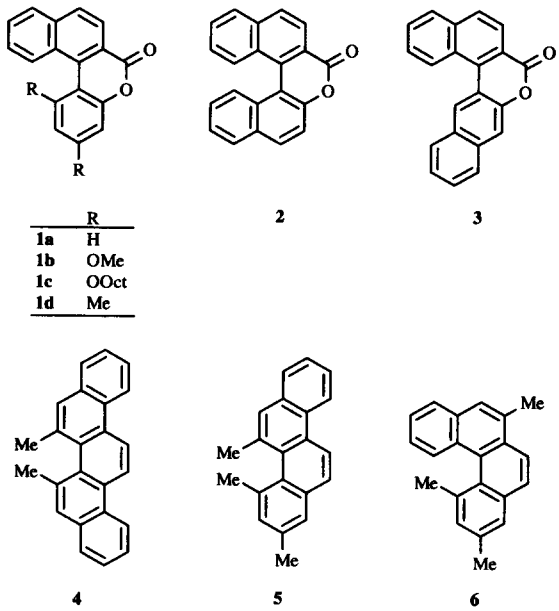


Fig. 1. Helically twisted aromatic fluorophores used in this investigation.

theoretical methods [4,5,9]. The preparative value of these bridged biaryls lies in the discovery that, out of this racemic mixture of interconverting enantiomers, they may be ring-opened such that essentially only one of the two possible atropisomeric cleavage products (which are now configurationally stable) results [4,5]. Similar biaryl lactones of synthetic importance are **2** and **3** [7].

Electron paramagnetic resonance (EPR) [10,11] and nuclear magnetic resonance (NMR) [12,13] are the only spectroscopic techniques to estimate the internal barrier to rotation of such conformationally unstable ('axial prostereogenic') compounds. However, fluorescence emission should also be sensitive to internal conformational changes in the excited state of a molecule. In order to test this assertion we investigated the fluorescence properties of the helically twisted lactones **1–3** and related isocyclic phenanthrene derivatives **4–6** (for their structures, see Fig. 1).

2. Methods

Absorption and fluorescence spectra were recorded on a Hitachi U3210 VIS/UV spectrophotometer and a SLM-Aminco-Bowman Series 2 luminescence spectrometer, respectively. To determine the fluorescence decay times, the single photon counting (SPC) spectrometer (Edinburgh Instruments, model 199S) with simultaneous acquisition of fluorescence and excitation (SAFE) was used [14]. The excitation and emission wavelengths were 337 and 430 nm, respectively, for all compounds measured. Time-dependent data were analyzed using a least-squares iterative deconvolution technique as described elsewhere [15]. Each reported decay time is the average of 10 measurements with values of $\chi^2 < 1.1$. The apparatus allows precise measurements of lifetimes with standard deviations $< 1\%$.

Fluorescence quantum yields were measured using 5×10^{-5} M quinine bisulfate in 1 N H_2SO_4 as reference compound and corrected according to the method of Parker and Rees [16]. Unless otherwise indicated, the concentration of all compounds was 5×10^{-5} M.

3. Results and discussion

3.1. Steady state spectra

Table 1 shows the absorption and emission maxima $\lambda_{abs/em}$ (nm) of the compounds **1a–d**, **2** and **3** measured in 1,4-dioxane at 20°C. In the case of absorption, only the band with the highest intensity is given, and emission showed only one broad transition in every case.

The positions of the maxima are in good agreement with the structures of the compounds: the larger or more stabilized/delocalized the π-system, the bigger is the Stokes shift observed in the spectra. Taking **1a** as a reference system, methyl substitution (**1d**) shifts the absorption and in particular the emission maxima to longer wavelengths. Changing from $+I$ to $-I/+M$ donors (**1b**, **1c**) amplifies these effects. The fact that the emission maxima are more affected than the absorption maxima leads to the conclusion that the fluorescing excited states are more stabilized by electron donor substitution of the aromatic system than the ground states. Additionally, alkoxy substitution results in a dramatic increase of the fluorescence intensity, whereas the emission intensity of compounds **1a** and **1d** is extremely weak.

