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The Synthesis of Some Benzanthrone Derivatives for Use as Dyes for Polymeric Materials

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ABSTRACT

Three new benzanthrone derivatives containing unsaturated groups have been synthesized and the possibility of their copolymerization with some vinyl monomers until coloured polymers are obtained has been investigated. These polymers have good resistance to wet treatments and to solvents because of dye inclusion in the polymer chain.

1 INTRODUCTION

We have previously reported[1,2] the synthesis of some 1,3,5-triazine derivatives. These dyes contained unsaturated groups in their molecule which made it possible for them to undergo copolymerization with different vinyl monomers. It was found that the polymers thus obtained had good colour resistance to wet treatments and to solvents.

It was therefore of interest to synthesize other dyestuffs on a similar basis, with a view to obtaining properties such as brightness of colour, thermostability, lightfastness and dyeing intensity.

Benzanthrone and its derivatives, have valuable properties and some of them are used for the mass colouration of polymeric materials and in other applications.[3] Benzanthrone was therefore used as the basis for the dye syntheses in this present investigation.

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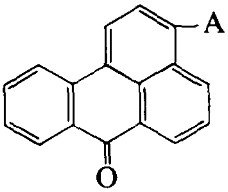
2 RESULTS AND DISCUSSION

Benzanthrone derivatives of the general formula **I** were synthesized:



(I)

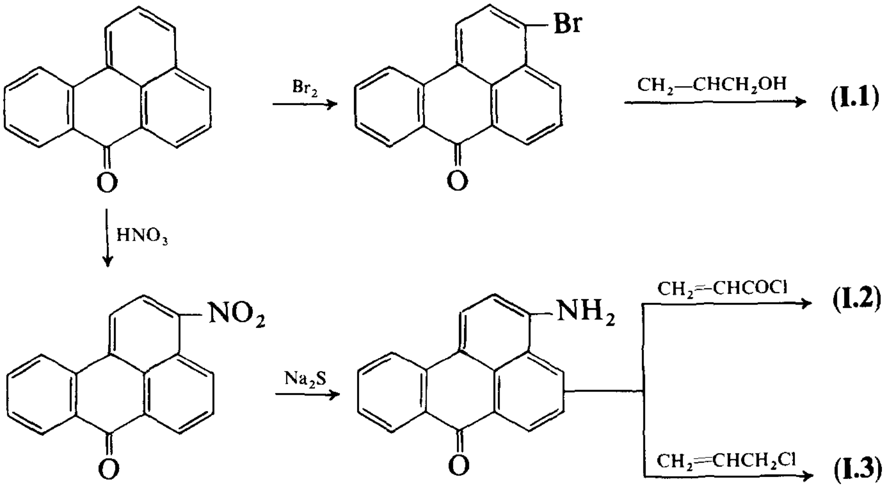
in which A is:

$—OCH_2CH{=}CH_2$ **(I.1)**

$—NHCOCH{=}CH_2$ **(I.2)**

and $—NHCH_2CH{=}CH_2$ **(I.3)**

The route employed in the synthesis was as follows:



Dye **I.1** was synthesized in two ways. Thus, 3-bromobenzanthrone was heated at 120–150°C for 4 h in allyl alcohol in NaOH, giving the product in 60% yield. Much better results were obtained using phase-transfer catalysis with 18-crown-6 at 50°C for 2 h when **I.1** was obtained in 94% yield.

Dye **I.2** was obtained by reaction of 3-aminobenzanthrone and acryloyl chloride ($CH_2{=}CHCOCl$) in pyridine and dye **I.3** by reaction of 3-aminobenzanthrone with allyl chloride ($CH_2{=}CHCH_2Cl$) in DMSO at 120°C in presence of sodium acetate and cupric acetate.

The syntheses were monitored by TLC on alumina and the dyes were purified by column chromatography and characterized by m.p., elemental analysis, NMR and IR spectra. Dyes **I.1–I.3** were, respectively, bright orange, yellow and reddish orange in hue and were fluorescent in organic solvents.

The copolymerization of the dyes with vinyl monomers such as styrene, methyl methacrylate and acrylonitrile in the presence of radical initiators was carried out. It was found that 0·05% concentration of the respective dye in the initial monomer mixture was sufficient to obtain brightly coloured polymers. These polymers retained their colour after five- to six-fold reprecipitation to remove unreacted dye, which indicates that the dye is chemically bound to the polymer chain. This was also established by means of spectrophotometric measurements, which showed that no changes occurred in the basic chromophore group of the dye, either during the process or as a result of the inclusion of the dye in the polymer chain. Colorimetric studies using the method of standard curves showed that the content of dye in the six-fold reprecipitated polymers was 91%, 65% and 69% for Dyes **I.1**, **I.2** and **I.3**, respectively.

