

STUDIES ON QUINOXALINE COLOURS.

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Quinoxaline colours belong to azine colours, and are derivatives of quinoxaline (according to Hinsberg). The only technically important dyestuff of this series is Flavinduline (B) $C_{26}H_{17}N_2Cl$ which was discovered by C. Schraube in 1893⁽¹⁾, and was obtained by the action of *o*-amidodiphenylamine on phenanthraquinone in glacial acetic acid solution, followed by boiling the reaction products with dilute hydrochloric acid.

The papers related to the quinoxaline colours which have been published are very poor and a few investigators have described only unsatisfactorily Flavinduline and its properties.

The present studies have been undertaken with the view to pursue the study in greater detail and to get more exact information as to the properties of quinoxaline and its derivatives, and especially as to their dyeing character which has been explained by "chromophore theory" or "quinoid theory".

First of all, the three condensations described in the experimental parts have been studied.

Experimental.

I. The reaction of phenanthraquinone on *o*-amidodiphenylamine in glacial acetic acid solution. Preparation of the dyestuffs. *Chloride*. A mixture of 1 part of *o*-amidodiphenylamine (5 g.), 1 part of phenanthraquinone (5 g.) and about 20 parts of glacial acetic acid (100 g.) is heated on the water bath until a sample shows no increase in intensity of colour. The melt is then boiled with 20 times its volume of water, acidified with HCl (38%, 30 g.), cooled, and filtered. The dye is precipitated from the filtrate with zinc chloride.

Bromide. According to the formation process of the chloride, the melt is boiled with HBr solution (48%, 40 g. in 1500 g. water), cooled, and filtered. The dyestuff is precipitated.

Iodide. The melt is boiled with HI solution (57%, 60 g. in 1500 g. water), cooled, and filtered. The dyestuff is precipitated.

Molecular weight.

		Calculated	Found
Chloride	$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$	460.5	448.1
Bromide	$C_{26}H_{17}N_2Br$	437.0	420.3
Iodide	$C_{26}H_{17}N_2I$	484.0	468.1

(1) E.P. 18374 (1893); U.S.P. 543784 (1975).

Analytical data (%).

	$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$		$C_{26}H_{17}N_2Br$		$C_{26}H_{17}N_2I$	
	Calculated	Found	Calculated	Found	Calculated	Found
C	67.75	66.20	71.39	71.20	64.46	64.25
H	3.69	4.60	3.89	5.30	3.51	4.09
N	6.08	6.79	6.39	6.20	5.78	6.11
Cl	15.42	15.77	Br 18.3	18.13	I 26.23	26.19

Properties. Form and colour.

$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$ yellowish red needles;
 $C_{26}H_{17}N_2Br$ brownish red needles;
 $C_{26}H_{17}N_2I$ glistening black needles.

Melting point. Melting points of these compounds are over 285°C., and difficult to be determined exactly.

Solubility.

Solvent	$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{26}H_{17}N_2Br$	$C_{26}H_{17}N_2I$
Water	very sol.	not very sol.	sparingly sol.
Alcohol	very sol.	sol.	sol.
Aniline	very sol.	very sol.	very sol.
Chloroform	sol.	sol.	sol.
Nitrobenzene	sol.	sol.	sol.
Acetone	sol.	sol.	sol.
Glacial acetic acid	very sol.	very sol.	very sol.
Benzene	insol.	insol.	insol.
Ether	insol.	insol.	insol.

Colour reaction in aqueous solutions.

Solvent	$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{26}H_{17}N_2Br$	$C_{26}H_{17}N_2I$
H ₂ O	reddish brown	reddish yellow	yellow
NaOH	greyish green	bluish yellow	yellowish brown
HCl	precipitate	precipitate	precipitate
H ₂ SO ₄ (conc.)	reddish yellow	yellow	pale yellow
	bluish red	brownish red	brownish red

Dyeing.

	Cotton	Silk	Wool
$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$	yellowish brown	reddish yellow	brown
$C_{26}H_{17}N_2Br$	pale yellowish brown	reddish yellow	yellowish brown
$C_{26}H_{17}N_2I$	pale yellow	reddish yellow	greenish brown

These Dyestuffs have good affinity, especially for silk and wool.

