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Novel Colorants Based on the 9-Oxo-1,9a,10-triaza-9-hydroanthracene Chromophoric System

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SUMMARY

The synthesis of 9-oxo-1,9a,10-triaza-9-hydroanthracene derivatives containing fused ring systems across the 2,3-positions, as examples of a new chromophore system is reported. In particular, the preparation, spectral features and application properties of dyes based on the phenanthro, acenaphtho and isatino derivatives of the above are described.

1. INTRODUCTION

The development of a new chromophore system suitable for the preparation of novel classes of dyes is one of the main research objectives in colour chemistry. We report here the preparation, spectral features and application properties of dyes based on 9-oxo-1,9a,10-triaza-9-hydroanthracene as the first example of the previously undescribed 8-oxo-1,5,8a-triaza-8-hydronaphthalene chromophore.

The new dyes, obtained by a novel double condensation of 2-methyl-3-amino-4-oxoquinazoline with polycyclic orthoquinones, are suitable for use as disperse or pigment colours.

The colour, application properties and end use of these dyes are related to the nature of the quinone moiety: the acenaphtho and phenanthro derivatives are suitable for use as disperse dyes whilst the isatino derivative has pigment characteristics. These dyes are mainly suitable for finishes where high light, sublimation fastness and brightness are required and have colours ranging from very greenish to reddish yellow.

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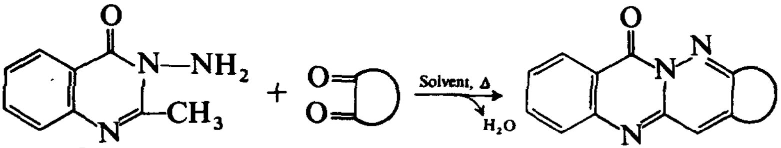
2. RESULTS AND DISCUSSION

9-Oxo-1,9a,10-triaza-9-hydroanthracene derivatives (**III**) are disperse dyes or pigments and can be obtained by reaction between the orthoquinones (**II**) and 2-methyl-3-amino-4-oxoquinazoline (**I**), as outlined in Scheme 1.

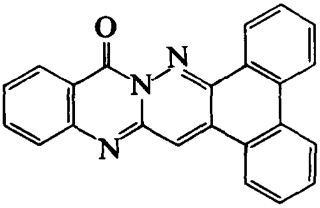


I **II** **III**

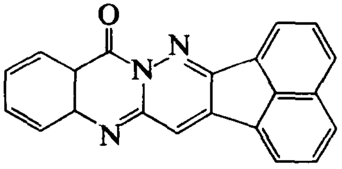
Scheme 1

By reaction of symmetrical polycyclic orthoquinones, such as phenanthro- and acenaphtho-quinones, with the quinazoline **I** two new disperse dyes (**IIIa** and **IIIb**) were obtained.

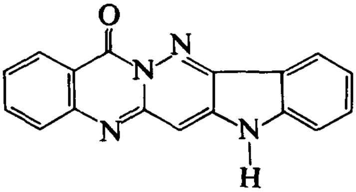
The use of an unsymmetrical orthoquinone containing a heteroatom and with a marked preferential reactivity of one of the two quinone groups, e.g. as in isatin, resulted in the formation of the deeply coloured product **IIIc**.



IIIa

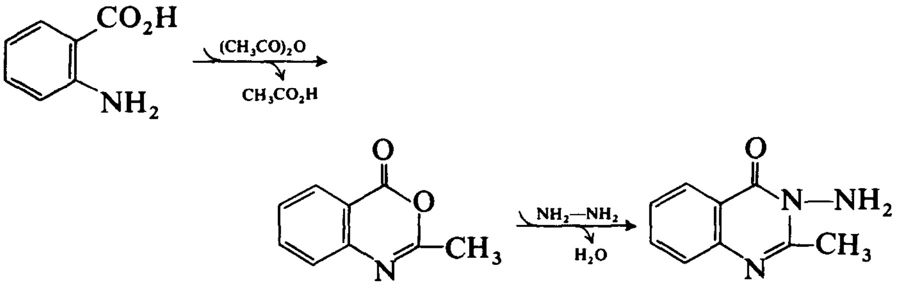


IIIb



IIIc

The quinazoline derivative (**I**) used as starting product in Scheme 1 is a white compound, readily obtainable in good yields by reaction of anthranilic acid with acetic anhydride and hydrazine (Scheme 2).[1]



