Disperse dyes based on 2-methyl-3-[3'-aminophthalimido]-4(3H)-quinazolinone

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Abstract: A series of new heterocyclic disperse dyes has been prepared by subsequent diazotization of 2-methyl-3-[3'-aminophthalimido]-4(3H)-quinazolinone and coupling with various mono- and di-N-substituted derivatives of aniline. All the disperse dyes were characterized by their percentage yield, melting point, UV-visible spectrum, elemental analysis, infrared spectrum and dyeing performance on nylon 66 and polyester fibres. The percentage dye bath exhaustion on different fibres was found to be reasonably good and acceptable. The dyed fibres showed fair to fairly good to good fastness to light and very good to excellent fastness to washing, rubbing, perspiration and sublimation.

Keywords: 3'-aminophthalimido; quinazolinone; synthesis; nylon 66 fibres; polyester fibres; dyeing properties.

INTRODUCTION

Disperse dyes from amino heterocycles, such as quinoline,1,2 isoquinoline,3 cinnoline,4 phthalazine, quinoxaline5–7 and quinazoline8,9 have been reported in the patent literature as being promising disperse dyes. It has been shown that dyes based on the 4-ketoquinazoline moiety10,11 possess good fastness properties and high stability. Phthalimide derivatives of 4-ketoquinazoline have been reported12 but the synthesis of 2-methyl-3-[3'-aminophthalimido]-4(3H)-quinazolinone and disperse dyes based on the same moiety have not been reported so far. In the present paper some disperse dyes based on this heterocyclic moiety are reported.

The substituents and their position were selected so as to increase their auxochromic effect in the final azo structure and so to have a variety of shades. The dyeing performance of these dyes were examined on nylon 66 and polyester fibres. Disperse dyes of the following structure were prepared.

where R= various mono and di-N-substituted aniline derivatives, as listed in Chart-I.

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Reaction scheme.

Chart I
EXPERIMENTAL

All melting points are uncorrected and are expressed in °C. The IR spectra were recorded on a Nicolet Impact – 400 D FT-IR spectrophotometer using the KBr pellets technique. The $^1$H-NMR spectra were recorded on a Hitachi R-1500 instrument, using TMS as the internal standard. Chemical shifts are given in δ (ppm). The absorption spectra of the dye solutions in DMF were recorded on a Shimadzu UV 240 instrument. Fastness test to light, sublimation and perspiration was assessed in accordance with AATCC/15/1985. The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC/88/1988, and the wash fastness test in accordance with IS: 765-1979.

Preparation of 3-amino-2-methyl-4(3H)-quinazolinone

The title compound was prepared following a sequence of reactions according to a procedure described in the literature.$^{13-16}$ Yield 80%, m.p. 143 °C, IR (KBr): 3496br cm$^{-1}$ (–NH stretching of –NH$_2$), 1696s cm$^{-1}$ (N–C=O) of quinazolinone and 1310 cm$^{-1}$ (C–H stretching of aromatic methyl). Mol. formula: C$_9$H$_9$N$_3$O. Found: %C: 68.61, %H: 5.34, %N: 15.57. Calcd.: %C: 68.97, %H: 5.75, %N: 16.09. $^1$H-NMR (CDCl$_3$): δ 7.28 to 8.29 ppm (4H, m, aromatic proton), δ 4.94 ppm (2H, s, aromatic amine) and δ 2.12 to 2.70 ppm (3H, s, aromatic methyl).

Preparation of 2-methyl-3-[3'-nitrophthalimido]-4(3H)-quinazolinone

The title compound was prepared according to a procedure described in the literature.$^{12}$ Yield 74 %, m.p. 194–5 °C; IR (KBr): 1530 cm$^{-1}$ and 1360 cm$^{-1}$ (–N=O stretching of aromatic nitro), 1696s cm$^{-1}$ (N–C=O) of quinazolinone and 1310 cm$^{-1}$ (C–H stretching of aromatic methyl). Mol. formula: C$_{17}$H$_{10}$N$_4$O$_5$. Found: %C: 57.92, %H: 2.44, %N: 15.47. Calcd.: %C: 58.29, %H: 2.86, %N: 16.00. $^1$H-NMR (CDCl$_3$): δ 7.27 to 8.26 ppm (7H, m, aromatic proton), δ 3.97 ppm (2H, s, aromatic amine) and δ 2.52 ppm (3H, s, aromatic methyl).

