October, 1980] *Bull. Chem. Soc. Jpn.*, ***53***, *3007—3011 (1980)* 3007

# Synthesis of Some Disperse Anthraquinone Dyes

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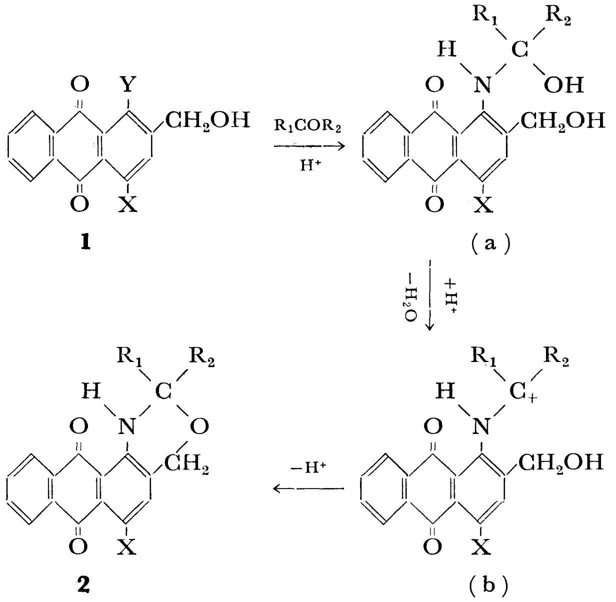
(Received October 22, 1979)

1-Hydroxy- and/or 1-aminoanthraquinones was allowed to react with formaldehyde in an alkaline medium to give 1-hydroxy- or 1-amino-2-hydroxymethyl-9,10-anthracenediols, which gave by air oxidation, (hydroxymethyl) anthraquinone derivatives. Interaction of 1-amino-2-(hydroxymethyl)anthraquinone or its 4-bromo derivative with carbonyl compounds in the presence of an acid catalyst gave 1,3-oxazine derivatives (**2**). The methylene group in position-2 of the 1,3-oxazine ring was found to be highly reactive and reacted with carbonyl compounds to form the corresponding 2-arylmethylene derivatives. Selective oxidation of dimethyloxazine derivatives with $SeO_2$ gave the corresponding dialdehyde, which interacted with aromatic amines to give the corresponding Schiff's bases. The bromine atom in the 6-position of **2** was easily replaced by aromatic amines to give blue disperse dyes.

Originally introduced as dyes for acetate fibers, disperse anthraquinone dyes are now used for a wide range of fiber types, such as polyamide, polyester, triacetate, and acrylics. The lightfastness of this class of disperse dyes is dependent on the substrate. Dyeings on acetate exhibit marginally higher lightfastness than those on nylon 66, while those on polyester are highest. Giles and Rahman[1)] suggest that one parameter controlling the lightfastness of a disperse-dyed fiber is the regain of the substrate. Hence the rate of photofading on polyester may be retarded because access of water vapour to the dye particle is restricted.

Most anthraquinone disperse dyes contain either one or two amino groups (free or substituted), usually in the 1- and 4-positions. The substitution pattern can have a marked effect on the lightfastness of such dyes as shown by nature and position of both *N*- and nuclear substituents.[2)] The aim of this work is to prepare some new disperse anthraquinone dyes provided by annellation of heterocyclic moiety namely the oxazine ring to the anthraquinone nucleus. The selection of oxazine ring is based on the fact that little is known in the literature concerning the structural factors that influence their application as disperse dyes for synthetic fibers. This paper is devoted for the chemistry of these dyes, while application and factors affecting fastness properties on synthetic fibers will be delt later. An extension of this area of investigation will be a comparison of the electron impact-induced fragmentation patterns of these dyes with their lightfastness on polyester.

1-Hydroxy- and 1-aminoanthraquinones react in an alkaline medium with formaldehyde or formaldehyde/aliphatic amines to give 2-(hydroxymethyl)- or 2-(aminomethyl)-substituted 9,10-anthracenediols which undergo an intramolecular redox reaction to yield the corresponding methyl-substituted anthraquinones.[3)] If the reaction is interrupted by oxidation, (hydroxymethyl)- or (aminomethyl)anthraquinones can be isolated[4)] (*cf.* Table 1). Interaction of carbonyl compounds with 1-amino-2-(hydroxymethyl)anthraquinone or its 4-bromo derivative in the presence of dilute hydrochloric acid as a catalyst gave 1,3-oxazine derivatives (**2**).[5)] The reaction mechanism probably involves an amino aldehyde addition reaction to give intermediate (a) which under acidic conditions loses water to form the carbonium ion (b). Deprotonation of this ion leads to the 1,3-oxazine derivatives (**2**). The reaction course can be represented as follows:



In favour of the formation of the postulated carbonium ion intermediate in the proposed mechanism is the fact that such reactions occured faster and with higher yields in case of ketones which gave the more stable tertiary carbonium ion. With formaldehyde, the reaction was found to be the lowest among the other aldehydes.