Fastness.

	$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{26}H_{17}N_2Br$	$C_{26}H_{17}N_2I$
Light	good	good	good
Washing	good	good	good
Soap	moderate	moderate	moderate
Alkali	moderate	moderate	moderate
Acetic acid	good	good	good
Sulphuric acid	good	good	good

II. The reaction of phenanthraquinone on *o*-amidomonomethylaniline in glacial acetic acid solution. Preparation of the dyestuffs. *Chloride.* A mixture of 1 part of *o*-aminomonomethylaniline (5 g.), 1 part of phenanthraquinone (5 g.), and about 20 parts of glacial acetic acid (100 g.) is heated on the water bath until a sample shows no increase in intensity of colour. The melt is then boiled with HCl solution (38%, 25 g. in 1500 c.c. water), and filtered. The dye is precipitated from the filtrate with zinc chloride.

Bromide. According to the formation process of the chloride, the melt is boiled with HBr solution (48%, 45 g. in 1500 c.c. water), and filtered while hot. The dyestuff is precipitated on cooling.

Iodide. The melt is boiled with HI solution (57%, 60 g. in 1500 c.c. water).

Molecular weight.

		Calculated	Found
Chloride	$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl$	397.59	406.38
Bromide	$C_{21}H_{15}N_2Br$	374.91	382.80
Iodide	$C_{21}H_{15}N_2I$	421.93	430.10

Analytical data.

	$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$		$C_{21}H_{15}N_2Br$		$C_{21}H_{15}N_2I$	
	Calculated	Found	Calculated	Found	Calculated	Found
C	63.39	64.09	67.21	66.89	59.72	59.04
H	3.77	4.02	4.00	4.81	3.55	4.16
N	7.40	7.20	7.46	7.53	6.63	6.64
Cl	17.80	18.05	Br 21.03	20.89	I 30.08	29.38
Zn	8.22	6.88				

Properties. *Form and colour.*

$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	brown needles ;
$C_{21}H_{15}N_2Br$	yellow needles ;
$C_{21}H_{15}N_2I$	glistening brownish red needles.

Melting point (Decomposition point).

$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	200–205°C.
$C_{21}H_{15}N_2Br$	216–217°C.
$C_{21}H_{15}N_2I$	195–200°C.

Solubility.

Solvent	$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{21}H_{15}N_2Br$	$C_{21}H_{15}N_2I$
Water	sol.	sol.	sol.
Alcohol	sol.	sol.	sol.
Aniline	very sol.	very sol.	very sol.
Chloroform	sol.	sol.	sol.
Nitrobenzene	sol.	sol.	sol.
Acetone	sol.	sol.	sol.
Glacial acetic acid	sol.	sol.	sol.
Benzene	insol.	insol.	insol.
Ether	insol.	insol.	insol.

Colour reaction in aqueous solution.

Solvent	$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{21}H_{15}N_2Br$	$C_{21}H_{15}N_2I$
H ₂ O	yellow, with greenish fluorescence	yellow, with greenish fluorescence	yellow, with greenish fluorescence
NaOH	pale green precipitate	pale yellowish brown precipitate	pale greyish yellow precipitate
HCl	reddish yellow	reddish yellow	reddish yellow
H ₂ SO ₄ (conc.)	brownish red	brownish red	brownish red

Dyeing.

	Cotton	Silk	Wool
$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	brown	yellow	yellow
$C_{21}H_{15}N_2Br$	brown	yellow	yellow
$C_{21}H_{15}N_2I$	brown	yellow	yellow

These dyestuffs have good affinity for cotton.

Fastness.

	$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$			$C_{21}H_{15}N_2Br$			$C_{21}H_{15}N_2I$		
	Cotton	Silk	Wool	Cotton	Silk	Wool	Cotton	Silk	Wool
Light	good	bad	bad	good	bad	bad	good	bad	bad
Washing	moderate	bad	bad	mod.	bad	bad	mod.	bad	bad
Soap	bad	bad	bad	bad	bad	bad	bad	bad	bad
Acetic acid	good	bad	bad	good	bad	bad	good	bad	bad
Sulphuric acid	moderate	mod.	mod.	mod.	bad	bad	mod.	mod.	mod.

