

Short Communication

Lightfastness and flash photolysis of disperse dyes on poly(ethylene terephthalate): indolizine derivatives

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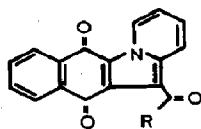
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Many factors influence the lightfastness of quinonoid-based disperse dyes on technologically important substrates such as poly(ethylene terephthalate) (PET) but it is normally the structure of the dye that is the one of greatest interest [1]. An example of this is shown in recent work on anthraquinone and benzanthrone disperse dyes in which it was found that the substitution of an anilino group *ortho* to a carbonyl group gave dyes of much higher lightfastness than if the same group had been amino or alkyl amino [2, 3]. Spectroscopic and laser flash photolysis studies suggested that the reason for high photostability of the anilino derivative is that this group induces a process of fast radiationless deactivation from the first excited singlet state [4 - 6].

Interestingly, a report in the patent literature suggested that the light stability of certain indolizine disperse dyes (I) may follow the same pattern of behaviour and so three typical indolizine disperse dyes, having R = -OEt, R = -NH₂ and R = -NHPH as substituents, were selected for study.



(I)

The data summarized in Table 1 show that the "anilino stabilizing effect" occurs with the indolizine dyes. It may also be noted that with respect to the lightfastness data the difference in the order of magnitude between the amino and anilino derivatives is nearer that of the benzanthrone dyes [2] than that of the anthraquinone dyes [3]. There is no obvious explanation for this difference but it must certainly be a feature that requires explanation when the mechanism of excited state deactivation is considered (see below).

TABLE 1

Effect of structure on the photochemical and spectroscopic properties of naphth[2,3-b]indolizine-6,11-dione derivatives

	R		
	-OEt	-NH ₂	-NHPh
I.S.O. light fastness grade [3]	<1	1	6
microsecond flash photolysis transients [4]	yes	yes	not observed
nanosecond flash photolysis transients [4]	yes	yes	not observed
fluorescence [5]	$\Phi_f = 0.16$	$\Phi_f = 0.03$	$\Phi_f < 0.001$
phosphorescence [5]	$\lambda_{\max} = 595 \text{ nm}$	not observed	not observed

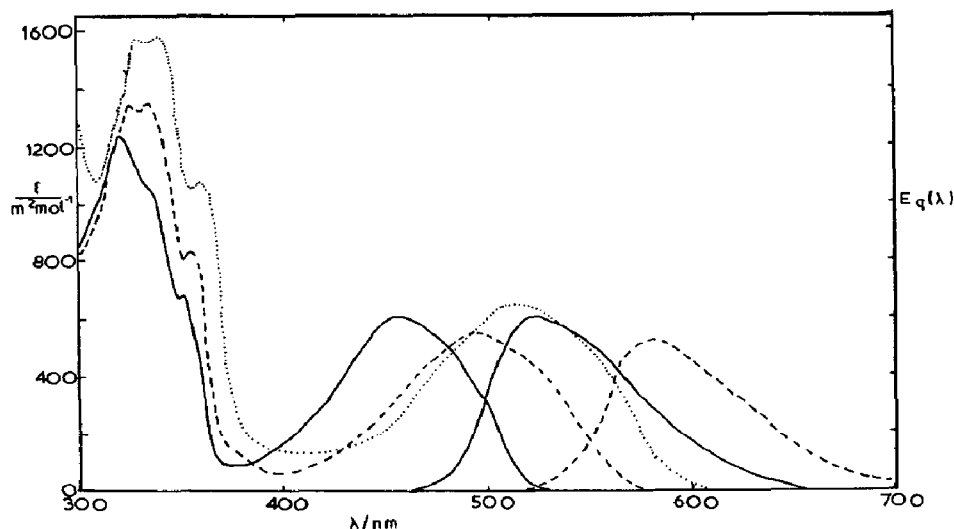


Fig. 1. Electronic absorption and fluorescence emission spectra of naphth[2,3-b]indolizine-6,11-dione 12-ethoxycarbonyl (—), 12-carbamoyl (---) and 12-phenylcarbamoyl (.....) in toluene.

