

Thermodynamic Studies of Disperse Dyes Synthesized From 3,5-dibromo amino benzaldehyde on Polyester Fabrics

By

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ABSTRACT

Ten azo dyes synthesized by coupling of diazotized 3, 5-dibromoaminobenzaldehyde to 3-acetamido N,-diethylaniline and their condensation with active methylene compounds have been thermodynamically studied. Replacement of the two bromo groups by cyano groups in the 3 and 5 positions of the 3, 5-dibromo aminobenzaldehyde affords another series of dyes with bathochromic shift of about 10 nm relative to the dibromo derivatives. The wash fastness properties of the dyes, are adequate, but their light fastness properties are quite low. The thermodynamic parameter values of these dyes were calculated and correlated with the structure of the dye on nylon 6.

INTRODUCTION

The easiest and perhaps the most versatile method of synthesizing method of synthesizing disperse dyes is based on diazotization and coupling reactions. It offers unique advantages of using few intermediate stages, coupled with the colour range obtainable and acceptable fastness properties.

Azo disperse dyes are classified under the donor acceptor chromogen. Here, the chromogen is characterized by having one or more substituents with lone pair of electrons (donor group) and one or more electron attracting substituents (receptor group) attached to the same conjugated π -electron system (conjugating bridge). Recent research efforts are concentrated on receiving the effects of donor and receptor strengths on the colour of the dye¹⁻⁴. Recently, some dyes based on 3-nitrobenzaldehyde as diazo component were reported⁵ and these dyes absorb in the visible region (570-660nm). In the present studies, 3,5-dibromo aminobenzaldehyde was used as diazo component and replacement of the two bromo groups by cyano groups were thermodynamically investigated. Also, the effects of changing these substituents on colour and fastness properties were investigated. The dye obtained by diazotizing the 3, 5-dibromo aminobenzaldehyde with 3-acetamido N, N-diethylaniline was condensed with active methylene compound such as indandione (I), 3-oxo $\Delta^{1,3}$ - indandione (II) 2, 2-indene-1,3-diyldene bispropanedinitrile (III) and malononitrile (IV) to obtain dyes in series 1. The bromo groups in dyes in series (1) were replaced by cyano groups to obtain the dyes in series (2). These dyes were applied to polyester and their fastness properties examined.

Results and Discussion

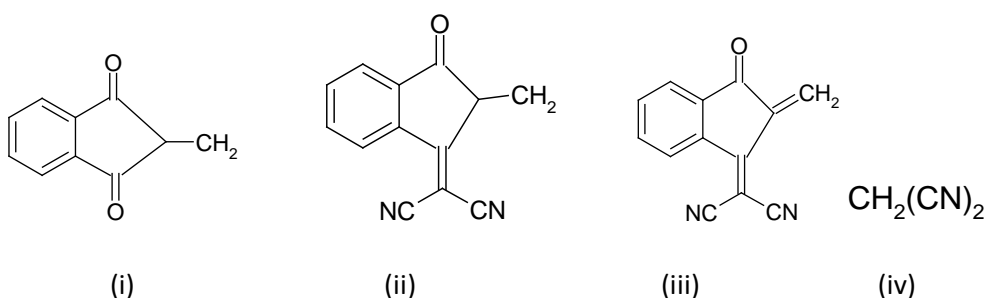
Synthesis of intermediates and dyes

Indandione (I), 3-oxo- $\Delta^{1,3}$ - indandione (II), and 2, 2 indene- 1, 3–diylidene bispropanedinitrile (III) were synthesized the method of (Bello et al1989)⁵. 3, 5-Dibromo para-aminobenzaldehyde was prepared by direct bromination of dimethylaminobenzaldehyde in glacial acetic acid over a period of 15 minutes. The product obtained was characterized by determining the melting point which agrees with the literature value⁷. The 3, 5-dibromo