The 1,3-oxazine ring is responsible for a considerable bathochromic shift in the absorption spectra of such derivatives as compared with the starting 1-amino-2-(hydroxymethyl)anthraquinones. The IR spectra indicated the presence of NH absorption bands beside the methylene hydrogen (*cf.* Table 2).

The methylene group in the oxazine nucleus proved to be active and react with carbonyl compounds in the presence of anhydrous zinc chloride as a catalyst to give the corresponding 2-arylmethylene derivatives (**3**). The reaction can be represented as follows:

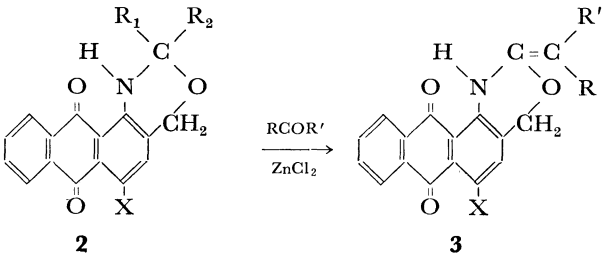


TABLE 1. (HYDROXYMETHYL)ANTHRAQUINONE DERIVATIVES (**1**)

| X | Y | Z | Mp<br>°C | Solvent of crystallization a) | Yield<br>% | Mol formula | N/% b) Calcd | N/% b) Found | $\lambda_{max}^{EtOH}$/nm (log $\varepsilon$) |
|---|---|---|---|---|---|---|---|---|---|
| H | $NH_2$ | H | 200—201 | A | 95 | $C_{15}H_{11}O_3N$ | 5.53 | 5.50 | 472(3.86) |
| $NH_2$ | $NH_2$ | H | 224—227 | B | 49 | $C_{15}H_{12}O_3N_2$ | 10.44 | 10.22 | 548(4.16) |
| H | $NH_2$ | $NH_2$ | 210 | C | 14 | $C_{15}H_{12}O_3N_2$ | 9.39 | 9.60 | — |
| Cl | $NH_2$ | $NH_2$ | 242 | C | 22 | $C_{15}H_{11}O_3NCl$ | 4.87 | 4.82 | 475(3.86) |
| Br | $NH_2$ | H | 242 | D | 94 | $C_{15}H_{10}O_3NBr$ | 4.22 | 4.17 | 472(3.86) |
| H | OH | H | 210—212 | B | 60 | $C_{15}H_{10}O_4$ | — | — | 408(3.83) |
| OH | OH | H | 203—205 | C | 38 | $C_{15}H_{10}O_5$ | — | — | 480(3.98) |

a) A, Ethanol; B, acetone; C, benzene; D, toluene. b) Satisfactory analyses for C, H, and Br were obtained.

TABLE 2. 1,3-OXAZINE DERIVATIVES (**2**)

