

## Disperse Dyes: Part XIX—Synthesis of Disperse Azo Dyes from 2-Amino-8H-pyrazolo (4,5-g) benzothiazole and Their Dyeing Properties

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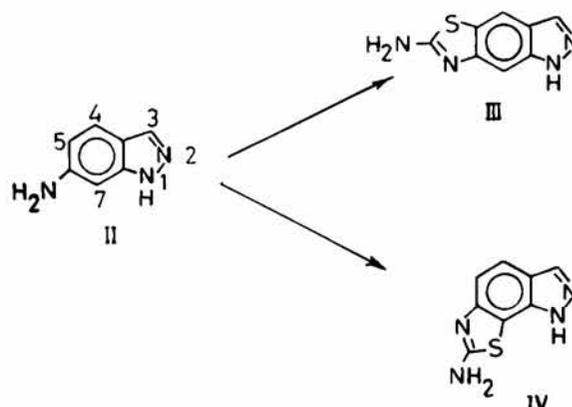
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2-Amino-8H-pyrazolo (4,5-g) benzothiazole has been synthesized in high yield (90%) by the action of ammonium thiocyanate and bromine in glacial acetic acid on 6-aminoindazole. An angular structure, based on NMR and mass spectral data, has been assigned to the resulting heterocyclic amine. The amine was diazotized in phosphoric acid (87%) and coupled with various coupling components in acetic acid-ethanol cosolvent. The dyeing properties of the dyes obtained have been studied.

Disperse dyes, synthesized in this laboratory from 6-aminoindazole, dyed polyester in yellow to orange shades of very good sublimation fastness<sup>1</sup>. It was of interest to extend the range of these dyes to include violets and blues. One way of achieving this result would be to annelate a thiazole ring to the indazole system and use this combined aminoheterocyclic compound as a diazo component in the synthesis of disperse azo dyes.

Following the classical method of synthesis of 2-aminobenzothiazole, 6-aminoindazole was treated with potassium or ammonium thiocyanate and bromine in glacial acetic acid. 6-Aminoindazole was synthesized by reducing 6-nitroindazole (I) with iron in aqueous medium<sup>2</sup>. The use of acetic acid or an electrolyte, such as ferric chloride, was found<sup>3</sup> to be beneficial, giving an yield of 70-75%. Raney nickel reduction<sup>4,5</sup>, although a little more involved, gave a higher yield (92%). The treatment of 6-aminoindazole with ammonium or potassium thiocyanate and bromine was expected to yield the desired compound by initial thiocyanation followed by ring closure. Since two *ortho* positions with respect to amino group are vacant, thiocyanation may occur on C-5 or C-7, and subsequent ring closure would lead to either to compound III or to compound IV.

Tarabasanu-Mihalai *et al.*<sup>5</sup> assigned the linear structure(III) to the product, largely on IR evidence. But some earlier reports on thiocyanation of 6-aminoindazole<sup>6,7</sup> claimed isolation of 7-thiocyanato-6-aminoindazole, the precursor of the angular structure(IV). The NMR studies proved this claim and we assigned an angular structure to the product with nomenclature 2-amino-8H-pyrazolo(4,5-g) be-



nzothiazole (IV). The NMR (in DMSO-*d*<sub>6</sub>, 60 MHz) spectra exhibited a singlet at  $\tau$  1.87 and two doublets at  $\tau$  2.33 and  $\tau$  2.72 respectively with coupling constant  $J = 10$  cps. The large coupling constant<sup>8</sup> indicated an *ortho* coupling (of protons at C-4 and C-5), proving the angular structure(IV) for the product. The amine (IV) gave satisfactory elemental analysis and mass spectrum exhibited  $M^+$ ,  $m/e$  190.

### Diazotization and Coupling of Amine (IV)

Diazotization of IV was carried out by two methods, the first one with nitrosyl sulphuric acid and the other one with sodium nitrite in 87% phosphoric acid. The phosphoric acid method was superior and gave the dyes in a better state of purity. After diazotization, the diazo mixture was directly added to the solution of the coupling components in a mixture of acetic acid and ethanol. The coupling components used were (1) N,N-dimethylaniline, (2) N,N-bis(oxyethyl)aniline, (3) N,N-bis(oxyethyl) *m*-toluidine, (4) N- $\beta$ -cyanoethyl-N- $\beta$ -acetoxyethylaniline, (5) 5-acetamido-2-methoxy-N- $\beta$ -cyanoethyl-N- $\beta$ -hydroxy-ethylaniline, and (6) N-ethyl-N- $\beta$ -cyanoethylaniline.

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Visible absorption spectra of the dyes varied from 505 to 555 nm (Table 1), showing a bathchromic effect of benzothiazole ring on the colour of the dyes, since the corresponding dyes from 6-aminoindazole gave absorption maxima at about 430 nm.

### Results and Discussion

Data regarding yields, melting points, elemental analysis, etc. of the dyes are given in Table 1.

Dyes D1 to D7 showed good substantivity to polyester (PES) and polyamide (PA) fibres. The dye bath exhaustion was good, except for dye D7 on PES. The sublimation fastness was very good for all the dyes. The light fastness, however, varied from fair to very fair (grade 3-4). Dye D7 giving a black shade (3%) on polyamide is of particular interest because of its attractive uncommon black shade. Data from dyeing trials are given in Table 2.

