

## Studies on Some Azonium Derivatives

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N-methyl-o-phenylene diamine has been condensed respectively with acenaphthenequinones, isatins and also phenanthraquinone to synthesise azonium derivatives possessing deep tinctorial properties. Although, the attempt has not been amply realised but two green compounds were obtained in the acenaphthenequinone series. Azonium compounds derived from isatins and phenanthraquinone are golden yellow to violet-brown and lighter in colour than those from the nearly corresponding acenaphthenequinones.

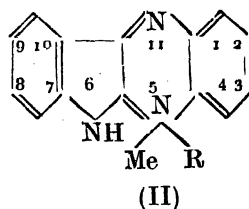
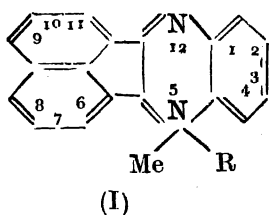
In view of the observations that the colour and dyed shade of 3-indole-2'-(4', 5', 6', and 7' -methyl-, chloro-, and methoxy)- thionaphthene-indigos<sup>1</sup> are deeper than those of the 2-(4-, 5-, 6-, and 7-methyl-, chloro-, and methoxy)-thionaphthene acenaphthylene-indigos<sup>2</sup>, an attempt was made to synthesise deep coloured azonium compounds from various acenaphthenequinones and isatins and also to study if the order of the colour change of the azonium derivatives of these two series is similar to that of the indole-indigos and acenaphthylene indigos (*loc. cit.*).

A few azonium derivatives<sup>3</sup> were previously obtained from acenaphthenequinones, which are yellow, deep violet and greenish-black products. In the isatin series, although azines<sup>4</sup> are reported which are sulphur yellow to red but no record of azonium derivatives could be traced. Naphthaflavindulins<sup>5</sup> containing various auxochromes and other groups were studied. These are dark brown to blue black products.

Now, N-methyl-o-phenylene-diamine<sup>6</sup> has been condensed with a few acenaphthenequinones. The azonium compounds obtained are:— (Ia). 5-N-methyl-, (Ib). 5-N-methyl-9-bromo-, (Ic). 5-N-methyl-11-methoxy-, and (Id). 5-N-methyl-8:9-dinitro-acenaphthaphenazonium chlorides, having the general formula, I, (R=Cl). These are deep green, darkish green, brown and darkish violet-brown crystalline products produced in 18 to 48% yield. The compounds are soluble in acetic acid and acetone except Ib which is sparingly soluble in acetone; the two chlorides, Ic and Id are soluble in ethanol whereas Ia and Ib are insoluble in the same. The corresponding nitrates of (Ia), (Ib), and (Id) (I, R=NO<sub>2</sub>) were also prepared. These are (Ie) 5-N-methyl-, (If). 5-N-methyl-9-bromo-, (Ig). 5-N-methyl-8: 9-dinitro-acenaphthaphenazonium nitrates. (Table II). The compounds

1. S. K. Guha, *This Journal*, 1944, **21**, 87; S. K. Guha *et al*, *Ibid*, 1955, **32**, 777; S. K. Guha *et al*, *Chem. Ber.*, 1961, **94**, 2295 and earlier papers.
2. S. K. Guha, *This Journal*, 1943, **20**, 37; S. K. Guha *et al*, *Ibid*, 1957, **34**, 771; S. K. Guha *et al*, *Chem. Ber.*, 1961, **94**, 3297 and earlier papers.
3. F. Ullmann and E. Cassirer, *Ber.*, 1910, **43**, 439; A. C. Sircar and S. K. Guha, *J. Chem. Soc.*, 1924, **125**, 335; S. K. Guha, *Ibid*, 1931, 582.
4. E. Schunck and L. Marchlewski, *Ber.*, 1896, **29**, 194; S. K. Guha, *This Journal*, 1936, **13**, 571; J. D. Tewari and S. B. Dutt, *National Acad. Science*, Allahabad, 1937, **71**, 58; D. Prashad, S. Sen and P. C. Dutt, *Ber.*, 1937, **7011**, 2363.
5. S. B. Dutt, *J. Chem. Soc.*, 1922, **121**, 1951.
6. E. H. Usherwood and M. A. Whitely, *J. Chem. Soc.*, 1923, **123**, 1069.

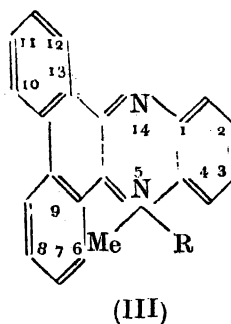
are yellowish-brown, yellow-orange and reddish-brown crystalline substances; soluble in acetic acid; the nitrates (Ie) and (If) are insoluble in ethanol whereas (Jg) is moderately soluble in the same.