Table 1
Absorption and emission maxima $\lambda_{abs/em}$ (nm), quantum yields Φ_f and decay times τ_f (ns) of the compounds **1a–d**, **2**, and **3** measured in 1,4-dioxane at 20°C. k_{fo} and k_{nr} (1/s) are calculated according to Eqs. (1) and (2). A dash means that the measurement was not possible due to low emission intensity

λ (nm)	1a	1b	1c	1d	2	3
abs	324	330	331	326	340	332
em	395	435	439	413	432	436
Φ_f	–	0.69	0.80	–	0.037	< 0.001
τ_f (ns)	–	6.24	6.62	–	0.42	–
k_{fo} (s^{-1})	–	1.10×10^8	1.21×10^8	–	8.81×10^7	–
k_{nr} (s^{-1})	–	5.04×10^7	2.98×10^7	–	2.29×10^9	–

Compounds **2** and **3** possess different aromatic systems, but the location of the bands indicates a similar delocalization/stabilization of the π-system.

3.2. Kinetic data

To gain detailed information about the processes which take part in the fluorescence deactivation of these compounds, fluorescence decay times and quantum yields of the chromophores were measured in 1,4-dioxane at 20°C (Table 1). Although emission spectra were recorded for the compounds **1a** and **1d**, the calculation of quantum yields and measurements of the decay times was not possible due to their low fluorescence intensities. This is a result of the fact that R = H and Me do not allow mesomeric stabilization of the π-system and therefore high emission intensities. The compounds **1b** and **1c** show a large fluorescence quantum yield with decay times > 6 ns. This behavior, in comparison with compounds **2** and **3** (small quantum yield with short fluorescence decay times), might be explained in terms of the electronic structure of the molecules. In the case of **1b** and **1c**, the electron pairs of the alkoxy groups can act as donors and therefore lead to a mesomeric stabilization of the whole π-system. In the case of compounds **2** and **3**, this stabilization is not possible and only weak emission is detectable.

The fluorescence rate constant k_f is

$$k_f = \frac{1}{\tau_f} = k_{fo} + k_{nr}, \qquad (1)$$

where k_{nr} denotes the sum of the various possible non-radiative deactivation processes (e.g. internal conversion (IC), intersystem crossing (ISC), collisions with solvent molecules), and k_{fo} represents the natural fluorescence constant, which can be calculated according to

$$k_{fo} = \frac{\Phi_f}{\tau_f}. \qquad (2)$$

The kinetic data show that the k_{fo} values are within a comparable range for **1b**, **1c**, and **2** (Table 1). The main difference occurs in the non-radiating deactivation processes; compound **2** is deactivated by about two orders of magnitude faster than the alkoxy lactones. The result is a weak fluorescence intensity with comparable k_{fo}.

3.3. Temperature dependence

To gain information about the dynamic behavior of the lactones, temperature dependent measurements of compounds **1b**, **1c**, and **2** were carried out in the range 20 to 60°C. The location and shape of the absorption spectra of all compounds showed no significant changes, emission maxima shifted at the most by 3 nm. These small changes imply that the energy of the electronic states is not affected by temperature changes. To describe the relation between the internal energy of the systems and the fluorescence decay times/quantum yields, we focussed our attention on the temperature dependence of the kinetic constants k_f, k_{fo}, and k_{nr}.

Table 2 shows the values for k_{fo} and k_{nr} at various temperatures calculated by using the Φ_f and τ_f data (Eqs. (1) and (2)). As expected, the rate of the non-radiative deactivation process k_{nr} increases with rising temperature in the case of all the three lactones **1b**, **1c**, and **2**, possibly due to the increase

Table 2
Fluorescence decay behavior of the compounds **1b**, **1c**, and **2** in terms of radiating and non-radiating decay constants (1/s) at various temperatures, measured in 1,4-dioxane. The temperature 'ependence of the kinetic constants is calculated according to Eq. (3)