| $R_1$ | $R_2$ | Mp<br>°C | Solvent of crystallization a) | Yield<br>% | Mol formula | N/% b) Calcd | N/% b) Found | $\lambda_{max}^{EtOH}$/nm (log $\varepsilon$) | $\nu$ (IR)<br>$cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| H | H | 250 | A | 85 | $C_{16}H_{10}O_3NBr$ | 4.07 | 4.33 | 489(3.69) | N-H 3320<br>C-O 1080 |
| $C_6H_5$ | $C_6H_5$ | 215 | B | 76 | $C_{28}H_{18}O_3NBr$ | 2.82 | 3.20 | 488(3.74) | N-H 3240<br>C-O 1090 |
| H | $C_4H_3O$ | 183 | C | 82 | $C_{20}H_{13}O_4NBr$ | 3.41 | 2.99 | 486(3.69) | N-H 3260<br>C-O 1100 |
| H | $C_{14}H_8NO_2$ | 168 | D | 72 | $C_{30}H_{17}O_5N_2Br$ | 3.01 | 3.06 | 488(4.14) | N-H 3300<br>C-O 1090 |
| H | *p*-$(CH_3)_2N$-$C_6H_4$ | 120 | B | 82 | $C_{24}H_{19}O_3N_3Br$ | 6.05 | 6.50 | 480(3.56) | N-H 3340<br>C-O 1090 |
| H | *o*-Cl-$C_6H_4$ | 95 | E | 86 | $C_{22}H_{14}O_3NClBr$ | 3.07 | 2.91 | 486(3.81) | N-H 3300<br>C-O 1080 |
| H | *p*-$NO_2$-$C_6H_4$ | 220 | D | 92 | $C_{22}H_{13}O_5N_2Br$ | 6.02 | 6.17 | 486(4.77) | N-H 3300<br>C-O 1100 |
| $CH_3$ | $CH_3$ | 160—162 | E | 92 | $C_{18}H_{14}O_3NBr$ 1) | 3.77 | 3.65 | 490(3.88) | N-H 3290<br>C-O 1100 |
| H | *o*-HO-$C_6H_4$ | 210 | D | 82 | $C_{22}H_{14}O_4NBr$ | 3.21 | 3.11 | 482(3.91) | N-H 3280<br>C-O 1090 |
| H | *p*-Cl-$C_6H_4$ | 180—182 | E | 80 | $C_{22}H_{14}O_3NClBr$ | 3.07 | 3.62 | 478(3.95) | N-H 3280<br>C-O 1100 |
| H | *p*-HO-$C_6H_4$ | 223—225 | F | 82 | $C_{22}H_{14}O_4NBr$ | 3.21 | 3.45 | 478(3.95) | N-H 3280<br>C-O 1060 |
| H | *p*-$CH_3$-$C_6H_4$ | 260 | G | 78 | $C_{23}H_{16}O_3NBr$ | 3.22 | 3.44 | 478(3.89) | N-H 3320<br>C-O 1100 |
| H | *m*-$NO_2$-$C_6H_4$ | 235 | D | 78 | $C_{22}H_{13}O_5N_2Br$ | 6.02 | 6.64 | 482(3.91) | N-H 3280<br>C-O 1060 |
| H | *o*-$NO_2$-$C_6H_4$ | 230—232 | D | 80 | $C_{22}H_{13}O_5N_2Br$ | 6.02 | 6.54 | 478(3.96) | N-H 3280<br>C-O 1100 |
| H | $C_6H_5$ | 220 | D | 83 | $C_{22}H_{14}O_3NBr$ | 3.33 | 2.99 | 488(3.86) | N-H 3300<br>C-O 1080 |
| H | $C_2H_5$ | 186 | D | 88 | $C_{18}H_{14}O_3NBr$ | 3.78 | 3.88 | 488(4.64) | N-H 3300<br>C-O 1100 |
| H | *p*-$CH_3O$-$C_6H_4$ | 220 | G | 90 | $C_{23}H_{16}O_4NBr$ | 3.11 | 3.45 | 488(3.93) | N-H 3300<br>C-O 1090 |
| H | *m*-HO-$C_6H_4$ | 230 | G | 88 | $C_{22}H_{14}O_4NBr$ | 3.21 | 3.41 | 488(3.93) | N-H 3300<br>C-O 1080 |
| $CH_3$ | $C_6H_5$ | 208 | G | 80 | $C_{23}H_{16}O_3NBr$ | 3.22 | 3.15 | 477(3.89) | N-H 3290<br>C-O 1080 |
| $C_6H_5$ | $\underset{\overset{\mid}{OH}}{CH}-C_6H_5$ | 135 | D | 78 | $C_{29}H_{20}O_4NBr$ | 2.66 | 3.03 | 488(3.64) | N-H 3300<br>C-O 1080 |
| H | H | 162 |  | 82 | $C_{16}H_{11}O_3N$ 2) | 5.28 | 4.94 | 495(3.95) |  |
| $CH_3$ | $CH_3$ | 155 |  | 91 | $C_{18}H_{15}O_3N$ 1) | 4.77 | 4.71 | 494(3.92) |  |
| H | $CH_3$ | 172 |  | 91 | $C_7H_{13}O_3N$ | 5.02 | 5.12 | 494(3.84) |  |
| H | $C_2H_5$ | 183 |  | 85 | $C_{18}H_{15}O_3N$ | 4.78 | 4.83 | 477(4.02) |  |
| H | $C_6H_5$ | 210 |  | 92 | $C_{22}H_{15}O_3N$ | 4.10 | 4.23 | 498(4.12) |  |

a) A, Toluene; B, benzene; C, dil methanol; D, dil acetic acid; E, acetone; F, dil ethanol; G, ethanol. b) Satisfactory analyses for C, H, and Br were obtained.