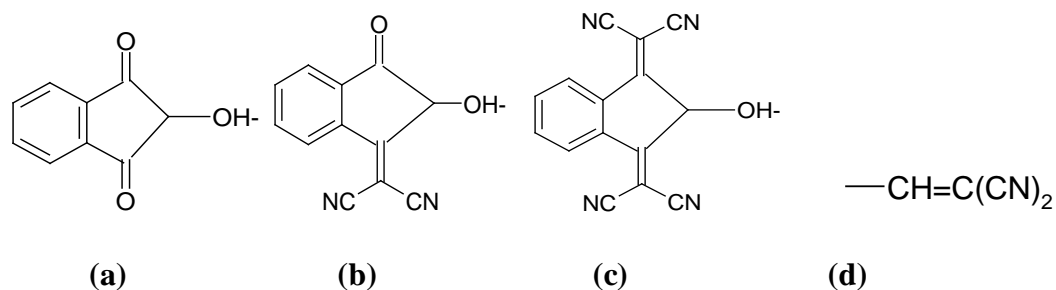
aminobenzaldehyde obtained was diazotized and coupled to 3-acetamido N, N-diethylaniline to get Dye 1. Dye 1 was there condensed with active methylene compounds.(I-IV)

Table 1: Yield and Characterisation Data for the Synthesized Dyes

Dye No.	Yield (%)	Molecular weight	M.Pt (°C)	Recrystallization solvent	Colour of crystals
1	4.0	495.9	100-103	Ethanol	Orange crystals
1a	3.8	623.9	150-151	Toluene	Grey crystals
1b	2.0	695.9	114	Ethanol	Dark crystals
1c	2.0	695.9	119-120	Toluene	Leaflet crystals
1d	11.0	543.9	215-217	Toluene	Blue powder
2	9.1	362.0	250.251	Toluene	Dark crystals
2a	13.5	490.0	313-314	Ethanol	Dark crystals
2b	28.7	526.0	307-310	Toluene	Blue crystals
2c	18.6	562.0	316-320	Toluene	Leaflet needles
2d	22.0	410.0	290-300	Ethanol	Dark crystals



(I) – (IV), to obtain dyes in series (1). The two bromo groups were then replaced with cryano groups to obtain another series of dye in (2). Yield, melting points and physical characterization and thermodynamic parameter values of the dyes are summarized in Table 1.



Visible absorption spectra of the dyes

The visible absorption properties of the dyes are measured in dimethylformamide (DMF) and the results obtained are summarized in Table 2, Dye (1) which was obtained by coupling 3, 5-dibromo aminobenzaldehyde with 3-acetamido-N, N-diethylaniline absorbs at 585nm and condensation of dye (1) with active methylene compounds to give Dye 1a, gave a slight bathochromic shift of 5nm from 585 nm to 590 nm and in fact when dye (1) was condensed with manolonitrile, there is no visible change (shift) in the observed λ_{\max} . Even with this, there is a reduction in the standard affinity from 13.86kJmol^{-1} to 13.2kJmol^{-1} . The insensitivity of the dyes in this group to a significant change in visible absorption wavelength may be due to high molecular mass bromo groups which can interfere with easy movement of the lone pair of electrons on the β -nitrogen. This will also prevent complete planarity of the chromogen and therefore limits the absorption maxima of the dyes despite the increasing electron withdrawing strength of the active methylene groups incorporated. The molar extinction coefficients of the dyes in this series are also low due to the same steric interference.

