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Synthesis of Diquino[2,3-*a*:2′3′-*c*]acridine-6,12,18(5*H*,14*H*,17*H*)trione (Triquinolonobenzene)

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ABSTRACT

The synthesis of triquinolonobenzene from 1,3,5-tribromobenzene and anthranilic acid is described. In contrast to the organic pigment quinacridone, the new compound is colorless, in accord with theoretical considerations.

1 INTRODUCTION

The outstanding lightfastness of the organic pigment quinacridone[1–3] (**I**) and its derivatives is attributed to the high degree of intermolecular hydrogen bonding between the carbonyl and amino groups in the crystal lattice. Correspondingly, intramolecular hydrogen bonding has been shown to be an important photostabilization characteristic for many commercial UV stabilizers.[4,5] Research was therefore undertaken to synthesize the intramolecularly hydrogen bonded quinacridone analog, triquinolonobenzene (**II**).

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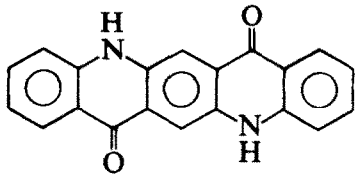
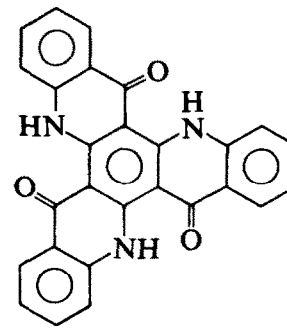


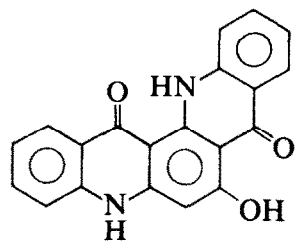
I



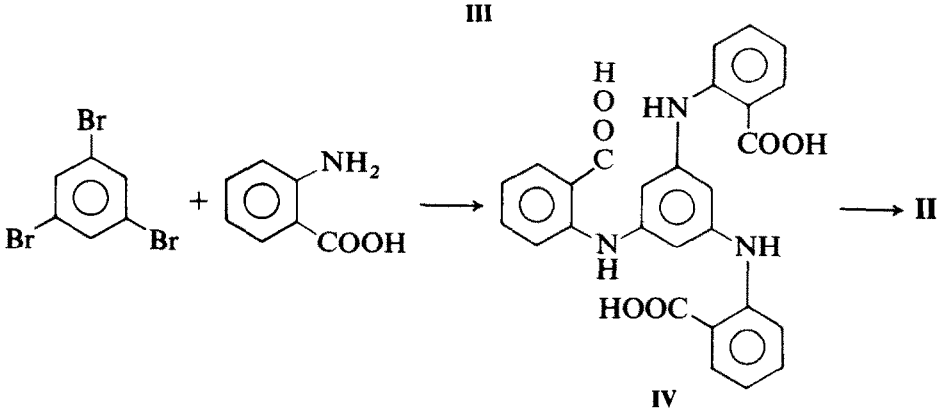
II

2 RESULTS AND DISCUSSION

A desired starting material, viz. the angular quinacridone derivative **III**, was synthesized using the literature procedure by reaction of phloroglucinol with anthranilic acid.[6-8] However, all attempts to replace the remaining hydroxyl group in **III** with a further anthranilic acid moiety were unproductive. Many other approaches to the synthesis of **II** were also unsuccessful, but a process was finally developed by reaction of 1,3,5-tribromobenzene with anthranilic acid. This gave the tricarboxylic acid **IV** in excellent yield, and cyclization of **IV** in polyphosphoric acid gave the desired compound **II**.

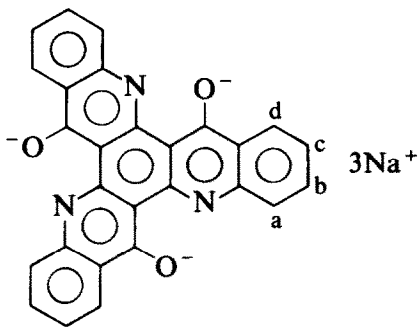


III



IV

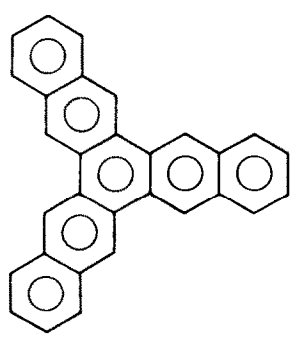
The bromine replacement was effected in refluxing 1-pentanol using an excess of anthranilic acid in the presence of anhydrous potassium carbonate and a copper/copper ion catalyst. The purified tricarboxylic acid **IV** showed correct elemental analysis and neutralization equivalent. Purified **II** showed correct elemental analyses and the sodium salt **V**, obtained by dissolving **II**