The resulting products are highly coloured and have high melting points. Their structures were established by elemental analyses as well as (IR) spectral data (*cf.* Table 3).

Oxidation of 2,2-dimethyl-1,2-dihydro-4*H*-anthra[1,2-*d*][1,3]oxazine-7,12-dione or its 6-bromo analogue with selenium dioxide gave the corresponding dialdehyde derivatives (**4c, d**).

The dialdehyde derivative (**4d**) was found to be highly reactive and condense readily with *o*-phenylenediamine, *p*-aminophenol, and *p*-anisidine to give the corresponding Schiff's bases (**5e—g**), respectively.

1,3-Oxazine derivatives prepared in this work and containing bromine atom in the 6-position were subjected to reaction with amines, whereby the bromine atom was substituted by amino group. The introduc-

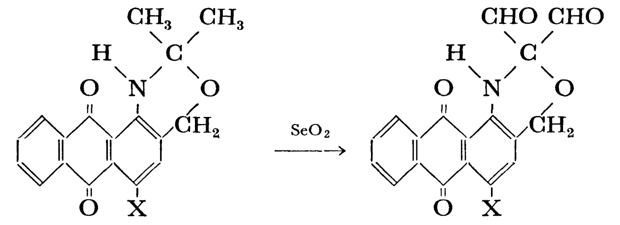


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Table 3. 2-Arylmethylene-1,3-oxazines (**3**)

| R | R′ | Mp<br>°C | Solvent of crystallization[a] | Mol formula | N%[b] | | ν (IR)<br>cm$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | | | Calcd | Found | |
| H | *p*-$CH_3O$-$C_6H_4$ | 260 | A | $C_{24}H_{16}O_4NBr$ | 3.09 | 3.87 | N-H 3400<br>C-O 1100<br>C=C 1660 |
| H | *p*-$CH_3$-$C_6H_4$ | 270 | B | $C_{24}H_{16}O_3NBr$ | 3.21 | 2.70 | N-H 3400<br>C-O 1060<br>C=C 1660 |
| H | *p*-HO-$C_6H_4$ | 280 | C | $C_{23}H_{14}O_4NBr$ | 3.21 | 3.34 | N-H 3400<br>C-O 1060<br>C=C 1670 |
| H | *o*-Cl-$C_6H_4$ | 285—288 | C | $C_{23}H_{13}O_3NBrCl$ | 3.00 | 2.54 | N-H 3400<br>C-O 1100<br>C=O 1670 |
| H | $C_6H_5$ | 295 | C | $C_{23}H_{14}O_3NBr$ | 3.24 | 2.94 | N-H 3400<br>C-O 1100<br>C=C 1670 |
| H | *o*-HO-$C_6H_4$ | 235 | A | $C_{23}H_{14}O_4NBr$ | 3.12 | 2.67 | N-H 3400<br>C-O 1100<br>C=C 1660 |
| $C_6H_5$ | $C_6H_5$ | 300 | C | $C_{29}H_{18}O_3NBr$ | 2.75 | 2·87 | N-H 3400<br>C-O 1110<br>C=C 1660 |
| H | $C_5H_5O$<br>(2-furyl) | >300 | D | $C_{21}H_{12}O_4NBr$ | 3.31 | 3.38 | N-H 3400<br>C-O 1100<br>C=C 1670 |
| $CH_3$ | $C_6H_5$ | 305 | E | $C_{24}H_{16}O_3NBr$ | 3.13 | 3.06 | N-H 3400<br>C-O 1110<br>C=C 1665 |
| H | $C_{14}H_8O_2N$<br>(1-amino-9,10-dioxo-2-anthryl) | 270 | A | $C_{31}H_{17}O_4N_2Br$ | 4.99 | 4.83 | N-H 3390<br>C-O 1100<br>C=C 1670 |
| H | *p*-$NO_2$-$C_6H_4$ | 283 | C | $C_{23}H_{13}O_5N_2Br$ | 5.87 | 5.71 | N-H 3390<br>C-O 1100<br>C=C 1660 |
| H | *m*-HO-$C_6H_4$ | 290 | A | $C_{23}H_{14}O_4NBr$ | 3.14 | 2.96 | N-H 3400<br>C-O 1060<br>C=C 1670 |
| H | *o*-$NO_2$-$C_6H_4$ | 265 | C | $C_{23}H_{13}O_5N_2Br$ | 5.87 | 5.43 | N-H 3400<br>C-O 1100<br>C=C 1680 |
| H | *m*-$NO_2$-$C_6H_4$ | 280 | F | $C_{23}H_{13}O_5N_2Br$ | 5.87 | 5.27 | N-H 3420<br>C-O 1100<br>C-C 1670 |
| H | *p*-Cl-$C_6H_4$ | 285 | C | $C_{23}H_{13}O_3NBrCl$ | 3.00 | 3.27 | N-H 3410<br>C-O 1100<br>C=C 1670 |