Table 2: Visible Absorption Spectra for the Dyes		
Dye No.	λ_{\max} in DMF/nm	molar extinction coefficient ($\lambda_{\max} \times 10^4$) $1\text{mol}^{-1}\text{cm}^{-1}$
1	585	1.289
1a	590	3.957
1b	592	9.554
1c	595	6.186
1d	585	4.131
2	610	5.147
2a	605	5.870
2b	600	7.416
2c	587	6.663
2d	600	8.590

The dicyano groups counterparts recorded higher λ_{\max} and molar absorption coefficient. This means that the rod like nature of the cyano group interfered to a lesser extent than the dibromo group. This is also a reflection of the thermodynamic parameter values, such as the partition coefficient (K) and the standard affinities ($\Delta\mu^{\theta}$) as shown in Table 3. These thermodynamic parameter values are relatively higher for Dye 2 series than Dye 1 series as shown in Table 3. It is also evident from the data on Table 2 that the bathochromic effect of the active methylene compounds incorporated into the acceptor half of the chromogen follows a similar pattern. The order of bathochromic shift of the dye follows; $c > b > d > a$ formyl-azo dye i. e. .
 Dye in $(c) > (b) > (d) > (a) >$ formyl-azo dye.

The reasons for the small bathochromic shift observed when the active methylene compounds are incorporated are clearly evident. Quantitatively, bathochromic shift is determined by two opposing factors at the acceptor ring; these are electron withdrawing strength of the acceptor group and the steric influence of the atoms attached to the ring. Dyes in (c); derived from 2, 2-indene-1,3-diylidene bispropandinitrile, though might suffer from steric hindrance due to the positioning of the two cyano groups at one carbon atom is not much affected adversely because of the rod-like shape of the cyano groups. Wherever this steric interference might incur

on the maximum wavelength (λ_{\max}) it is always counter balanced by strong electron – withdrawing affinity of maximum cyano group. A strong electron-withdrawing group attached to the acceptor ring in such a situation is believed to lead to increased conjugation thus lowering the ionization potential across the molecules and therefore bringing about a bathochromic shift.

Table 3: Percentage dye exhaustion on polyester					
Dye No.	Percentage exhaustion (%E)	Molecular weight	Shade on polyester	K lkg⁻¹	$\Delta\mu^{\theta}$ kJmol⁻¹
1	65	495.9	Pink	92.85	13862.7
1a	53	623.9	Light pink	56.38	12336.4
1b	36	659.9	Bright pink	28.13	10209.22
1c	38	659.9	Dull pink	30.64	10470.7
1d	60	543.9	Light violet	75.0	13209.5
2	70	362.0	Purple	116.7	14562.26
2a	63	490.0	Blue	85.13	13597.2
2b	80	526.0	Blue	200	16210.5
2c	90	562.0	Bright blue	450	18691.5
2d	60	410.0	Blue violet	75.0	13209.5

K = partition coefficient, $\Delta\mu^{\theta}$ = standard affinity Shade= hue of the colour on fabric

Table 4: Wash and light fastness properties of the dyes on polyester

Dye No.	Change in colour (%)	Staining on white polyester	Light fastness rating
1	3	4	3.4
1a	3	3-4	2-3
1b	3-4	4	2
1c	4-5	4	2
1d	4-5	4-5	2-3
2	2-3	4	3
2a	3	3	2-3
2b	3-4	3-4	2
2c	2-3	4-5	3-4
2d	3-4	4	3

Member of dyes in series (b); derived from 3-oxo Δ^1 , indandione gave more bathochromic colours than member of dyes in (a); derived from indandione simply because the former has two cyano groups, i.e. increased conjugation than the latter.

Dye exhaustion on polyester fibre

The percentage dye exhaustion was determined by applying the dyes on polyester using the exhaustion method. The dyeing was carried out at 95°C with a liquor ratio of 1:50. The optical density of the dye bath was determined before dyeing and after dyeing. From these two measurements, the percentage dyes exhausted (%E) on to the fibre was calculated

$$\% (E) = \frac{D_A - D_B}{D_A} \times \frac{100}{1} \%, \text{ which is related to absorbance as}$$

$$\% (E) = \frac{A_o - A_t}{A_o} \times \frac{100}{1} \%$$

Where A_o =absorbance at time zero, A_t =absorbance at time t

and the thermodynamic parameters such as partition coefficient (K) and standard affinities of the dyes on polyester were also determined. The results obtained are summarized in Table 3.

