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Light absorption and stability properties of some near-IR indamine dyes related to Bindschedler's green

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This paper is dedicated to Dr. Geoff Hallas on the occasion of his retirement from the Department of Colour Chemistry, University of Leeds, in recognition of the major contribution he has made to dye chemistry.

Abstract

Symmetrical indamine (quinoneimine) cationic dyes related to Bindschedler's Green have been synthesised by condensing 3-substituted *NN*-dialkylanilines with their corresponding 4-nitroso derivatives in acetic anhydride. The light absorption and general stability properties of the dyes have been examined. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Indamine dyes; Bindschedler's Green analogues; Near-infrared dyes

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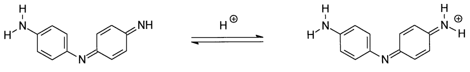
1. Introduction

The indamine, or quinonediimine dyes, are typified by Phenol Blue **1** (*N*-*p*-aminophenylbenzoquinonediimine), which may exist in the neutral form shown or, after facile protonation, as its more bathochromic cation **2**. In some cases an indamine may exist only in the cationic form, the best known example being Bindschedler's Green **3** [1], a particularly long wavelength absorbing dye. Bindschedler's Green was originally synthesised by the oxidation of a mixture of *NN*-dimethyl-p-phenylenediamine and *NN*-dimethylaniline [1], and gives a deep green solution that absorbs in the near infrared (λ_{max} 725 nm in water).



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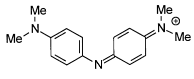

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In general the indamines are hydrolytically unstable, both in acidic and alkaline solution, and because of this, compounds of this type have largely found use as transient intermediates in the synthesis of other, more stable, classes of dye, such as the oxazines, phenazines and phenothiazines [2], rather than as colorants in their own right. However, they do find use in oxidative hair dyeing [3].

Although Bindschedler's Green has been known for many years, relatively little is known about its analogues and about the influence of substituents on its visible absorption spectroscopic properties and hydrolytic stability. Given that this system has attractive light absorption characteristics for

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near-infrared dye applications (e.g. long wavelength absorption, high extinction coefficient, narrow absorption band, and absence of secondary visible absorption bands), we were interested in examining the technical potential of this class of chromophore more closely. Consequently we have synthesised a range of substituted analogues of Bindschedler's Green and have examined the influence of substituents on light absorption characteristics and stability.

2. Experimental

2.1. *General procedure for 4-nitroso-*NN-*dialkyanilines*

The appropriate *NN*-dialkylaniline (0.02 mol) was dissolved in concentrated hydrochloric acid (12 ml) and cooled in an ice bath. A solution of sodium nitrite (1.6 g, 0.023 mol) in water (10 ml) was added slowly, ensuring the temperature did not exceed 5°C. The solution was stirred for 1 h and sodium chloride (1.5 g) was added. The resultant precipitate was filtered off, washed with a little water and dried in a vacuum desiccator. The products were obtained in yields ranging from 22% to 82% and were used directly for the synthesis of the indamine dyes without further purification.

2.2. *General procedure for synthesis of indamine dyes*

A mixture of the appropriate *NN*-dialkylaniline (0.002 mol) and its 4-nitroso derivative (0.002 mol) in acetic anhydride (2 ml) was stirred at room temperature until the reaction was judged to be complete by t.l.c. analysis. The optimum reaction times are summarised in Table 1. The dyes were isolated by one of the following procedures, and their structures confirmed by mass spectrometry. Isolated yields and characterisation data for the dyes **4** and **5** are summarised in Table 1.

2.2.1. *Procedure (i)*

Water (20 ml) was added to the viscous reaction mixture and the solution stirred for several hours to ensure complete hydrolysis of the acetic anhydride. Sodium acetate (0.4 g) was added, and after stirring for a further hour, the solution was filtered and the filtrates extracted with dichloromethane to remove the dye. The dichloromethane extracts were combined and dried over anhydrous magnesium sulphate, and then filtered through a bed of neutral alumina (ca. 5 g) to adsorb the dye. After washing the intensely coloured alumina through with dichloromethane to remove impurities, the indamine dye was washed from the alumina with methanol. Evaporation of the methanol under vacuum afforded the pure dye as its acetate salt (single green spot on t.l.c).