Diazotization of 2-methyl-3-[3'-aminophthalimido]-4(3H)-quinazolinone

Diazotization of the title compound was carried out by the usual method.$^{17}$

Coupling of the diazo solution with N-(2-hydroxyethyl)aniline (Formation of D$_1$)

N-(2-Hydroxyethyl)aniline (0.37 g, 0.0027 mol) was dissolved in hydrochloric acid (10 % w/v). The solution was diluted with water (6 ml) and cooled to 0–5 °C. To this well stirred solution, a freshly prepared diazo solution at 0–5 °C was added dropwise in about 45 min, whereby the temperature was maintained below 5 °C. Stirring was continued for 24 h at 0–5 °C maintaining the pH in the range 5.0 to 6.0 by the addition of the required amount of an ice-cold solution of sodium carbonate (10 % w/v). The product was filtered, washed several times with water and dried at 40 °C. The brown solid thus obtained was dissolved in a minimum amount of dimethylformamide and precipitated by the addition of chloroform. Yield 75 %, m.p. 198–199 °C, IR (KBr): 3453br cm$^{-1}$ (–NH stretching), 1696s cm$^{-1}$ (N–C=O) of quinazolinone and 1310 cm$^{-1}$ (C–H stretching of aromatic methyl) and 1559s cm$^{-1}$ (–N=N– stretching of azo group). Mol. formula: C$_{25}$H$_{20}$N$_6$O$_4$. Found: %C: 63.72, %H: 3.87, %N: 17.44. Calcd.: %C: 64.10, %H: 4.27, %N: 17.95.
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<th>Dye</th>
<th>Coupling component R</th>
<th>Mol. formula</th>
<th>Mol. wt g/mol</th>
<th>Yield %</th>
<th>M.p. °C</th>
<th>λ\text{max}/nm (log ε)</th>
<th>%Found (% Calcd.)</th>
<th>%Exhaustion</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>N*</th>
<th>P*</th>
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<td>C_{25}H_{20}N_{6}O_{4}</td>
<td>468</td>
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<tr>
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<td>C_{26}H_{22}N_{6}O_{4}</td>
<td>482</td>
<td>72</td>
<td>185–8</td>
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<td>77</td>
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<td>71</td>
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<td>\textit{N. N}-bis(2-hydroxyethyl)-\textit{m}-chloroaniline</td>
<td>C_{27}H_{23}N_{6}O_{5}Cl</td>
<td>546.5</td>
<td>84</td>
<td>183–5</td>
<td>465 (4.45)</td>
<td>58.89 (59.29)</td>
<td>68</td>
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<td>\textit{N. N}-bis(2-hydroxyethyl)-\textit{m}-toluidine</td>
<td>C_{28}H_{26}N_{6}O_{5}</td>
<td>526</td>
<td>75</td>
<td>200–2</td>
<td>475 (4.32)</td>
<td>63.49 (63.88)</td>
<td>78</td>
<td>73</td>
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<td>D7</td>
<td>\textit{m}-acetamido-\textit{N. N}-bis(2-hydroxyethyl)-aniline</td>
<td>C_{29}H_{27}N_{7}O_{6}</td>
<td>569</td>
<td>72</td>
<td>160–2</td>
<td>478 (4.15)</td>
<td>60.75 (61.16)</td>
<td>74</td>
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<td>D8</td>
<td>\textit{N}-methyl-\textit{N}-(2-cyanoethyl)-aniline</td>
<td>C_{27}H_{21}N_{7}O_{3}</td>
<td>491</td>
<td>80</td>
<td>190–2</td>
<td>482 (4.27)</td>
<td>65.60 (65.99)</td>
<td>73</td>
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<td>D9</td>
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<td>C_{28}H_{23}N_{7}O_{3}</td>
<td>505</td>
<td>76</td>
<td>195–8</td>
<td>486 (4.21)</td>
<td>66.19 (66.53)</td>
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<td>530</td>
<td>82</td>
<td>189–90</td>
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<td>65.29 (65.66)</td>
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<td>80</td>
<td>182–5</td>
<td>510 (4.32)</td>
<td>62.09 (62.42)</td>
<td>80</td>
<td>78</td>
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<tr>
<td>D12</td>
<td>\textit{N. N}-bis-(2-acetoxyethyl)-\textit{m}-chloroaniline</td>
<td>C_{31}H_{27}N_{6}O_{7}Cl</td>
<td>630.5</td>
<td>72</td>
<td>190–2</td>
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<td>58.62 (59.00)</td>
<td>85</td>
<td>81</td>
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<td>\textit{m}-acetamido-\textit{N. N}-diethylaniline</td>
<td>C_{29}H_{27}N_{7}O_{4}</td>
<td>537</td>
<td>75</td>
<td>185–8</td>
<td>450 (4.15)</td>
<td>64.43 (64.80)</td>
<td>73</td>
<td>70</td>
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<td>D14</td>
<td>\textit{m}-propionamido-\textit{N. N}-diethylaniline</td>
<td>C_{30}H_{29}N_{7}O_{4}</td>
<td>551</td>
<td>70</td>
<td>180–2</td>
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<td>64.97 (65.34)</td>
<td>70</td>
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</table>