Scheme 2

Whilst it is well known that the amino group in the quinazoline derivative **I** undergoes condensation reactions with carbonyl compounds such as aldehydes, reactions at the methyl group of **I** have not been previously described. We now wish to report that by using an inert, high-boiling solvent in condensation reactions of **I**, both the methyl and the amino groups can be condensed with aromatic carbonyl groups. e.g. orthoquinones.

Preparation of the 9-oxo-1,9a,10-triaza-9-hydroanthracene derivatives in high yields is readily effected, by condensation of aromatic quinones with **I**, in high-boiling, inert solvents—such as dichlorobenzene or nitrobenzene—at reflux. Pure products are obtained by hot-solvent washing or crystallization from, for instance, methanol, acetic acid or dichlorobenzene.

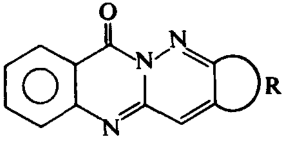
In this manner, the new products **IIIa**, **IIIb** and **IIIc** were obtained. These products were crystalline, soft powders, brightly coloured with pure hues ranging from greenish-yellow (**IIIb**) to golden-yellow (**IIIa**) and reddish-yellow (**IIIc**). The nature of the quinone moiety is related, not only to hue and other application properties of the dyes (Tables 1 and 2), but also to the end use: whilst the phenanthro and acenaphtho derivatives are suitable for use as disperse dyes, the isatino derivative has pigmentary properties and is thus suitable for use in the colouration of paints, printing inks, enamels and plastics.

The 9-oxo-1,9a,10-triaza-9-hydroanthracene derivatives (**III**) can be considered as particular derivatives of a more general chromophoric system based on 2,3:6,7-bis-annelated derivatives of 8-oxo-1,5,8a-triaza-8-hydronaphthalene (**VII**), according to the general Scheme 3.

By the route shown in Scheme 3, a variety of derivatives **VII** can be obtained from various reactive α-aminoacids (**IV**) and α,β-diketones (**VI**). When R_1 and R_2 in **IV** and R_3 and R_4 in **VI** are aromatic systems (which

TABLE 1

9-Oxo-1,9a,10-triaza-9-hydroanthracene Derivatives



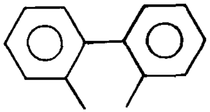
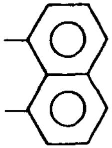
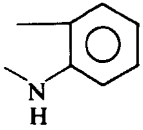
Compound	R	Crystn solvent	Yield (%)	M.p. (°C)	Molecular formula	Elemental analysis (%) Calc. Found C	H	N	Molecular ion M^+	$\lambda_{max}(H_2SO_4)$ (nm)
IIIa		CH_3COOH	75	>300	$C_{23}H_{13}N_3O$	79·5 79·5	3·75 3·7	12·1 12·05	347	415–443
IIIb		*o*-Dichlorobenzene	70	>300	$C_{21}H_{11}N_3O$	78·5 78·5	3·4 3·4	13·1 13·0	321	383–407
IIIc	 N H	Nitrobenzene	60	>300	$C_{17}H_{10}N_4O$	71·3 71·25	3·5 3·5	19·6 19·5	286	400–463

