

## THE LIGHT FASTNESS AND FLASH PHOTOLYSIS OF BENZANTHRONE DISPERSE DYES ON POLY(ETHYLENE TEREPHTHALATE)

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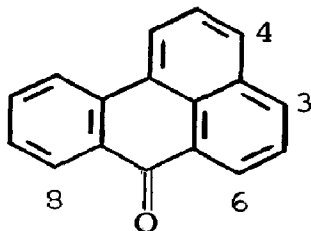
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### Summary

The I.S.O. light fastness grade of 15 benzanthrone disperse dyes on poly(ethylene terephthalate) (PET) fabric has been determined and the flash photolysis behaviour of benzanthrone dyes in PET film has been examined. The dyes of poor light fastness all show transient absorption on flash photolysis and the transients observed on flashing films dyed with benzanthrone and its 3-methoxy-, 6-hydroxy- and 6-amino-derivatives are identified as the triplet states of the dyes. 6-Anilino- and 8-hydroxy-benzanthrone, on the other hand, have good light fastness and films dyed with these derivatives show no transient absorption on flash photolysis. The higher light fastness of PET dyed with 6-anilino- and 8-hydroxybenzanthrone is attributed to the low triplet yields of these dyes.

### Introduction

The light stability of benzanthrone (I) derivatives varies markedly



with molecular structure, both in solution [1, 2] and on polyester fabric [3]. For example, one might expect, by analogy with the behaviour of the benzophenones [4], that substitution of amino or hydroxyl groups *ortho* to carbonyl in the 6 position of the benzanthrone nucleus would lead to high light stability, owing to rapid deactivation of the photo-excited dye within the singlet manifold. However, no significant increase

in light stability is observed [1 - 3]. On the other hand, substitution of an anilino group in the 6 position, or substitution of hydroxyl or amino groups in the 8 position, does lead to an increase in light stability and, in solution at least, this increase appears to be due to rapid deactivation of the photo-excited dye within the singlet manifold [1, 3].

Here we present further light fastness data for benzanthrone disperse dyes in poly(ethylene terephthalate) (PET) and report on a flash photolysis study of these dyes in PET film.

## Experimental

### *Benzanthrone*

6-Acetamidobenzanthrone was prepared from the 6-amino derivative by reaction with acetic anhydride. The product was crystallized three times from acetic acid, m.p. 225 - 226 °C, lit. [5] 224 - 225 °C.

6-*p*-Toluidinobenzanthrone (m.p. 134 - 135 °C, lit. [6] 131 - 132 °C) and 6-*p*-chloroanilinobenzanthrone (m.p. 215 - 216 °C lit. [6] 217 - 218 °C) were prepared by the same general method as that employed earlier [1] for synthesis of the 6-anilino derivative. 6-Benzamidobenzanthrone was the gift of Imperial Chemical Industries Ltd (m.p. 208 - 209 °C lit. [5] 204 - 205 °C). The source and purification of the other benzanthrone has been described elsewhere [1, 7].

### *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 polyester fabric (Terylene, I.C.I.) was dyed under pressure at 130 °C for 1 h, rinsed, reduction cleared and soaped. Plasticizer-free 50  $\mu$ m thick PET film (Melinex, I.C.I.), was dyed in the same way until the absorbance of the dye at 347 nm (the wavelength of the incident light from the frequency doubled ruby laser) was about 1.8.

### *Light fastness determination*

Irradiation was performed in a "Xenotest 150" fadeometer and light fastness was assessed by the I.S.O. test method [8]. The black body temperature of the irradiated surfaces was 35 °C and the effective humidity, determined by the red azoic standard, was 40%.

### *Flash photolysis*

Flash photolysis was performed on the laser nanosecond flash photolysis apparatus described earlier [1]. The dyed films were fixed at an angle of 45° to the laser beam and were in free equilibrium with air.

TABLE 1

I.S.O. light fastness grades and flash photolysis behaviour of benzanthrone disperse dyes on PET

Compound	Light fastness grade	Flash photolysis transients
benzanthrone	1	strong
3-methoxy-	3 - 4	strong
4-hydroxy-	1	strong
4-anilino-	2	weak
6-hydroxy-	1 - 2	strong
6-amino-	1 - 2 RD	strong
6- $\gamma$ -methoxy-propylamino-	1 - 2	strong
6-acetamido-	2	strong
6-benzamido-	2 - 3	weak
6-anilino-	6 - 7	not observed
6- <i>p</i> -anisidino-	6 - 7	—
6- <i>p</i> -toluidino-	6 - 7	—
6- <i>p</i> -chloroanilino-	6	—
8-hydroxy-	8	not observed
8-amino-	2 RD	weak

## Results and Discussion

The I.S.O. light fastness grades of the benzantrones in PET are shown in Table 1. Interestingly, the light stability of the dyes in PET appears to parallel that in solution [2] and this is confirmed by Fig. 1. The results also show, however, that if a benzanthrone dye is to have satisfactory light fastness on PET ( $>4$ ) its quantum yield of disappearance in methanol must be less than about  $10^{-4}$ . Indeed, although in solution the 4-anilino- and 8-amino-benzantrones are an order of magnitude more stable to light than benzanthrone itself [2], the increase in light stability is insufficient to make these derivatives technically useful as disperse dyes for PET.