*All the melting points are uncorrected, λ\text{max} in DMF; N* – nylon; P* – polyester;
RESULTS AND DISCUSSION

Heterocyclic compounds of 2-methyl-3-[3’-aminophthalimido]-4(3H)-quinazolino-
ne were prepared by the condensation of 3-amino-2-methyl-4(3H)-quinazolinone with
3-nitrophthalic anhydride followed by reduction with Fe/HCl in methanol.

A series of disperse dyes (D1 to D14) was prepared by diazotization of 2-me-
thyl-3-[3’-aminophthalimido]-4(3H)-quinazolinone and coupling with various couplers,
as listed in Chart I. Diazotization was carried out by the usual procedure using sodium ni-
trate and hydrochloric acid and the coupling was done in a moderately acidic medium at
0–5 ºC. The characterization data, absorption maxima (λ_max) and logarithm of molar ex-
tinction coefficient (log ε) of the 2-methyl-3-[3’-aminophthalimido]-4(3H)-quinazolinone
dyes are given in Table I. Dyeing of nylon 66 and polyester fibres with all the dyes was car-
rried out following a high temperature dyeing technique using a glycerin bath “Labora-
tory High Temperature Dyeing Machine” containing twelve beakers. The absorption max-
ima of the disperse dyes (D1 – D14) were recorded in DMF. The absorption maxima were
in the range of 450 nm to 510 nm. The dyes were characterized by their infrared spectrum,
all the dyes showed characteristic bands at 1559s cm⁻¹ (–N≡N–) stretching. The dyes D3
and D12 showed a band at 836s cm⁻¹ for C–Cl stretching. The dye D8, D9 and D10 showed
a broad band at 2240–2260 cm⁻¹ for (–C≡N) stretching.

These dyes were applied on nylon 66 and polyester fibres as disperse dyes, which
gave variety of hues ranging from golden yellow, light brown to dark brown.