a) A, Dil acetic acid; B, toluene-pet. ether; C, DMF; D, pyridine; E, benzene-pet. ether; F, 1-butanol. b) Satisfactory analyses for C, H, and Br were obtained.

TABLE 4. BLUE ANTHRA[1,2-*d*][1,3]OXAZINE-7,12-DIONE DISPERSE DYES (**6**)

| $R_1$ | $R_2$ | R | Mp °C | Yield % | Mol formula | N/%[a)] Calcd | N/%[a)] Found | $\lambda_{max}^{EtOH}$/nm (log $\varepsilon$) | $\nu$ (IR) $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ | $CH_3$ | $C_6H_5$ | 180 | 85 | $C_{24}H_{20}O_3N_2$ | 7.29 | 7.36 | 620(4.02) | N-H 3290<br>C-O 1110 |
| $CH_3$ | $C_6H_5$ | $C_6H_5$ | 170 | 82 | $C_{29}H_{22}O_3N_2$ | 6.27 | 5.65 | 609(3.85) | N-H 3400<br>C-O 1090 |
| $C_6H_5$ | $C_6H_5$ | $C_6H_5$ | 125 | 78 | $C_{34}H_{24}O_3N_2$ | 5.51 | 5.80 | 608(3.79) | N-H 3400<br>C-O 1090 |
| $CH_3$ | $CH_3$ | *o*-$ClC_6H_4$ | 120 | 68 | $C_{24}H_{19}O_3N_2Cl$ | 6.69 | 6.46 | 578(3.96) | N-H 3410<br>C-O 1100 |
| $CH_3$ | $C_6H_5$ | *o*-$ClC_6H_4$ | 130 | 60 | $C_{24}H_{19}O_3N_2Cl$ | 5.85 | 5.36 | 608(3.84) | N-H 3400<br>C-O 1100 |

a) Satisfactory analyses for C, H, and Cl were obtained.

tion of the amino group in the 6-position changes the colour of the molecule to the intense blue shade. The reaction is carried out by heating the bromo derivative of 1,3-oxazines (**2**) with the amine derivative in an alkaline solution and in the presence of a copper salt as catalyst to give anthraquinone disperse dyes (**4**) (*cf.* Table 4). Such amination can be carried on the brominated 1-amino-2-(hydroxymethyl)anthraquinone derivative and the oxazine ring can be further constructed by the action of carbonyl compounds.

As the previously prepared anthraquinone derivatives are water insoluble they were tested as disperse dyes for dyeing synthetic fibers in shades ranging from yellowish brown to intense blue. Samples of polyamide, polyester and acrylic fibers were dyed satisfactory using these derivatives. A comprehensive application program involving such disperse dyes is now in progress with the aim of investigating the relation between structure, fastness properties, and dyeing behaviour. This forthcoming study will include a comparison of the electron impact induced fragmentation patterns of these dyes with their lightfastness on polyester fibers.

## Experimental

The infrared absorption spectra were determined with a Unicam SP 1200 spectrophotometer using the KBr wafer technique. Absorption spectra in visible region were determined with a Unicam SP 8000 ultraviolet recording spectrophotometer. All melting points are uncorrected.

*(Hydroxymethyl)anthraquinone Derivatives (1).* Dissolve (0.1 mol) of 1-amino(or 1-hydroxy)anthraquinone derivatives in about 160 ml (0.1 mol dm$^{-3}$ KOH) and 150 ml ethanol, warm the solution and pass nitrogen gas through it for about 15 min. Add formaldehyde solution (40%, 0.1 mol), followed by addition of sodium dithionite solution (0.1 mol in about 40 ml 0.2 mol dm$^{-3}$ KOH) and pass nitrogen gas for further 12 min. The reaction mixture was oxidized by air for about 30 min. The product was filtered, dried and crystallized from the proper solvent. The results are given in Table 1.