Table 1
Preparative details and characterisation data for dyes **4** and **5**

Compound	Reaction time (h)	Isolation procedure	Yield (%)	Mass spectrum (electrospray)
4a	2	(i)	22	Found: $m/Z = 310$; $C_{20}H_{28}N_3$ reqs. $M = 310$
4b	3	(ii)	77	Found: $m/Z = 424$; $C_{24}H_{34}N_5O_2$ reqs. $M = 424$
4c	3	(i)	5	Found: $m/Z = 378/380$; $C_{20}H_{26}N_3Cl_2$ reqs. $M = 378/380$
4d	2	(i)	17	Found: $m/Z = 422$; $C_{28}H_{44}N_3$ reqs. $M = 422$
4e	4	(i)	[a]	[a]
5a	3	(ii)	[a]	[a]
5b	4	(ii)	62	Found: $m/Z = 532$; $C_{32}H_{46}N_5O_2$ reqs. $M = 532$

[a] Could only be isolated in solution.

2.2.2. *Procedure (ii)*

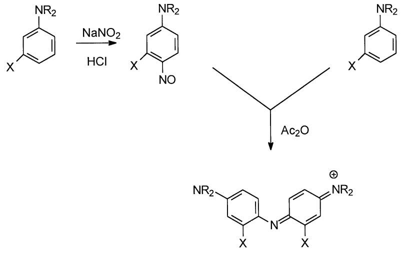
The viscous solution was hydrolysed with water as described in (i), and zinc chloride (0.54 g, 0.004 mol) was added and the mixture stirred for 1 h. The precipitated zinc chloride double salt of the indamine was filtered off, washed with a little water and dried in a vacuum desiccator.

3. Results and discussion

3.1. *Synthesis*

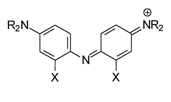
The synthesis of indamines can be effected by various routes. Witt was the first to describe the condensation of 4-nitroso-*NN*-dialkylanilines with anilines having a free para position to give indamines [4]. Nietzki showed that the same chromophoric system could be formed by oxidative coupling of *p*-phenylenediamines with anilines under neutral conditions [5], and Ullman found that similar oxidative coupling between a *m*-phenylenediamine and 4-*NN*-dialkylaminophenol under alkaline conditions could also lead to indamines [6]. Traditionally, Bindschedler's Green is made by the second oxidative coupling method, but as this can lead to complex mixtures from which it is difficult to isolate pure dye it is not suitable for preparation of substituted analogues. We therefore examined the first method, and by following the procedure that we used for similar condensation reactions of 4-nitroso-*NN*-dialkylanilines with acridinium salts [7], it was possible to prepare the substituted dyes **4** and **5** in reasonable yields. Thus the procedure summarised in Scheme 1 was employed, the condensation reaction being effected at room temperature using acetic anhydride both as solvent and dehydrating agent.

Although t.l.c. and absorption spectroscopic analysis indicated in most cases reasonable conversion to the indamine dye, isolation and purification of the dye was problematical. Thus a closer study was made of the parent dye **4a**, the *NN*-diethyl analogue of Bindschedler's Green. In the early literature the use of zinc chloride to precipitate cationic indamine dyes as their less water soluble zinc chloride double salts is suggested. However, this proved unsuccessful in the case of **4a**, as minimal precipitation was found to occur. Instead it was found to be more appropriate to extract the dye as its acetate salt into dichloromethane, in which it had reasonable solubility. T.l.c. analysis of the extracts on alumina showed the presence of two fast moving yellow impurities, with the dye cation strongly retained by the adsorbent. This afforded a convenient means of purification. Thus the dye solution could be filtered through a short column of neutral alumina, when subsequent washing with dichloromethane removed the soluble impurities from the strongly adsorbed dye. The dye could then be extracted from the alumina with methanol, giving a solution of the pure acetate salt. It was notable that whereas solutions of **4a** in methanol were relatively stable (slight colour change over days), solutions in dichloromethane degraded rapidly, the bright green colour turning brown in an hour or two. This is presumably due to traces of acidic impurities that are frequently present in dichloromethane. Whereas extensive degradation of the dye occurred when dichloromethane solutions were evaporated to dryness under vacuum, similar solutions in methanol could be evaporated to give the dye as dark green solid. However the solid dye was not stable unless stored under refrigeration and showed signs of degrading to brown products after a few hours standing.