The marked difference in lightfastness between the indolizine derivatives is not apparently related to a difference in the nature of their photoexcited states since the magnitude of the absorption coefficient of their long wavelength bands (Fig. 1) shows that their lowest energy states are all $\pi\pi^*$ in nature. Similarly the lowest triplet must also be $\pi\pi^*$. This follows from the spectroscopic data (Fig. 1 and Table 1) which shows that the singlet-triplet splitting in the ethoxy derivative is quite large ($\sim 3000 \text{ cm}^{-1}$). The amino and anilino derivatives must also have lowest energy triplet states of the $\pi\pi^*$ type. As the conjugation of a π -system is extended, so the energy

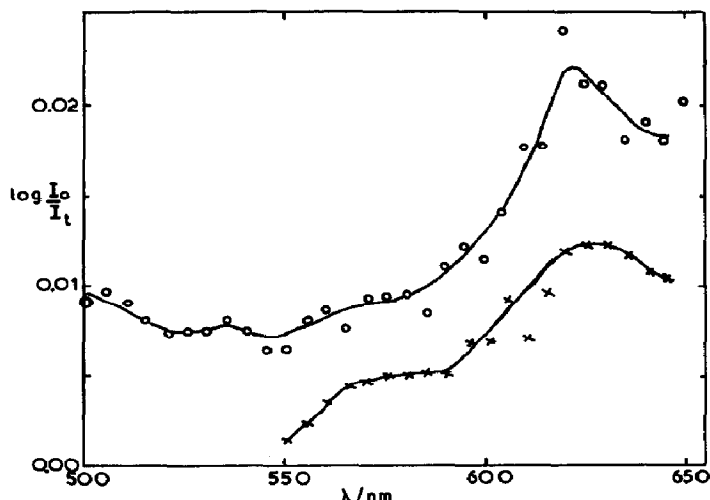


Fig. 2. End-of-pulse transient absorption observed on laser flash photolysis of 12-ethoxycarbonylnaphth[2,3-b]indolizine-6,11-dione (○) and 12-carbamoylnaphth[2,3-b]indolizine-6,11-dione (×) on polyester film.

of the $\pi\pi^*$ level is lowered while the higher energy $n\pi^*$ triplet remains unaffected [7].

The spectroscopic data show that the ethoxy and amino derivatives both have significant fluorescence quantum yields while no fluorescence emission was observed from the anilino derivative (Table 1). Since the extinction coefficients of the absorption spectra show that the radiative lifetimes of the singlet states of all three derivatives are similar, this must mean that the rate of radiationless deactivation of the lowest excited singlet state of the anilino derivative is much faster than that of the other two. A further significant result is that while the ethoxy and the amino derivatives show transient absorption on flash photolysis in toluene and on polyester film (Fig. 2 and Table 1), no transient absorption was observed with the anilino derivative. This indicates that the photoexcited dye is rapidly deactivated in a PET environment and is thus consistent with our view that this rapid deactivation is the main factor responsible for high lightfastness [2, 6, 8].

Finally, it is interesting to note that while the anthraquinone and benzanthrone analogues of the anilino derivative probably owe their high light stability, at least in part, to their ability to form a six membered intra molecular hydrogen bonded ring in the photoexcited state [8], clearly this is not possible with the corresponding indolizine. Any mechanistic explanation for rapid deactivation of these anilino derivatives must therefore include consideration of this particular compound and it is to this end that our current studies in this field are directed.

Experimental

Dyes

The ethoxy derivative (12-ethoxycarbonylnaph(2,3-6)-indolizine-6,11-dione) was prepared from 2,3-dichloronaphthoquinone, ethylacetoacetate and pyridine [9]. Recrystallization from ethanol gave orange needles m.p. 157 - 158 °C (lit. 157 - 158 °C [9]). Alkaline hydrolysis of the ethoxy derivative gave the acid (I; R = -OH) which was converted to the acid chloride (I; R = -Cl) by treatment with thionyl chloride. Reaction of the acid chloride with ammonia in *o*-dichlorobenzene gave the amino derivative (12-carbamoylnaph(2,3-6)indolizine-6,11-dione). Recrystallization from *o*-dichlorobenzene gave red needles, m.p. 314 °C (lit. 314.5 °C [9]). The anilino derivative (12-phenyl-carbamoylnaphth(2,3-6)indolizine-6,11-dione) was prepared from 2,3-dichloronaphthoquinone, ethylacetoacetanilide and pyridine [10]. Recrystallization from dioxane gave bluish-black needles, m.p. 258 °C (lit. 256 - 257 °C [11]).

Dyeing method

The crystalline dyes were ground with a few drops of Dispersol VL (I.C.I.) and made up into a dyebath containing dispersing agent and potassium dihydrogen phosphate. The PET fabric (Terylene, I.C.I.) was dyed under pressure at 130 °C for 1 hour. Plasticizer-free PET film (Melinex, I.C.I.), was dyed in the same way.

References

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- 10 U. S. Pat. 2,772,274 (General Aniline and Film Corp.).
- 11 Br. Pat. 1,046,643 (Ciba-Geigy Ltd.).