Anticipating the production of deeper coloured azonium derivatives in the isatin series from analogy of the colour of indole-indigos (loc. cit) the following compounds represented by the formula II, ( $R=Cl$ ) were prepared: (IIa) 5-N-methyl-, (IIb) 5-N-methyl-9-chloro-, (IIc) 5-N-methyl-9-bromo-, (IId) 5-N-methyl-9-iodo- (IIe) 5-N-methyl-9-nitro-, (IIf) 5-N-methyl-7:9-dibromo-, (IIg) 5-N-methyl-7-nitro-9-bromo-, (IIh) 5-N-methyl-7:9-dinitroindophenazonium chloride.

These compounds are brownish-yellow, golden yellow, brown and violet-brown crystalline substances obtained in 36-66% yield; soluble in acetic acid and ethanol except (IId), 9-iodo derivative which is moderately soluble in acetic acid and (IIf), 7:9-dibromo compound and (IIh), 7:9-dinitro derivative which are moderately soluble in ethanol. The compounds are also soluble in acetone except (IId), 9-iodo compound and (IIe) 9-nitro derivative which are respectively insoluble and moderately soluble in the same. The corresponding nitrates of the compounds (IId) and (IIg) (II,  $R=NO_3$ ) were also obtained as yellow-orange and orange needles respectively. The products (III) 5-N-methyl-9-iodo-, and (IIj) 5-N-methyl-7-nitro-9-bromo-indophenazonium nitrates, are soluble in ethanol. The iodo-nitrate is moderately soluble and the nitro-bromo compound is soluble in acetic acid.

Lastly, from phenanthraquinone (IIIa) 5-N-methyl-phenanthraphenazonium chloride (III,  $R=Cl$ ) and (IIIb) nitrate, ( $R=NO_3$ ) were prepared for a comparative study of colour of the parent compounds of the three series studied here. These are yellowish



brown and brown crystalline substances obtained in 22-24% yield. Both the chloride and the nitrate are soluble in ethanol, chloroform, acetone and benzene; moderately soluble in acetic acid,

The azonium derivatives described here are all insoluble in petroleum ether. These also yield characteristic colour reaction with cold strong sulphuric acid. The dyed shades of a few selected compounds were developed on wool from an acid bath at 70-80° which are all even but lighter than the original substances. Even then the shades obtained from the compounds Ia, Ib, Id, II<sub>f</sub>, and II<sub>g</sub> are quite satisfactory. The absorption maxima values (Table I) were determined in acetone except that of Ib, found in methanol.

It was concluded from a comparison of colour, dyed shade and absorption maxima data of some of the azonium derivatives (Table I), that methyl-acenaphthaphenazonium chlorides are deeper in colour than those of the available nearly corresponding methyl-indophenazonium chlorides and also methyl-phenanthraphenazonium chloride (cf. the reverse order of the colour change of acenaphthylene-, and indole-indigos, (loc. cit ).

TABLE I

Compounds.	$\lambda_{\text{max}}$ .
5-N-methyl-acenaphthaphenazonium chloride (Ia)	632.5 m/ $\mu$
5-N-methyl-indophenazonium chloride (II <sub>a</sub> )	416
5-N-methyl-9-bromo-acenaphthaphenazonium chloride (Ib)	640
5-N-methyl-9-bromo-indophenazonium chloride (II <sub>c</sub> )	424
5-N-methyl-8:9-dinitro-acenaphthaphenazonium chloride (Id)	492
5-N-methyl-7:9-dinitro-indophenazonium chloride (II <sub>h</sub> )	418
5-N-methyl-7:9-dibromo-indophenazonium chloride (II <sub>f</sub> )	508
5-N-methyl-7-nitro-9-bromo-indophenazonium chloride (II <sub>g</sub> )	490
5-N-methyl-phenanthraphenazonium chloride (III <sub>a</sub> )	397

## EXPERIMENTAL

The azonium chlorides and nitrates recorded in Table II were obtained by heating equimolecular proportion of acenaphthenequinone (or isatin or phenanthraquinone) and N-methyl-o-phenylene diamine hydrochloride, denoted by 'M' in glacial acetic acid (2 ml) solution in presence of strong hydrochloric or nitric acid (0.2—0.4 ml) for about 5 min. only. The condensed products gradually separated on cooling in crystalline form; in some cases removal of the solvent was necessary for crystallisation and in others addition of a little water or suitable solvent precipitated the condensed product; collected and crystallised from glacial acetic acid unless otherwise stated.

The deep green compound (Ia) was precipitated by water from the concentrated acetic acid solution and crystallised. The darkish green product (Ib) was precipitated by acetone and crystallised from dilute acetic acid. The brown derivative (Ic) separated, on concentration, as a sticky mass which was extracted with chloroform and left overnight; the product deposited was crystallised from the same.

The brownish-yellow substance (II<sub>a</sub>) was obtained by adding water to the concentrated solution as a sticky mass which was extracted with aqueous acetone and crystallised therefrom.