T (°C)	**1b**		**1c**		**2**	
	$k_{fo} \times 10^8$	$k_{nr} \times 10^7$	$k_{fo} \times 10^8$	$k_{nr} \times 10^7$	$k_{fo} \times 10^7$	$k_{nr} \times 10^9$
20	1.099	5.040	1.213	2.980	8.810	2.293
30	1.085	7.270	1.181	4.830	7.429	2.783
40	1.048	10.18	1.125	7.650	6.000	3.273
50	1.042	14.21	1.065	10.04	5.185	3.652
60	1.009	19.94	0.983	14.86	4.231	3.804
$m_{fo/nr}$	205	−3317	504	−3835	1170	−1257

in collisions with solvent molecules. Molecule **2** exhibits a special behavior, because k_{nr} is about two orders of magnitude larger and the temperature sensitivity of k_{nr} is about three times smaller than the corresponding data for **1b** and **1c**. The deactivation may therefore mainly be caused by solvent quenching mediated by the alkoxy groups, whereas in the case of compound **2** a different deactivation process, with a different temperature dependence dominates. Surprisingly, the radiative deactivation constant k_{fo} shows the opposite trend for all compounds: the higher the temperature, the smaller the rate constant becomes. Also for the radiative deactivation route, lactone **2** deviates significantly. The temperature sensitivity of k_{fo} is markedly higher than for the other molecules.

To quantify the temperature behavior of a rate constant, semi-logarithmic plots were generated using the Arrhenius-type equation

$$\ln k_{fo/nr} = m_{fo/nr}\frac{1}{T} + C, \tag{3}$$

where

$$m_{fo/nr} = -\frac{E_a}{R}. \tag{4}$$

The slope m_{fo} or m_{nr} of each linear equation describes the temperature sensitivity of the corresponding kinetic processes (Table 2), E_a is the Arrhenius activation energy.

3.4. Temperature dependence and structure

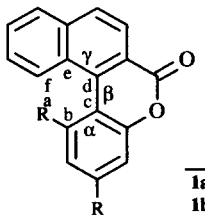
The temperature dependence of the non-radiating part of the fluorescence deactivation can be easily interpreted considering the fact that collisions between solvent molecules and the chromophore play an important role together with processes like internal conversion and intersystem crossing. The higher the temperature, the more deactivating collisions take place and the faster the IC and ISC processes become.

The radiative deactivation constant k_{fo} is commonly accepted in the literature to be temperature independent [17,18]. However, in the case of the present compounds, k_{fo} is temperature dependent with a sign opposite to the one generally predicted: the higher the temperature, the longer the natural lifetime becomes. This situation can be formally described by a negative Arrhenius activation energy according to Eqs. (3) and (4).

To analyze this atypical situation, we investigated the temperature dependence of non-twisted aromatic molecules like anthracene and phenanthrene. In these cases, a normal behavior of k_{nr} and no temperature dependence of k_{fo} was found [19]. We therefore conclude that the temperature dependence of k_{fo} may not only be related to the electronic structure, but also to the 3D structure of the molecules.

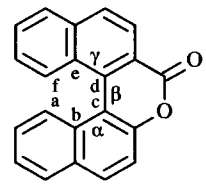
As mentioned before, all investigated molecules are helically twisted. To quantify the internal strain of the molecules, the sum of the dihedral angles of the 'inner spiral loop' [6] [α(abcd) + β(bcde) + γ(cdef)] and the individual values α, β, and γ can be used. Table 3 shows representative dihedral angles for the compounds **1a–1d**, and **2**. Comparing these structures, a clear ranking of the internal strain within the molecules can be found. Thus, a qualitative classification is possible. Substituting the reference compound **1a** by two methyl groups to give **1d**

Table 3
Representative dihedral angles α(abcd), β(bcde), and γ(cdef) describing the internal distortion around the central biaryl axis of the compounds **1a** [8], **1b** [6], **1c** [20], **1d** [7], and **2** [7], as determined by X-ray diffraction. Σ = total sum of the dihedral angles α, β and γ. For **3**, an X-ray structure was not achieved



1a-d

	R
1a	H
1b	OMe
1c	OOct
1d	Me



2

	1a	**1b**	**1c**	**1d**	**2**
α	– [a]	6.0°	9.7°	12.4°	14.9°
β	26.0°	32.2°	32.3°	34.1°	29.5°
γ	15.7°	17.2°	13.2°	15.0°	18.6°
Σ	–	55.4°	55.2°	61.5°	63.0°

[a] Not determined, since hydrogen atoms were not refined.

increases the internal strain more than alkoxy substitution (compounds **1b** and **1c**), for which the strain should be similar. Having identical electronic structures, the differences are only caused by the flexible alkyl chain. The increase in strain between **1c** and **2** should be relatively large. In this case, however, the electronic structure of the system markedly changes.