In our earlier work [2], we have shown that in solution the light stability of the benzantrones is determined by the triplet yield of the dyes, the lower the triplet yield, the higher the light stability. That this also applies to light stability in PET is shown by the laser flash photolysis experiments.

On laser flash photolysis of benzanthrone and its 3-methoxy-, 6-hydroxy- and 6-amino-derivatives in PET film a long-lived ( $t_{1/2} > 10 \mu\text{s}$ ) transient is formed in less than about 100 ns after the flash. Comparison of the absorption spectra of the transients (Figs. 2 and 3) with the triplet-triplet absorption spectra of the dyes [1] reveals the identity of the transients as the triplet states of the dyes. Long-lived ( $t_{1/2} > 10 \mu\text{s}$ )

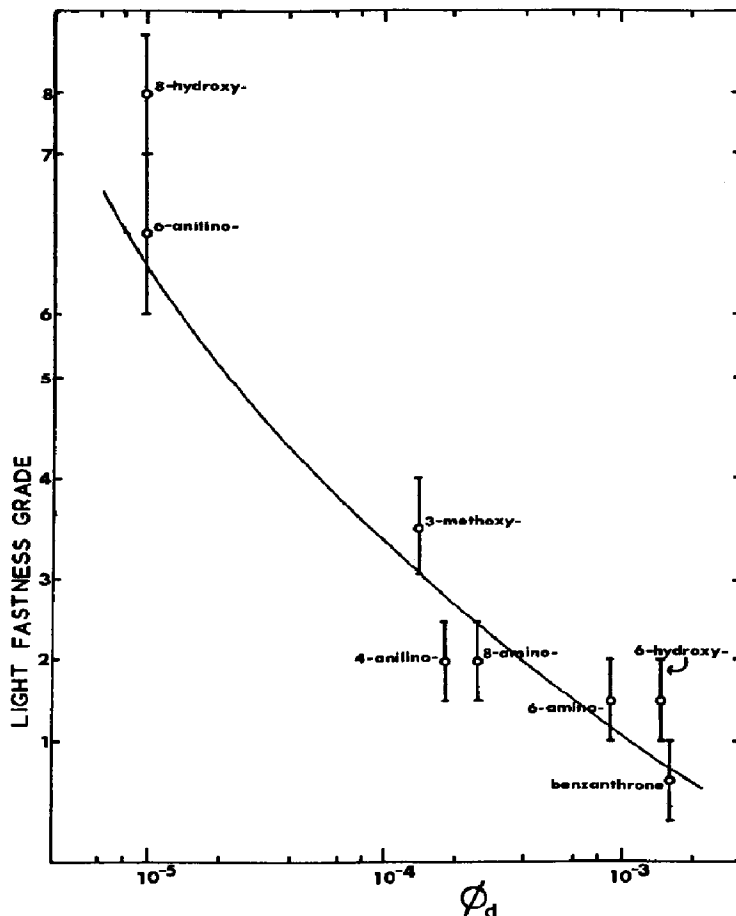


Fig. 1. Relationship between the quantum yield of disappearance of benzantrones in methanol [2] and their light fastness on polyester fabric. The light fastness grades are spaced according to the fastness ratio between successive standards [9].

transient absorption is also observed on flashing a number of other fugitive dyes under these conditions (Table 1). However, no transient is detected on flashing the light-fast 6-anilino- or 8-hydroxybenzantrones showing that, in a polymeric environment as in solution, the high light stability of the 6-anilino- and 8-hydroxy-derivatives is due to their low triplet yields.

One may conclude, therefore, that despite the many factors which can affect the light fastness of dyes in textile fibres [10], the main factor which determines the light fastness of the benzantrones examined in this work is the triplet yield of the dyes, a factor which until recently [3], has been largely neglected.

This work also further illustrates the potential utility of the laser flash photolysis technique as a tool for the investigation of the photochemistry of dyes in their textile environment. The technique has already been used to advantage in studies concerned with the