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TABLE II

Azonium derivatives	Reactants (g)	Appearance; shade on wool.	M.P.° C; Colour in strong sulphuric acid		Analysis %Nitrogen		
			Yield (g), (%)		Mol. formula	Found	Reqd.
Ia	Acenaphthenequinone (0.182) + M(0.158)	Deep Green; green	283-284; 0.13, (42.6)	Brown yellow	C <sub>19</sub> H <sub>13</sub> N <sub>2</sub> Cl	8.87	9.19
Ib	3-Bromo-acenaphthenequinone (0.261) + M(0.158)	Darkish green; darkish green.	220-221; 0.07, (18.2)	Brown	C <sub>19</sub> H <sub>12</sub> N <sub>2</sub> Cl Br	7.51	7.3
Ic	1-Methoxy-acenaphthenequinone (0.106) + M(0.079)	Brown.	124-125; 0.08, (48)	Red-brown	C <sub>20</sub> H <sub>15</sub> ON <sub>2</sub> Cl	8.07	8.37
Id	3:4-Dinitro-acenaphthenequinone (0.272) + M(0.158)	Darkish violet-brown; brown	284-285; 0.16, (40.5)	Yellow-brown	C <sub>19</sub> H <sub>11</sub> O <sub>4</sub> N <sub>4</sub> Cl	14.55	14.19
Ie	Acenaphthenequinone (0.182) + M (0.158)	Yellowish brown. on rubbing yellow	250-251; 0.12, (36.3)	Orange	C <sub>19</sub> H <sub>13</sub> O <sub>3</sub> N <sub>3</sub>	12.31	12.68
If	3-Bromo-acenaphthenequinone (0.2) + M(0.14) in 5ml acetic acid	Yellow-orange	228-229; 0.14, (34.2)	Red brown	C <sub>19</sub> H <sub>12</sub> O <sub>3</sub> N <sub>3</sub> Br	10.41	10.24
Ig	3:4-Dinitro-acenaphthenequinone (0.272) + M(0.158)	Reddish-brown	288-289 (d); 0.15, (35.6)	Lemon yellow	C <sub>19</sub> H <sub>11</sub> N <sub>5</sub> O <sub>7</sub>	16.71	16.62
IIa	Isatin (0.147) + M(0.158)	Brownish-yellow; lemon yellow	257-258; 0.16, (59.4)	Orange yellow	C <sub>15</sub> H <sub>12</sub> N <sub>3</sub> Cl	15.72	15.54
IIb	5-Chloro-isatin (0.181) + M (0.158)	Bright golden yellow.	248-249; 0.11, (36.1)	Orange	C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> Cl <sub>2</sub>	13.65	13.81
IIc	5-Bromo-isatin (0.226) + M (0.158)	Brownish-yellow; light brown.	250-251; 0.16, (45.2)	Yellow-brown	C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> Cl Br	12.46	12.05
IId	5-Iodo-isatin (0.273) + M (0.158)	Brownish-yellow, deeper than IIc	above 300; 0.17, (42.9)	Brown	C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> Cl I	10.28	10.61
IIe	5-Nitro-isatin (0.192) + M (0.158)	Brown; on rubbing darkish brown	above 300; 0.21, (66.9)	Orange	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> N <sub>4</sub> Cl	12.25	17.8
IIf	5:7-Dibromo-isatin (0.31) + M (0.158)	Deep violet-brown; brownish-red	273-274; 0.26, (60.9)	Yellowish-brown	C <sub>15</sub> H <sub>10</sub> N <sub>3</sub> Cl Br <sub>2</sub>	9.41	9.82
IIg	5-Bromo-7-nitro-isatin (0.271) + M(0.158)	Darkish violet-brown; chocolate brown.	above 300; 0.21, (53.3)	Do	C <sub>15</sub> H <sub>10</sub> O <sub>2</sub> N <sub>4</sub> Cl Br	13.92	14.23
IIh	5-7-dinitro-isatin (0.237) + M (0.158)	Dark brown; on rubbing yellowish-brown; yellow.	246-247; 0.21, (58.4)	Deep yellow	C <sub>15</sub> H <sub>10</sub> O <sub>4</sub> N <sub>5</sub> Cl	19.62	19.47
IIi	5-Iodo-isatin (0.273) + M (0.158) in 7 ml acetic acid	Bright yellow-orange	above 300; 0.05, (16.9)	Yellowish-brown	C <sub>15</sub> H <sub>11</sub> O <sub>3</sub> N <sub>4</sub> I	12.95	13.27
IIj	5-Bromo-7-nitro-isatin (0.271) + M(0.158)	Orange	243-244; 0.22, (52.4)	Yellow-orange	C <sub>15</sub> H <sub>10</sub> O <sub>3</sub> N <sub>5</sub> Br	16.21	16.66
IIIa	Phenanthraquinone (0.21) + M (0.158)	Yellowish-brown, yellow	186-187; 0.08, (24.7)	Red-brown	C <sub>21</sub> H <sub>15</sub> N <sub>2</sub> Cl	8.41	8.47
IIIb	Phenanthraquinone (0.21) + M (0.158)	Brown; on rubbing yellow orange.	198.199 0.08 (22.4)	Red-brown	C <sub>21</sub> H <sub>15</sub> O <sub>3</sub> N <sub>3</sub>	11.91	11.76