III. The reaction of naphthoquinone on *o*-amidodiphenylamine in glacial acetic acid solution. Preparation of the dyestuffs. *Chloride.* A mixture of 1 part of *o*-amidodiphenylamine (5 g.), 1 part of naphthoquinone (5 g.) and about 20 parts of glacial acetic acid (100 g.) is heated on the water bath until the sample shows no increase in intensity of colour. The melt is then boiled with 20 times its volume of water acidified with HCl (38%, 30 g.), cooled, and filtered. The dye is precipitated from the filtrate with zinc chloride.

Bromide. According to the formation process of the chloride, the melt is boiled with HBr solution (48%, 40 g. in 1500 g. water), filtered, and cooled. The dyestuff is precipitated.

Iodide. The melt is boiled with HI solution (57%, 60 g. in 1500 g. water).

Molecular weight.

		Calculated	Found
Chloride	$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	410.75	392.5
Bromide	$C_{22}H_{15}N_2Br$	387.05	378.8
Iodide	$C_{22}H_{15}N_2I$	434.07	430.6

Analytical data (%).

	$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$		$C_{22}H_{15}N_2Br$		$C_{22}H_{15}N_2I$	
	Calculated	Found	Calculated	Found	Calculated	Found
C	64.27	64.30	68.21	67.51	60.82	61.03
H	3.68	3.63	3.91	5.57	3.48	3.38
N	6.82	6.80	7.24	7.23	6.45	6.39
Cl	17.26	17.52	Br 20.65	19.74	I 29.24	29.16
Zn	7.95	7.58				

Properties. *Form and colour.*

$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	madder brown needles ;
$C_{22}H_{15}N_2Br$	vistoris lake needles ;
$C_{22}H_{15}N_2I$	vandyke red needles.

Melting point (decomposition point).

$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	278—279°C.
$C_{22}H_{15}N_2Br$	281—282°C.
$C_{22}H_{15}N_2I$	220—221°C.

Solubility.

Solvent	$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{22}H_{15}N_2Br$	$C_{22}H_{15}N_2I$
Water	very sol.	very sol.	very sol.
Alcohol	sol.	sol.	sol.
Aniline	very sol.	very sol.	very sol.
Chloroform	insol.	insol.	insol.
Nitrobenzene	sol.	sol.	sol.
Acetone	sol.	sol.	sol.
Glacial acetic acid	sol.	sol.	sol.
Benzene	insol.	insol.	insol.
Ether	insol.	insol.	insol.

Colour reaction in aqueous solution.

Solvent	$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{22}H_{15}N_2Br$	$C_{22}H_{15}N_2I$
H ₂ O	yellowish red	brownish yellow	reddish yellow
NaOH	bluish yellow (black ppt.)	pale yellow (yellowish green ppt.)	yellow (red ppt.)
HCl	reddish yellow	reddish yellow	pale yellow
H ₂ SO ₄	brownish red	brownish red	pale red

Dyeing.

	Cotton	Silk	Wool
$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	pale sudan brown	capucin yellow	deep fresh colour
$C_{22}H_{15}N_2Br$	sudan brown	golden yellow	ocher red
$C_{22}H_{15}N_2I$	pale sudan brown	pale capucin yellow	seashell colour

These dyestuffs have good affinity for silk, wool, and especially for cotton.

Fastness.

		$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{22}H_{15}N_2Br$	$C_{22}H_{15}N_2I$
Light	Cotton Silk Wool	good moderate moderate	good moderate moderate	good moderate moderate
Washing	Cotton Silk Wool	good bad bad	good bad bad	good bad bad
Soap	Cotton Silk Wool	bad bad bad	bad bad bad	bad bad bad
Acetic acid	Cotton Silk Wool	good bad moderate	good bad moderate	good bad moderate
Sulphuric acid	Cotton Silk Wool	good bad moderate	good bad moderate	good bad moderate