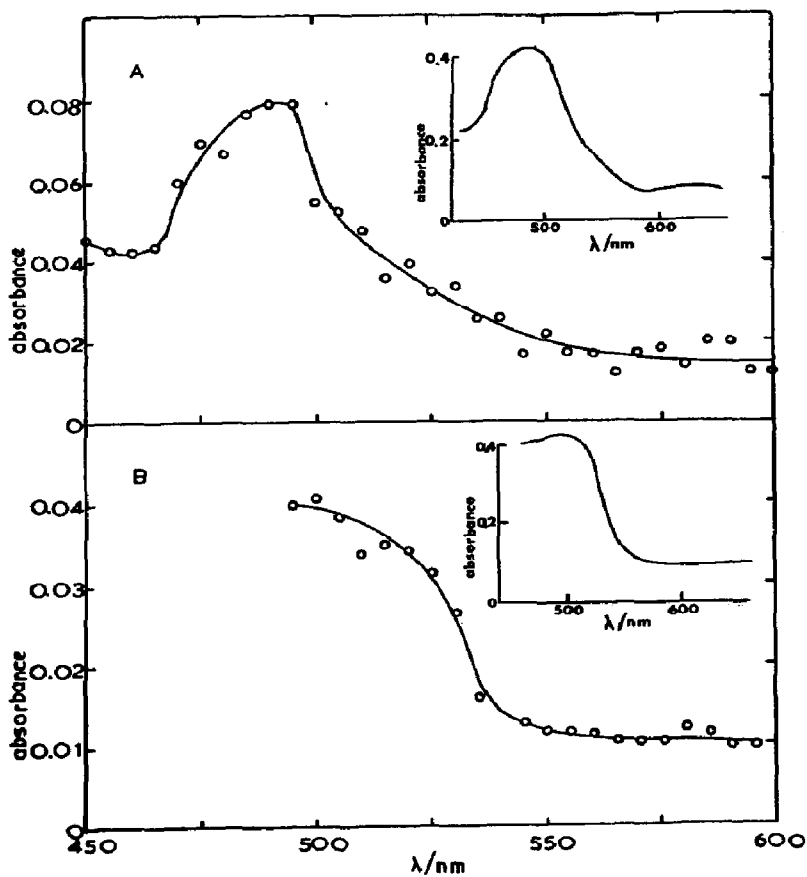


Fig. 2. Absorption spectrum of the transient formed on laser flash photolysis of benzanthrone (A) and 3-methoxybenzanthrone (B) in PET film. The triplet-triplet absorption spectrum of benzanthrone and 3-methoxybenzanthrone in benzene [1] are shown in the inset to A and B respectively.

light fastness of indolizine disperse dyes in PET [11] and the problem of phototendering [12].

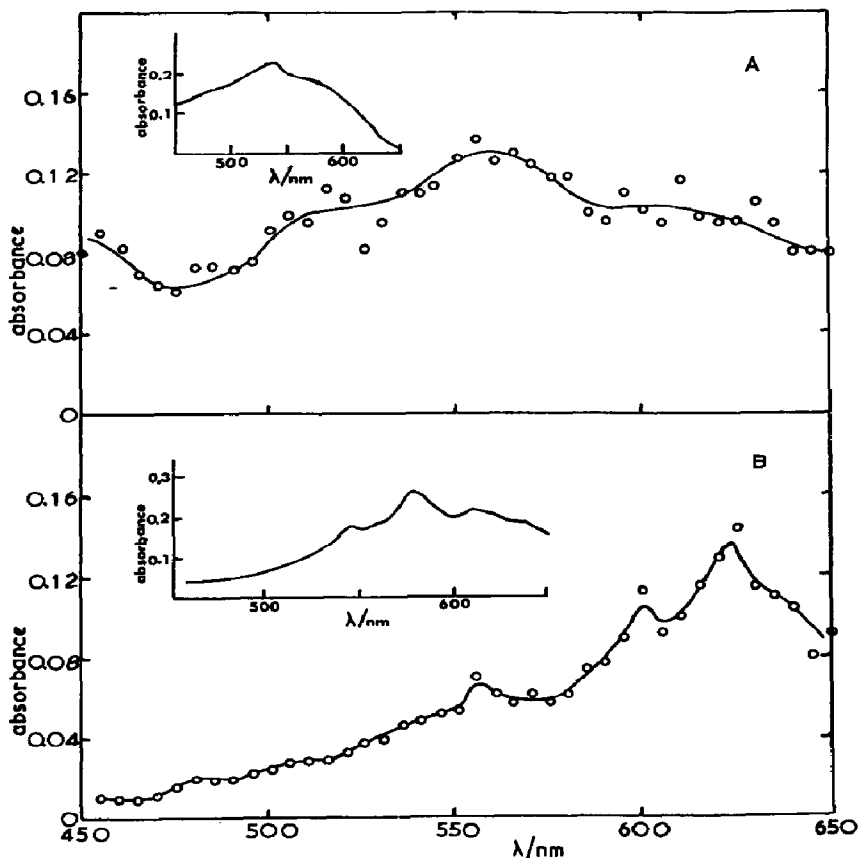


Fig. 3. Absorption spectrum of the transient formed on laser flash photolysis of 6-hydroxybenzanthrone (A) and 6-amino benzanthrone (B) in PET film. The triplet-triplet absorption spectrum of 6-hydroxybenzanthrone and 6-amino benzanthrone in benzene [1] are shown in the inset to A and B respectively.

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