This qualitative description of the internal strain can be confirmed by the temperature dependence of k_{fo}, expressed as m_{fo} in Table 2. Between **1b** and **1c**, an increase by a factor of 2.5, but between **1b** and **2**, an increase by a factor of 5.7 has been found. The data do not exactly reflect the classification derived from the X-ray data, but verifies the difference between compounds **1b** and **1c** on the one side and compound **2** on the other side.

With the assumption that the temperature dependence of k_{fo} might reflect the internal strain of the molecules, the opposite sign of m_{fo} compared to m_{nr} has to be interpreted. This can be done considering the fact that the molecules are not static (like in simple geometry optimizations). Due to the thermal energy, the molecules vibrate around their global energy minimum. The higher the temperature of the environment, the more vibronically excited states are populated. Stating that the vibronic ground state of a molecule represents 'ideal' conditions for fluorescence deactivation, the bending of the π-system (due to high temperature) decreases the possibility of radiative deactivation.

In order to check whether the observed temperature dependence of k_{fo} is a lactone-specific or a more general phenomenon, we investigated these properties for a different isocyclic compound class lacking the 'ester linkage'. Fig. 1 shows three methyl-substituted phenanthrene derivatives (**4–6**), which should be helically twisted without any hetero-atoms involved. The measurements were carried out in n-butanol in a temperature range of 20–50°C. The concentration of the dyes was 2×10^{-5} M in every case.

All three compounds show only weak fluorescence intensities ($\Phi_f < 0.1$), apparently due to the lack of mesomeric stabilization via alkoxy + *M* donors (as for **1b** and **1c**). In the case of the derivatives **4** and **5**, the temperature dependence of k_{fo} is within experimental error. This is probably caused by the fact that in both cases the π-system is not as much involved in the helimerization process as in the case of the lactones. However, for compound **6**, the aromatic system should be more strongly bent. Therefore it is not surprising that a temperature dependence of k_{fo} exists. The resulting value (m_{fo} = 408) has the same sign and lies in the range of the alkoxy-substituted lactones. The internal strain of these compounds should therefore be comparable. We conclude that the influence of temperature on the spectroscopic behavior is not so much dependent on the contribution of the lactone ring, but rather on the strain in the total aromatic system.

4. Conclusion

The aim of this investigation was the application of fluorescence methods to access the intramolecular dynamics of helically twisted aromates. For that purpose, two different effects have to be considered. On the one hand, the compounds must show a sufficiently high fluorescence quantum yield that allows temperature-dependent measurement of the fluorescence properties. When this electronic condition is fulfilled, a steric contribution to the dynamic behaviour of the molecules may become important.

Considering both electronic and structural contributions we propose that the strain within a fluorescing molecule may be described qualitatively using the temperature dependence of the radiative deactivation constant k_{fo}. The larger the temperature dependence, the larger is the internal motion barrier of the molecule. We started to verify this proposal by using two different types of classes of molecules with and without hetero-atoms in the aromatic system. Special care has to be taken when comparing systems with different electronic structures. So, this investigation is currently extended to additional compounds with comparable electronic structures but different steric contribution to the overall effect and, vice versa, with a similar strain, but different electronic conditions.

The fact that the m_{fo} values have positive signs (k_{fo} becomes smaller with rising temperature) leads to the proposal that a pre-equilibrium precedes the photophysical process. We are currently investigating this more closely on the basis of a kinetic model which should simulate the individual components leading to this unusual type of fluorescence deactivation.

Acknowledgements

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