On the Influence of Intra- and Inter-Molecular Hydrogen Bonding on the Excited State Lifetime of Indigo Dyes

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It is shown that intramolecular hydrogen bonding can give rise to very fast nonradiative desactivation of the S_1-state of indigo dyes. In those derivatives, which lack the possibility of internal hydrogen bonds, hydrogen bonding to suitable solvent molecules can provide the channel for fast radiationless transitions. As a consequence, drastic effects on the S_1-state lifetime are observed both as a function of solvent and/or temperature.

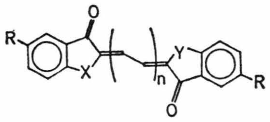
Introduction

According to theory, internal rotation should be a degree of freedom which is very effective in accepting energy during the process of radiationless transitions [1]. Prevention of this motion, either by means of chemical bonds or by imbedding into a rigid solvent, therefore decreases the rates of nonradiative transitions and increases concomitantly both, the quantum yield of fluorescence and the excited state lifetime. Intramolecular hydrogen bonding seems to be sufficient to hinder internal rotation in the case of indigo dyes. Whilst one observes photoinduced trans → cis-isomerisation in compound III, no evidence for this process is found in I or II [2] (cf. Table 1). Lifetime measurements in EtOH at room temperature somewhat contradict this picture in as far as compound III lives much longer in the S_1-state than compounds I and II do [3]. In order to decide whether the hydrogen bonds act as strong coupling modes (as was e. g. suggested by Küttner et al. [4]) and thereby compensate the effect of stabilization of the molecular frame, we studied the influence of solvent and temperature onto the S_1-state lifetime of both the indigo-dyes I – III a as well as their vinylogue analogues IV and V. By comparison of the results of both series, we are able to distinguish between the influence of either inter- and intramolecular hydrogen bonding.

Experimental

The fluorescence decay curves were determined by the single photon timing technique [5]. Whenever the decay time was less than the f.w.h.m. of the exciting pulse, the lifetime was determined by Laplace transformation [6] and crosschecked by direct convolution of the excitation profile with the decay function $\exp(-t/\tau)$. In those cases, in which the signal-to-noise ratio was too low for a precise determination of τ, only the upper limit for τ was included in Table 1. The dye samples were provided by the

Table 1. Structure of the indigo dyes studied.



	I	II	III	III a	IV	V
n	0	0	0	0	1	1
X	N–H	N–H	S	S	S	N–H
Y	N–H	S	S	S	S	N–H
R	$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-$	$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-$	$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-$	CH_3-CH_2-	$\begin{array}{l}CH_3\\ \quad\diagdown\\ \qquad CH-CH_2-CH_2-\\ \quad\diagup\\ CH_3\end{array}$	H–

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courtesy of Professor W. Lüttke, Organic Chemistry Institute, University of Göttingen. They were used as donated without further purification; their synthesis is described in [7]. Solvents used were spectrograde as supplied by Merck. PMMA-samples were prepared as described in [8].

Results and Discussion

Inspection of Table 1 brings up several points which are intriguing at a first sight:

(i) Whilst at room temperature, the indigo (I) and cibaviolet (II) derivatives show a lifetime of less than 20 psec in both EtOH and benzene, the one of the thioindigo derivative (III) is about 300 psec in EtOH. In benzene as solvent the lifetime is even raised to 9.3 nsec.

(ii) Upon cooling of the ethanolic solutions, the lifetimes rise, as expected, but the large differences between I or II and III, respectively, remain. Corresponding to a lifetime of less than 1 nsec, the fluorescence quantum yield is low both in I and II. In compound III, on the other hand, radiationless processes seem less important at 77 K, because the lifetime is up to 8.3 nsec.

As benzene does not give rigid glassy solutions at low temperatures but crystallizes, the temperature dependence of the lifetimes could not be determined in this solvent.

(iii) The vinylogue analogues IV – V also show a solvent dependent S_1-state lifetime. In EtOH (300 K) we find lifetimes of less than 1 nsec for both compounds. In benzene (300 K) the decay time is increased to about 2.5 – 3 nsec.

(iv) In a PMMA-matrix, the lifetimes of the thio-indigoderivatives, are nearly as high as in rigid ethanolic solution at 77 K.