Scheme 1.

Syntheses of the various symmetrical analogues **4b–h** and **5** were then investigated. Thus the terminal *N*-alkyl functionality was varied, as were the substituents X situated ortho,ortho (with respect to the central nitrogen atom. Acetylamino and hydroxy groups were considered as electron donating substituents and chlorine as an electron withdrawing group. It was anticipated that substituents in these positions would affect the colour and stability properties of the chromophore not only by their electronic effects, but also through their steric interactions with the central nitrogen atom of the indamine system. Although in all cases the appropriate nitroso compound could be prepared in reasonable yields, some of the condensation reactions proved very inefficient and, for example, in the case of the chloro dye **4e** and the bis-tetrahydroquinoline dye **5a** pure solid dyes could not be isolated. However, solutions of the pure dyes in methanol could be obtained, albeit transiently, from which their λ_{max} values were determined.



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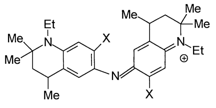
a: R = Et ; X = H
b: R = Et ; X = NHAc
c: R = Et ; X = Cl
d: R = *n*-Bu ; X = H
e: R = *n*-Bu ; X = Cl
f: R = Et ; X = OH
g: R = Et ; X = CO_2H
h: R = Et ; X = SO_3H



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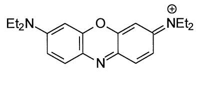
a: X = H
b: X = NHAc



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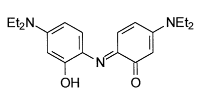

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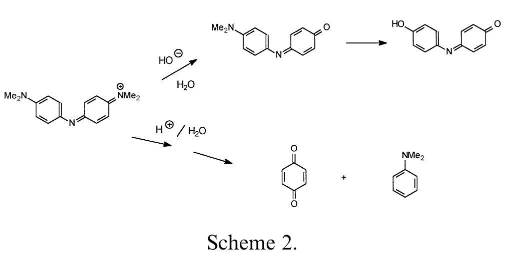
The condensation reaction between *NN*-diethyl-3-hydroxy-4-nitrosoaniline and *NN*-diethyl-3-hydroxyaniline proved unsuccessful, as the product, although intensely coloured, absorbed at much shorter wavelengths (ca. 100 nm) than expected for the indamine structure **4f**. Subsequent investigation showed the product to be the oxazine **6** formed by cyclisation of the initially formed indamine. The alternative hypsochromic neutral indoaniline **7** was discounted, as electrophoresis showed the product to be positively charged. Such a cyclisation is not surprising given the strongly dehydrating conditions used for the condensation [8].

In the case of derivatives **4g** and **4h**, although the requisite nitroso intermediates could be prepared in reasonable yields, subsequent condensation reactions of these with the parent anilines were unsuccessful under the reaction conditions employed. This indicates the sensitivity of the reaction to steric and electronic effects. Steric inhibition due to the bulky carboxylic and sulfonic acid groups in **4g** and **4h** is self-evident. However, the bis(acetylamino) dye **4b** has similar steric crowding yet is formed in good yield. This apparent anomaly can be attributed to the high nucleophilic reactivity of 3-acetylamino-*NN*-diethyl-aniline, which will facilitate its reaction with the nitroso compound, whereas with **4g** and **4h** the corresponding anilines will have a reduced nucleophilic reactivity. The dichloro substituted dyes **4c** and **4e** are formed in poor yields for similar steric reasons, although their somewhat lower steric requirement did enable the reaction to proceed to a limited extent.

3.2. Stability properties

The instability of the indamine system appears to be largely due to its susceptibility to hydrolysis, both under acidic and alkaline conditions. Under alkaline conditions Bindschedler's Green is first converted to phenol blue and then indophenol by successive loss of dimethylamine [9]. However, acid hydrolysis occurs much more easily, and the principal degradation products have been shown to be *p*-benzoquinone and *NN*-dimethylaniline [1] [5]. These hydrolysis reactions are summarised in Scheme 2.