It can be observed from Table 3 that, to a large extent, the exhaustion of the dye onto the fabric is inversely proportional to the molecular weight of the dyes in series 1, while the percentage exhaustion for series 2 is directly proportional to the molar mass of the dye. It can also be observed that the percentage exhaustion of the dyes based on 2, 2-indene-1, 3-diylidene bispropanedinitrile proved to have higher substantivity than their 3-oxo- Δ^1 , 3 indandione counterpart, in some cases even better than the dyes based on indandione. This can be explained by the fact that both indandione and 3-oxo- Δ^1 , 3 indandione are having at least an oxygen atom in their structure. This can participate in hydrogen bond formation inside the fibre structure, while 2, 2-indene-1, 3-diylidene bispropanedinitrile does not carry any oxygen atom or hydrogen-bonding heteroatoms in its structure. This hydrogen bonding capability of the former dyes can hinder their diffusion onto the fibre as reported by Glenzel *et al*⁸. Another possible explanation is that, oxygen being more spherical than cyano group, can contribute to more molar volume factor and therefore less substantive⁹. This explanation can be extended to explain why the 3, 5-dicyano dyes are more substantive than the 3, 5-dibromo derivatives. All these explanations are further reflected in the values of thermodynamic parameters of the dyeing process on polyester. Dye 2c which has a standard affinity of about 18.7 kJmol^{-1} has the highest exhaustion of 90 %, while its

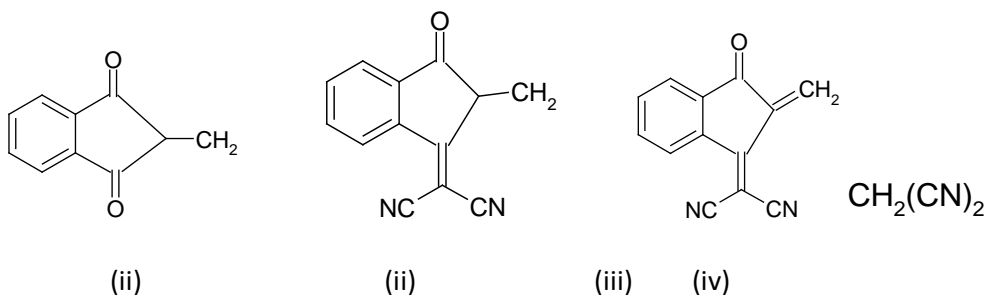
counterpart in series i.e. 1c has standard affinity of 10.4 kJmol^{-1} , with percentage exhaustion of 38.

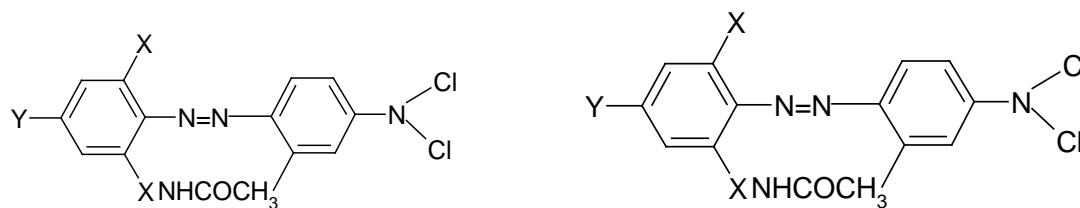
Fastness properties of the dyes

Both the wash and light fastness properties of the dyes synthesized were determined using the standard methods⁹. The results obtained are summarized in Table 4. It is generally observed that the wash fastness for the 3, 5-dibromo derivatives recorded better washing fastness than their dicyano counterparts. This can be explained from the point of view of the large molecular weight of the former which afforded their low diffusion and higher resistance to washing. The light fastness recorded by the dyes generally was not very impressive for all as shown in Table 4.