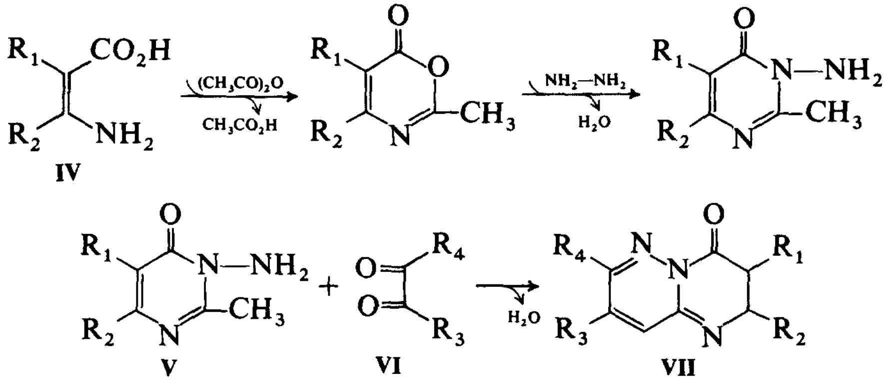
TABLE 2

Application Properties as Disperse Dyes or Pigments of Anthracene Derivatives **IIIa**, **IIIb**, **IIIc**

Sample	*Lightfastness (Xenotest)*								*Sublimation*		*Washing*[a] *Pes–cotton 60°C*			*Rubbing Pes–cotton*		*Migration PVC*
	Pes			*Pes–cotton*			*PVC*		*Pes*							
									Intensity 1/3					*Dry*	*Wet*	
	1/6	*1/3*	*1/1*	*1/12*	*1/6*	*1/3*	*Mass*	*Tint*	*180° × 30 s*	*210° × 30 s*						
IIIa	6–7	6–7	5	4–5	5	5	2–3	2–3	5/5	4–5/4–5	4–5	5	5	4–5	4	1–2
IIIb		6	5	4	4–5	5	2	1	4–5/4–5	4/3–4	4–5	4	4	4	2–3	2
IIIc							5	4–5								3–4

Applications on Pes is referred to 5 g of pure product (dyestuff) on 100 g of Pes.

[a] Washing test: ISO 105/4; values shown refer to loss in depth of original sample.



Scheme 3

can be fused, monocyclic or polycyclic, with or without heteroatoms), the above sequence of reactions can be used to derive a variety of coloured compounds.

Moreover, due to the lack of symmetry in the chromophore structure **VII** we may anticipate the formation of good dyes with a pure hue, either when R_3 and R_4 in **VI** are the same, as, for example, as part of a symmetrical ring system, or when R_3 and R_4 in **VI** are different, i.e., they are part of an unsymmetrical ring system. In the latter case, one carbonyl group of the orthoquinone system must be much more reactive than the other: as, for example, in isatin as used in this present study. The dyes **IIIa, IIIb** and **IIIc** were characterized by means of their mass, UV–visible, ^{13}C-NMR and IR spectral data; their application properties as disperse and pigment dyes are given in Table 2.

2.1. Spectral features

Mass spectra

Molecular ions of dyes **IIIa**, **IIIb** and **IIIc** agreed with the proposed structures (Table 1).

^{13}C-NMR spectra

These were obtained on products **IIIa** and **IIIb** to confirm in more detail the proposed structures. Working with Broad Band and Off-Resonance Proton Decoupling Techniques, we could distinguish between carbon atoms bearing hydrogen and those not substituted by hydrogen atoms. The decoupled spectrum of (**IIIa**) can be divided into two groups of peaks, namely those due to H-bearing carbon-13 atoms and those due to the ten carbon atoms not substituted by hydrogen atoms (see section 3). However, because of the closeness of the chemical shifts in the aromatic range, assignments of non-hydrogen substituted carbons remain speculative. For the compound **IIIc**, only the chemical shift and partially relative multiplicity (s,d) were assigned, because Off-Resonance data exhibited an overlapping of peaks with uncertain assignment, in the range between 131·8 and 131·0.

IR spectra

Spectra of dyes **IIIa, IIIb** and **IIIc** (Fig. 1), show the absence of saturated C—H bonds in the range at 2090 cm^{-1}, whilst at 3050 cm^{-1} aromatic and at 3220 cm^{-1} unsaturated C—H stretching are observed.

Carbonyl stretching frequencies were apparent at 1720–1700 cm^{-1} for the phenanthro and acenaphtho derivatives and at 1690–1700 cm^{-1} for the isatino derivative.