*1,3-Oxazine Derivatives (2).* A mixture of 1-amino-2-(hydroxymethyl)-4-bromo (or non-brominated) anthraquinone (0.1 mol) and the carbonyl compounds (0.1 mol) was dissolved in dioxane (80 ml) in presence of 10 ml HCl (1 mol dm$^{-3}$). The mixture was concentrated, cooled and then added to excess of cold water. The product was filtered, washed with water and dried, then crystallised from suitable solvent. The results are listed in Table 2.

*2-Arylmethylene-1,3-oxazines (3).* A mixture of 6-bromo-1,2-dihydroanthra[1,2-*d*][1,3]oxazine-7,12-dione (250 mg, 0.1 mol) and the carbonyl compound (0.1 mol) was fused for about 5 min in the presence of anhydrous zinc chloride (0.5 g). The melt was triturated with ethanol to dissolve the excess aldehyde, then filtered, washed with hot water and dried. The product was crystallized from the proper solvent. The results are given in Table 3. 2,2-Diformyl-1,2-dihydro-4*H*-anthra[1,2-*d*][1,3]oxazine-7,12-dione and its 6-bromo-analogue (**4c, d**) and the corresponding Schiff's bases (**5e**—**g**).

0.01 Mol of the dimethyl derivative (II, $R_1=R_2=CH_3$; X=H or Br) was dissolved in ethanol and the solution was added to a solution of $SeO_2$ (0.02 mol) in ethanol. The reaction mixture was boiled under reflux for 1.5 h. The solution was cooled and the precipitated selenium was eliminated by filteration. The filtrate was concentrated and cooled, then the product was collected and crystallized from ethanol.

**4c**; mp 95 °C; $\nu$ NH 3300, $\nu$ C–O 1110, and $\nu$ -COH 1730 cm$^{-1}$. Found: N, 3.99%. Calcd for $C_{18}H_{11}NO_5$: N, 4.36%.

**4d**; mp 112 °C; $\nu$ N–H 3280, $\nu$ C–O 1110, and $\nu$ -C–H 1730 cm$^{-1}$. Found: N, 2.99%. Calcd for $C_{18}H_{10}NO_5Br$: N, 3.50%.

0.1 Mol of the dialdehyde (**4d**) was condensed with 0.2 mol of *o*-phenylenediamine, *p*-aminophenol and *p*-anisidine by the usual way to give the corresponding Schiff's bases (**5e**—**g**) respectively.

**5e**; mp 105 °C; $\nu$ NH 3400, $\nu$ C–O 1100, and $\nu$ C=N 1550 cm$^{-1}$. Found: N, 7.92%. Calcd for $C_{24}H_{14}O_3N_3Br$: N, 8.26%.

**5f**; mp 120 °C; $\nu$ NH 3290, $\nu$ C–O 1080, and $\nu$ C=N 1550 cm$^{-1}$. Found: N, 8.12%. Calcd for $C_{30}H_{20}O_5N_3Br$: N, 8.35%.

**5g**; mp 118 °C; $\nu$ NH 3300, $\nu$ C–O 1150, and $\nu$ C=N 1550 cm$^{-1}$. Found: N, 7.41%. Calcd for $C_{32}H_{23}O_5N_3Br$: N, 7.92%.

*Blue Anthra*[1,2-d][1,3]*oxazine*-7,12-*dione Disperse Dyes.* A mixture of 6-bromo-1,3-oxazine derivative (0.02 mol) and the amine derivative (0.02 mol) was dissolved in ethanol (50 ml). The solution was turned alkaline by the addition of sodium carbonate. Copper carbonate (1 g) was added and the reaction mixture was refluxed for 4 h, whereby the brown colour was changed to deep blue. The mixture was filtered while hot and the filtrate was concentrated and diluted with cold water to give a blue precipitate. It was filtered, washed with water and dried. The product was crystallized from dilute ethanol. The results are given in Table 4.

*Application of the Prepared Anthraquinone Derivatives as Disperse Dyes.* These derivatives could be used for colouring synthetic fibers, *e.g.* polyamide. This is done by immersing the textile material in a dyebath containing an aqueous dispersion of these dyes and an ionic surface-active reagent. The dyeing process was performed by boiling for 45 min. The fibers are soaped and rinsed with cold water then dried and tested for light and wash fastness.

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