Conclusion

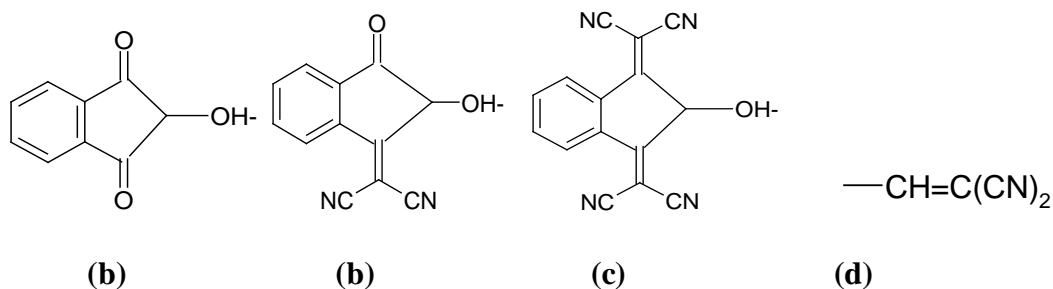
It can be concluded from the study that the incorporation of electron withdrawing group with bulky dibromo groups leads to interference of the free movement of the electron from the β -nitrogen atom and to obtain highly bathochromic dyes less bulky and rod-like cyano groups are preferred. This is demonstrated by the standard affinities of the dyes on polyester fabric. i. e. those Dyes with high exhaustion recorded high standard affinities and indeed high values of partition coefficient. However, the relatively low molecular weight of cyano group had negative effect on the washing and to some extent also on the light fastness properties.





(1) Y = CHO, X = Br

(2) Y = CHO, X = CN



Experimental

3, 5-dibromo para-amino benzaldehyde

This was prepared by dissolving 68.39g (0.43 moles) of bromine in 40CC glacial acetic acid. The solution was then added dropwise to 30g of 4-dimethylamine benzaldehyde (0.2 moles) in 96cm³ glacial acetic acid over a period of 15 minutes. After a further 45 minutes of stirring and cooling in an ice bath, orange crystals were obtained. It was washed thoroughly with benzene and then dried overnight over sodium hydroxide. The product obtained after drying was then heated for 3 hours at 135°C. Yield, 50.3g (89.7%), and M.pt. 148-149°C (Lit. 7 149.5-150°C).

Diazotization of 3,5-dibromo amino benzaldehyde

3, 5-Dibromo amino benzaldehyde 5.58g (0.02 moles) was dissolved in a mixture of 25cc acetic acid and 6cm³ water. The solution was cooled with stirring to 12°C. To this solution was added dropwise 1.5g (0.02 mole) sodium nitrite dissolved in 10cm³ of water. 10cm³ of HCl was

then added immediately and the mixture maintained at 10-20°C for 15 minutes. Excess nitrous acid was destroyed with a small amount of urea. The solution was diluted with 200cm³ of ice water to obtain a clear solution of the diazonium salt.

Coupling of the Diazonium Salt with 3-acetamido-N, N-diethylaniline was dissolved in a mixture of 300cm³ of ice water and 5cm³ HCl. To this solution was added gradually the solution of the diazonium salt. The pH was maintained at 4 by adding sufficient quantities of sodium acetate. Stirring was continued for 2 hours. The dye obtained was filtered out, washed thoroughly with water and then recrystallized from ethanol.

Synthesis of dyes in series (2)

Replacement of the dyes in series (1) with cyano groups to get dyes in (2) was carried out by reacting equimolar amount of the dye and cuprous cyanide in dimethylformamide under reflux for 30 minutes. The suspension formed was poured into 100cm³ cold water. The precipitated solid was washed thoroughly with water and then dried overnight. Pure samples were obtained by recrystallisation from toluene.

Condensation of dye (1) with active methylene compounds

This was done by following the procedure used by Bello et al⁶.

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