A very intense band at 1540 cm^{-1} was common to all the products **IIIa, IIIb** and **IIIc**, and we consider it to be characteristic of the 9-oxo-1,9a,10-triaza-9-hydroanthracene chromophore, because it seems to be independent of the quinone rings. Several bands were observed between 1660 and 1450 cm^{-1}, varying from medium to intense, and are relatable to the stretching of the complex double-bond system in these structures.

2.2. Application and properties

The phenanthro derivative, **IIIa**, on polyester (Pes) gave a bright golden-yellow dyeing with pale green fluorescence and having excellent fastness to light and sublimation. When applied to polyester/cotton blends by a Dybln-type application process, the resultant dyeing had good fastness to light, washing, dry and wet rubbing.

The acenaphtho derivative, **IIIb**, similarly gave a very greenish fluorescent yellow on polyester and a lemon yellow on polyester/cotton blends.

The isatino derivative, **IIIc**, was a pigmentary crystalline, reddish-yellow material, easily grindable and dispersible, with good fastness to bleeding; on plasticized polyvinyl chloride it exhibited good migration fastness and good overspray on baking enamels.

The isatino derivative has the lowest molecular weight of the dyes studied and is also the least symmetrical structure; nevertheless it has pigmentary features whilst the phenanthro and acenaphtho derivatives