The data in Table I reveals that the position of the value of λ_max depends on the nature
of the substituents at the terminal amino group as well as on the phenyl ring. A bathochromic shift was observed, the magnitude of which depended on the nature of sub-
stituents at the terminal amino group. The following trend was observed.

\[
\begin{align*}
N-\text{H} & < N-\text{CH}_3 \\
\text{CH}_2\text{CH}_2\text{OH} & < \text{CH}_2\text{CH}_2\text{OH} \\
N-\text{C}_2\text{H}_5 & < \text{CH}_2\text{CH}_2\text{OH} \\
N-\text{CH}_2\text{CH}_2\text{OH} & < \text{CH}_2\text{CH}_2\text{OH}
\end{align*}
\]

D-1 (λ_max = 460nm) D-2 (λ_max = 465nm) D-3 (λ_max = 468nm) D-4 (λ_max = 471nm)

Similarly, in case of cyano substituted derivatives of aniline, a bathochromic shift was observed in the following order:

\[
\begin{align*}
N-\text{CH}_3 & < N-\text{C}_2\text{H}_5 \\
\text{CH}_2\text{CH}_2\text{CN} & < \text{CH}_2\text{CH}_2\text{CN} \\
N-\text{CH}_2\text{CH}_2\text{CN} & < \text{CH}_2\text{CH}_2\text{CN}
\end{align*}
\]

D-8 (λ_max = 482nm) D-9 (λ_max = 486nm) D-10 (λ_max = 486nm)

A bathochromic shift was also observed on introduction of –NHCOCH₃ into the
phenyl ring at the ortho position to the azo group (D-4 to D-7). A similar comparison of
D-13 and D-14 also showed a bathochromic shift on displacing –NHCOCH₃ with
–NHCOCH₂H₅. Introduction of a methyl group in the phenyl ring ortho to the azo group
also showed a bathochromic shift of 4 nm (D-4 and D-6). On the other hand, a
hypsochromic shift was observed with the introduction of a chlorine group into the phenyl
ring (D-4 to D-5 and D-11 to D-12).
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<th>Dye</th>
<th>Light fastness</th>
<th>Washing fastness</th>
<th>Rubbing fastness</th>
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<td>P*</td>
<td>N*</td>
<td>P*</td>
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</table>

N* – nylon, P* – polyester
The data of percentage exhaustion on the nylon 66 and polyester fibres were calculated by a known method\(^{19}\) and are given in Table I. The higher percentage exhaustion on the nylon 66 fibres is to be expected due to its relatively open structure.\(^{20}\)

Data of the fastness properties given in Table II show that the light fastness ranges from fair to fairly good to good for all the disperse dyes. The higher the rating is, the better is the fastness. The fastness to washing, rubbing, perspiration and sublimation are very good to excellent for all the prepared disperse dyes. The fastness to washing was determined using cotton fabric for the evaluation of the staining. This indicates the good penetration and affinity of these disperse dyes for the fibres.

CONCLUSION

Disperse dyes based on 2-methyl-3-[3'-aminophthalimido]-4(3H)-quinazolinone were synthesized. These dyes gave mostly golden yellow and light brown to dark brown shades on nylon 66 and polyester fibres having very good to excellent washing fastness properties on both substrates. The dyes have better exhaustion on nylon than on polyester, probably due to the greater accessibility of the pore structure in nylon.

Acknowledgement: One of the authors (Vijay H. Patel) is thankful to the Gujarat Government for a Research Fellowship.

IZVOD

DISPERZNE BOJE ZASNOVANE NA DERIVATIMA

2-METIL-3-[3'-AMINOFTALIMIDO]-4(3H)-HINAZOLINONA

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Синтезоване су нове хетероцикличне дисперзне боје сукуцесивним диазотовањем 2-метил-3-[3'-аминофталимидо]-4(3H)-хиназолинона и куповањем са различитим моно- и ди-N-супституисаним дериватима анилине. Све дисперзне боје окрашени су својим процентним приношом, тачком топљења, UV-Vis спектром, елементалном анализом и IR спектром, као и спо собности бојења влакана од најлона 66 и полиестера. Процен тно испитивање купата за бојење различитих влакана показало се релативно добро и прихватљиво. Обојена влакна показала су добр о до врло добр о отпорност на светлост, као и врло добр о до одличну отпорност на прашење, тржење, зној и сублимацију.

(Примљено 10. јануара, ревидирано 27. јула 2002)

REFERENCES