In our opinion all these observations can be understood on ground of the following model. In compound I and II intramolecular hydrogen bonding acts as a strong accepting mode and thereby determines the rate of the dominating radiationless deactivation process, i. e. internal conversion $S_1 \rightarrow S_0$. Since even one internal hydrogen bridge is obviously efficient enough to reduce the lifetime to less than 20 psec at 300 K, no major difference in the lifetime can be observed between compound I and II, respectively. In accordance with this, no variation in lifetime should be recorded, when one switches between two solvents which differ in their ability to generate intermolecular hydrogen bonding. In compound III and III a, on the other hand, the intramolecular decay channel should be exceeded in importance by the intermolecular decay channel, whenever the solvent is such that intermolecular hydrogen bonds can be established. A variation of the saturated side chains does not modify the general behaviour of the dyes. As can be seen from the data of III and III a respectively, in the Tables 2 and 3 and Fig. 1 however, it has an effect on the kinetics of the excited molecule. Whether this change is due to the electron donating power of the alkyl-groups and whether there is a position-dependent effect is to be investigated.

Table 3. Activation energies for the thioindigo derivatives derived from Figure 1.

	III	III a	IV
E_A $T < 140$ K	340 cm^{-1}	220 cm^{-1}	220 cm^{-1}
E_A $T > 140$ K	2430 cm^{-1}	3520 cm^{-1}	3520 cm^{-1}

The compounds IV and V have in common that neither one of them can have an internal hydrogen bridge, i. e. the effects discussed in connection with compound III should also show up, as they do.

Further evidence for the assumption that intermolecular hydrogen bonding is the most important factor for the acceleration of internal conversion $S_1 \rightarrow S_0$ can be deduced from the temperature dependence of the lifetime in ethanolic solution. In

Table 2. Fluorescence lifetimes in nanoseconds of the dyes I—V in different solvents at 77 and 300 K respectively.

		I	II	III	III a	IV	V
ethanol	300 K	–	–	0.35	0.6	<1	<1
	77 K	0.6	0.7	8.3	13.5	13.4	
PMMA	300 K	decomp.	decomp.	6	12.5	11	
	77 K						
benzene	300 K	<1	<1	9.3	9.0	2.9	2.4

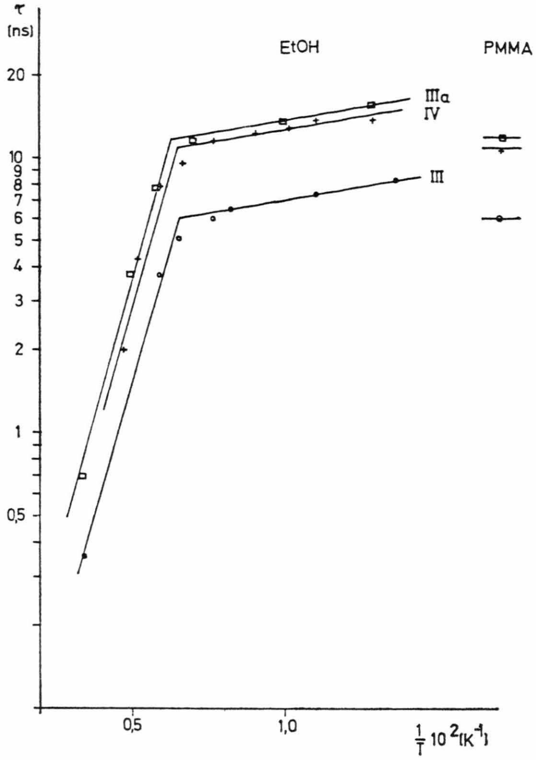

Fig. 1. Temperature dependence of the fluorescence lifetimes of compounds III, IIIa and IV in ethanolic solution.

an Arrhenius type plot (Fig. 1) all thio-compounds show the same general pattern: at higher temperatures $\ln \tau$ correlates linearly with $1/T$, the slope being the same for all three (for the activation energies see Table 3). Below the softening point of the solvent, the slope is much smaller. A correlation between τ and $\eta^{2/3}$, as it was discussed by Förster and Hoffmann[9] for triphenylmethane dyes could not be verified.

An alternative interpretation of the temperature dependence of the rate of the radiationless process is offered by Fischer and van Dyne[10]. Their model takes into account the solute-solvent interaction and the relaxation of the solvent cage upon excitation of the solute. The activation energy observed is correlated to the stabilisation of the solute. In the low temperature region the molecular relaxation process is on a faster time scale than the rearrangement of the solid matrix. This results in the relatively small activation energies of 250 cm^{-1}. At temperatures higher than the softening point however, the solvent relaxation time is considerably shorter and the activation energy is therefore raised to about 3000 cm^{-1}.

On the other hand, the properties of PMMA as a solvent are hardly changed between 77 and 300 K and therefore the lifetimes are essentially independent of temperature.

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