V

in DMSO-d_6 + NaOD, gave a 250-MHz ^{1}H-NMR spectrum exhibiting two multiplets centered at δ 7·21 (3H) and 7·55 (3H) assigned to H_c and H_b, respectively, and two doublets centered at 7·69 (3H) and 8·32 (3H) assigned to H_a and H_d, respectively. The assignments were made with the aid of homonuclear decoupling experiments and a spectral comparison with the model compound, 4-quinolone. The mass spectrum of **II** showed the molecular ion peak at *m/z* 429·1114 (calculated value 429·1111). Other prominent mass spectra peaks were at *m/z* 401, 372 and 344. The UV–visible spectrum of **II** in DMF showed λ_{max} (log ε) at 369 nm (4·37); 354 nm (4·57); 323 nm (4·96) and 264 nm (4·79).

Although the angular quinacridone derivative **III**, unlike **I**, is only weakly colored [longest wavelength absorption band in DMF 391 nm (4·20)], the colorless nature of **II** was initially unexpected. However, the fact that the corresponding hydrocarbon naphtho(2′,3′:6,7)pentaphene **VI**[9,10] is also



VI

colorless [longest wavelength absorption band in benzene 389 nm (3·32)[10]] is in accord with the relationship of the visible spectra of **I** [longest wavelength absorption band, in DMF 519 nm (4·12)[3]] and its equivalent hydrocarbon, pentacene [longest wavelength absorption band in benzene 575 nm (4·12)[11]]. Molecular orbital calculations[12,13] which were performed on **I–III, VI** and pentacene are in full agreement with these experimental observations. The calculations successfully predict the hypsochromic character of the quinolone molecules relative to their corresponding hydrocarbons as well as the blue shift of **II** relative to **III**.

3 EXPERIMENTAL

3.1 General

A Bruker WM-250 spectrometer was used for recording the ^{1}H-NMR spectra, with tetramethylsilane as an internal standard. The UV spectrum was measured on a Beckman DK spectrophotometer. The mass spectrum was recorded on a Du Pont 21-110B high-resolution mass spectrometer.

3.2 1,3,5-Tri(*o*-carboxyanilino)benzene (IV)

A stirred mixture of 47·2 g (0·15 mol) of 1,3,5-tribromobenzene, 92·3 g (0·67 mol) anthranilic acid, 92·3 g (0·67 mol) anhydrous potassium carbonate, 1·2 g spongy copper,[14] 1·5 g cuprous chloride, 0·3 g cupric acetate monohydrate, and 263 ml 1-pentanol was refluxed for 5 h. At the end of the reflux period generation of water stopped: the volume of collected product water was 9·9 ml or 97·8% of the theoretical requirement. To the mixture was added 300 ml water and the 1-pentanol was steam-distilled off. The resulting solution (about 500 ml) was clarified by filtration, and the filtrate neutralized to pH 7 with concentrated hydrochloric acid. The precipitated solid was isolated by filtration, washed free of acid with water and dried at 82°C. The yield was 66·4 g (91·6%). A sample of the crude acid was extracted with boiling 80% acetic acid and then recrystallized twice from a 1·7:1 mixture of DMF/H_2O. M.p. > 300°C.

Analysis Calcd for $C_{27}H_{21}N_3O_6$: C, 67·1; H, 4·4; N, 8·7. Found: C, 67·1; H, 4·4; N, 8·7%.

3.3 Diquino[2,3-*a*:2′,3′-*c*]acridine-6,12,18(5*H*,14*H*,17*H*)trione (II)

To 400 g of stirred polyphosphoric acid protected from atmospheric moisture was added 4 g of **IV**, and the mixture was heated for 0·5 h to 150°C and

maintained at 140–150°C for 4 h. The mixture was cooled to 40–50°C and water was slowly added, maintaining the temperature below 60°C, until the vigorous hydrolysis reaction had ceased, after which an excess of water was added. The product was separated by filtration, then washed with water until free of acid, and dried at 80°C. The yield of the colorless product was 3·46 g (97·5%). A similar cyclization of the purified acid gave a 100% yield. Of this material, 200 mg were recrystallized from 800 ml DMF. M.p. >300°C.

Analysis Calcd for $C_{27}H_{15}N_3O_3$: C, 75·5; H, 3·5; N, 9·8. Found: C, 75·2; H, 3·6; N, 10·0%.

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