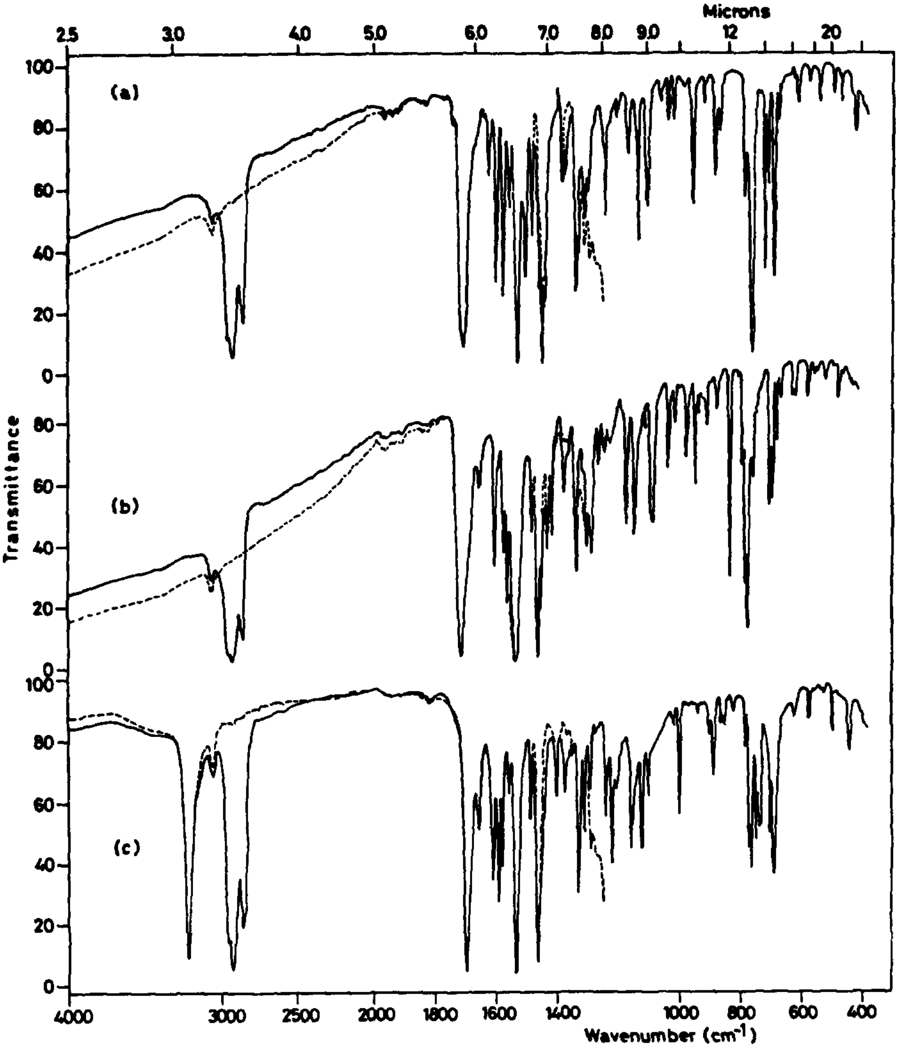


Fig. 1. IR spectra of phenanthro (a), acenaphtho (b) and isatino (c) derivatives **IIIa**, **IIIb** and **IIIc** in nujol (———) and in perfluorokerosine (· · · ·).

acted as disperse dyes: we explain this fact by suggesting the formation of a strong intermolecular H-bonding between a carbonyl of one molecule and the proton of the secondary amino groups of another dye molecule.

3. EXPERIMENTAL

Melting points, determined on a Tottoli apparatus, are uncorrected.

Visible absorption spectra were recorded on a Pye–Unicam SP 1800 spectrophotometer, using H_2SO_4 (96%) as solvent.

Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer as muls in nujol and in perfluorokerosine, with KBr windows.

Low-resolution mass spectra were recorded on a Varian MAT CH5 spectrometer, with coupled data Spectro-System SS200 (ionization potential electron impact 70 eV; direct sample insertion).

^{13}C-NMR spectra were recorded on a Brucker WH-90 spectrometer in Broad Band and Off-Resonance Proton Decoupling, using CF_3COOD as solvent from internal tetramethylsilane (TMS).

Fastness properties were measured according to UNI standards.

3.1. Preparation of 2-methyl-3-amino-4-oxo-quinazoline

Anthranilic acid (27·4 g, 0·2 mol) was refluxed for 3 h in acetic anhydride (82·6 g, 0·8 mol). The crude product (33 g) obtained by dry evaporation, and hydrazine hydrate (98 %), 14·7 g (0·3 mol), and methanol, 50 ml, were stirred at 20 °C with external cooling, and then at 40 °C for 20 min and finally at reflux temperature for 30 min.

The pure white product (m.p. 147–148 °C) was isolated by filtration and washing with methanol (26 g; 74 % yield).

3.2. Preparation of products IIIa, IIIb, IIIc: general method

2-Methyl-3-amino-4-oxo-quinazoline and an equimolar amount of the appropriate orthoquinone (phenanthraquinone, acenaphthenequinone or isatin) were refluxed in a high-boiling solvent (e.g. dichlorobenzene, nitrobenzene) for 6–8 h with removal of water by distillation. Crude products were isolated by filtration followed by washing with *n*-heptane and methanol (Table 1). Pure products were obtained by recrystallization from acetic acid for the phenanthro derivative (**IIIa**), dichlorobenzene for the acenaphtho derivative (**IIIb**) or nitrobenzene for the isatino derivative (**IIIc**).

The nature of products **IIIa** and **IIIb** was confirmed by ^{13}C-NMR (s = singlet, d = doublet).

IIIa: δ_C = 159·3 (s), 149·3 (s), 147·5 (s), 141·6 (d), 139·3 (s), 139·0 (s), 137·6 (d), 135·9 (d), 135·6 (s), 135·1 (s), 131·7 (d), 131·6 (d), 131·4 (d), 130·9 (d), 129·0 (d), 128·1 (d), 126·9 (s), 126·3 (d), 125·6 (d), 125·3 (s), 120·3 (d), 117·5 (d), 116·8 (s).

IIIb: δ_C = 159·6 (s), 158·9 (s), 147·9 (s), 146·0 (s), 141·1 (s + d), 138·7 (s), 135·7 (d), 134·1 (d), 132·5 (s), 131·8 (s), 131·4, 131·2, 131·0, 129·3 (d), 129·0 (s), 128·6 (d), 126·5 (d), 120·3 (d), 117·0 (s), 114·4 (d).

ACKNOWLEDGEMENT

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REFERENCE

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