Thus the general instability of the indamines during isolation and storage is more likely to be due to acid-catalysed hydrolysis, and the reaction most probably involves protonation of the central nitrogen atom which would accelerate nucleophilic addition of a water molecule to the chromophore. If this were the case, then one might expect substituents ortho to the central nitrogen to sterically inhibit protonation and thus increase stability, and in agreement with this it was found that the acetylamino- and chloro-substituted derivatives **4b**, **5b** and **4c**, **4e**, respectively, were noticeably more stable than the parent unsubstituted dyes, and could be left longer in solution before degradation became apparent. In addition, the acetylamino derivatives were significantly more stable than the chloro compounds. The latter observation could be due to additional protection of the central nitrogen from protonation by intramolecular hydrogen bonding, as shown in Fig. 1 for **4b**.



Scheme 2.

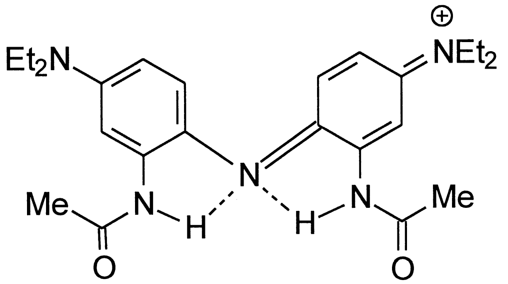


Fig. 1. Possible intramolecular hydrogen bonding in **4b**.

Nevertheless, the stabilities of the substituted derivatives were much too low for any of the dyes to have technical value.

3.3. Colour properties

The visible absorption spectroscopic properties of dyes **4** and **5** are summarised in Table 2. The Bindschedler's Green system should be well suited to the application perturbational MO theory (Dewar's rules), as it is an *alternant* chromophore and is electronically symmetrical [10]. Thus the system may be indexed as shown in Fig. 2, and this shows the positions ortho to the central nitrogen to be *unstarred* positions. Thus electron donor groups and electron acceptor groups attached to these carbon atoms should, respectively, induce hypsochromic and bathochromic shifts of the first absorption band [10].

In agreement with this, it can be seen that the chloro-substituted dyes **4c** and **4f** absorb some 16–17 nm to longer wavelength than their parent unsubstituted dyes **4a** and **4d**. In the case of the acetylamino-subsituted dye **5b** there is a small hypsochromic shift (4 nm) induced by the electron donating substituent, again in agreement with PMO theory. However there is no shift in the case of the dye **4b**. A possible explanation for the apparent lack of effect of the acetylamino group is that intramolecular hydrogen bonding of the type shown in Fig. 1 would induce a bathochromic effect (due to an increase in the positive character of the central unstarred nitrogen atom) which would then offset the expected hypsochromic electron donating effect of this substituent.

Table 2
Visible absorption spectroscopic properties of the indamine dyes in methanol

Compound	λ_{max}/nm)	ε_{max}/(l mol^{-1} cm^{-1})
4a	727	150,000
4b	727	100,000
4c	744	80,000
4d	738	150,000
4e	754	[a]
5a	750	[a]
5b	746	100,000

[a] Could only be isolated in solution.

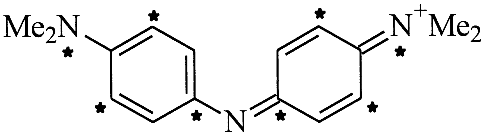


Fig. 2. "Starring" sequence in the Binschedler's Green chromophore.

Modification of the terminal *N*-alkyl groups has the expected effect on λ_{max} values, and thus the *NN*-dibutylamino-substituted dyes are approximately 10–11 nm more bathochromic than their *NN*-diethylamino counterparts. The annelated dyes **5** containing N-ethyl-2,2,4-trimethyltetrahydroquinoline residues are even more bathochromic, as would be expected from the sterically enhanced electron donating effect of the amino nitrogen atoms.

4. Conclusions

The indamine system, as represented by the Bindschedler's Green analogues **4** and **5**, provides bathochromic dyes absorbing in the 720–750 nm range with high extinction coefficients (ca. 10^5 l mol^{-1} cm^{-1}). The effects of substituents on λ_{max} values are consistent with PMO theory. The stability of the system is increased by ring substituents ortho to the central nitrogen atom, and the acetylamino group is more effective in this respect than chlorine. However, improvements in hydrolytic stability are marginal and none of the dyes investigated had sufficient stability for them to be of any practical value as near infrared absorbing materials.

Acknowledgements

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