Considering that the copolymerization process was not optimized and that these investigations are of a preliminary nature, it is likely that the lower percentage of **I.2** and **I.3** is due to the fact that a part of the dye reacts with the formation of oligomers which are removed during the precipitation. More detailed investigations dealing with the kinetics of the binding of dyes to the polymer chain, the optimum concentration for obtaining deep colours, as well as the influence of the dyes on the properties of the polymer, will be the subject of future reports.

From the initial results reported here, it can be generally concluded that benzanthrone-based dyes, having intensive bright colours and an ability to copolymerize, are suitable for the coloration of polymeric materials either through copolymerization or as polymer dyes.

3 EXPERIMENTAL

All melting points are uncorrected (in °C). Absorption spectra were recorded on a Perkin–Elmer spectrophotometer, IR on Specord (GDR) and NMR spectra on a JEOL-JNM-PS-100.

3-Bromobenzanthrone[4] and 3-aminobenzanthrone[5] were synthesized by described procedures.

3.1 3-Allyloxybenzanthrone (I.1)

3-Bromobenzanthrone (0·06 mol) was dissolved in DMF at 50°C and to the solution was added 0·13 mol allyl alcohol, 0·2 mol KOH and 2 g 18-crown-6.

The mixture was stirred at 50°C for 2 h and was then added to dilute hydrochloric acid (pH = 3). The dye precipitated as an orange yellow solid and this was filtered and dried at 30–40°C in vacuum. The product (94%, m.p. 149–150°C) was purified by column chromatography on alumina to give **I.1** m.p. = 152–153°C (λ_{max} in methanol, 450 nm).

Calculated for $C_{20}H_{14}O_2$: C, 83·9; H, 4·9.
Found: C, 83·6; H, 4·6%.
NMR: 4·5 (d, 2H); 5·1–5·5 (m, 2H); 5·8–6·3 (m, 1H); 7·1–8·6 (m, 8H).
IR: 1580 ($CH_2{=}CH$), 1130–1180 cm^{-1} (C—O—C).

3.2 3-Allylaminobenzanthrone (I.3)

To a solution of 1·6 g 3-aminobenzanthrone in 40 ml DMSO were added 0·51 g sodium acetate and 0·13 g cupric acetate, followed by dropwise addition of 1 ml allyl chloride. The mixture was heated at 120°C for 3–4 h, until evolution of HCl ceased. After cooling, the mixture was kept for 3 h at room temperature before pouring onto water. The product was filtered and dried under vacuum at 30–40°C (yield 90%). It was purified by column chromatography on alumina to give **I.3**, m.p. 200–201°C (λ_{max} in methanol 470 nm).

Calculated for $C_{20}H_5NO_2$: N, 4·9.
Found: N, 5·0%.
NMR: 4·5–4·8 (2H); 5·2–5·6 (m, 2H); 5·9–6·1 (m, 1H); 6·4 (1H).
IR: 3350 (—NH); 1590 cm^{-1} ($CH_2CH{=}CH$—).

3.3 3-Acrylaminobenzanthrone (I.2)

To a solution of 0·02 mol 3-aminobenzanthrone in 50 ml dioxane was added 0·045 mol acryloyl chloride, The mixture was refluxed until evolution of HCl ceased. Trimethylamine (6·8 ml) was then added and heating continued for a further 3 h. The yellowish-orange precipitate was filtered and purified by column chromatography on alumina to give **I.2**, m.p. 185–188°C (λ_{max} in methanol 418 nm).

Calculated for $C_{20}H_{13}NO_2$: N, 4·7.
Found: N, 4·8%.
NMR: 5·1–5·6 (m, 2H); 5·8–6·1 (m, 1H); 6·3–6·5 (1 H).
IR: 3400 (NH), 1650 (CONH), 1590 cm^{-1} ($CH{=}CH_2$).

3.4 Copolymerization of the dyes with vinyl monomers

Styrene or methyl methacrylate (10 g), 2% benzoylperoxide and 0·01 g of dye **I.1**, **I.2** or **I.3** were mixed in an ampoule flushed with pure dry N_2. The ampoule was sealed and heated for 8 h at 80°C. The coloured transparent polymers thus obtained were dissolved in benzene or chloroform and precipitated with methanol. This operation was repeated 5–6 times, until the filtrate was colourless. The polymers thus obtained were dried under vacuum to constant weight and the percentage of chemically bound dye determined by the standard curve method (using solutions of 1 g polymer in 25 ml solvent).

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