### Experimental Procedure

**6-Aminoindazole(II)**—A mixture of water (25 ml) and iron filings (2.5 g, etched) was heated under stirring

to 40°C, 6-Nitroindazole (1.63 g, 0.01 mol) was added in small portions and the temperature of the reaction mixture was raised to 90°C. Acetic acid (1 ml) was added and the reaction mixture was further stirred for 1 hr at 90-95°C. The iron sludge was removed by filtering the hot reaction mixture. The filtrate was made alkaline (pH 9) by adding sodium carbonate. The precipitated iron salt was removed by filtration and the filtrate was cooled to 0°C for 2 hr, when 6-aminoindazole separated as a crystalline precipitate. The residues (iron sludge) from the first and second filtrations were combined and boiled with water (30 ml), and filtered hot. The filtrate on concentration and cooling gave an additional amount of 6-aminoindazole. The combined yield of the product was 1 g (75.2%); m.p. 209°C (lit.<sup>2</sup> m.p., 209°C).

Alternatively, 6-nitroindazole (4 g) was reduced with Raney nickel (1.5 g) in methanol under hydrogen pressure of 30 atm at 40°C for 8 hr. After the reaction was over, the catalyst was removed by filtration, the filtrate concentrated to one third volume and diluted with 3 volumes of water. On cooling to 10°C, the

Table 1—Yields, Melting Points and Analysis of Azo Dyes Derived from 2-Amino-pyrozolobenzothiazole

Dye No.	Coupling component	Yield %	M.P. °C	$\lambda_{\max}$ nm	Molecular formula	Required		Found	
						N%	S%	N%	S%
D1*	N,N-Bis( $\beta$ -hydroxyethyl) aniline	60	250	520	C <sub>18</sub> H <sub>18</sub> N <sub>6</sub> O <sub>2</sub> S	21.99	8.37	22.0	8.2
D2	N,N-Bis( $\beta$ -hydroxyethyl) <i>m</i> -toluidine	72	240	535	C <sub>19</sub> H <sub>20</sub> N <sub>6</sub> O <sub>2</sub> S	21.2	8.07	20.8	8.6
D3	N,N-Bis( $\beta$ -acetoxyethyl) aniline	73	190	510	C <sub>22</sub> H <sub>22</sub> N <sub>6</sub> O <sub>4</sub> S	16.54	6.3	16.3	6.0
D4	N,N-Bis( $\beta$ -acetoxyethyl) <i>m</i> -toluidine	70	175	525	C <sub>23</sub> H <sub>24</sub> N <sub>6</sub> O <sub>4</sub> S	16.09	—	16.2	—
D5	N-Ethyl-N- $\beta$ -cyanoethyl-aniline	83	196	512	C <sub>19</sub> H <sub>17</sub> N <sub>7</sub> S	26.1	8.53	26.1	8.2
D6	N- $\beta$ -Hydroxyethyl-N- $\beta$ -cyanoethyl- <i>m</i> -acetamido- <i>o</i> -anisidine	69	210	555	C <sub>22</sub> H <sub>22</sub> N <sub>8</sub> O <sub>3</sub> S	23.43	6.7	23.3	6.8
D7	N- $\beta$ -Acetoxyethyl-N- $\beta$ -cyanoethyl-aniline	75	120	505	C <sub>21</sub> H <sub>19</sub> N <sub>7</sub> O <sub>2</sub> S	22.63	7.38	22.2	7.5

\*D1 as a representative was analyzed for C and H. C<sub>18</sub>H<sub>18</sub>N<sub>6</sub>O<sub>2</sub>S requires C, 56.54% and H, 4.71%; found C, 56.6 and H, 4.71%.

Table 2—Shades and Fastness of Azo Dyes Derived from 2-Amino-pyrozolobenzothiazole (IV)

Dye No.	Colour of dye, 1 % shade		Pick up		Light fastness		Sublimation fastness
	Polyester	Polyamide	Polyester	Polyamide	Polyester	Polyamide	Polyester
D1	Corinth	Corinth	1	4	2	3	4-5
D2	Corinth	—	2-	—	1	—	4-5
D3	Red-orange	Brownish-red	2+	4	3-4	3	4-5
D4	Brown	Red-brown	4	4	3-4	3	4-5
D5	Brown-red	—	2+	—	3-4	—	4-5
D6	Brown-red	Red-brown	—	4	—	3.4	—
D7	Blue-black	Black	4	4	3-4	3.4	4-5

product got precipitated out and was filtered and dried; yield, 3 g (92%); m.p., 204-205°C. After crystallization from ethanol it melted at 209°C.

**2-Amino-8H-pyrazolo(4,5-g)benzothiazole (IV)**—To a solution of 6-aminoindazole (1.33 g, 0.01 mol) in acetic acid (20 ml), ammoniumthiocyanate (2.28 g, 0.03 mol) was added, maintaining the temperature below 35°C. After the addition was over, the mixture was stirred for 1 hr at room temperature. A solution of bromine (2.4 g, 0.03 atom) in glacial acetic acid (10 ml) was added dropwise to the above reaction mixture over 15-20 min. It was then stirred at room temperature for 6 hr, diluted with water (30 ml), heated to 90°C and filtered hot. The filtrate, on careful neutralization with sodium carbonate, yielded a buff coloured product. It was isolated by filtration, washed with water (100 ml) and dried at 80°C; yield, 1.71 g (90%); m.p., 315°C (DMF : EtOH) (lit.<sup>6</sup> m.p., 315°C). C<sub>8</sub>H<sub>6</sub>N<sub>4</sub>S requires N, 29.47% and S, 16.84%; found N, 29% and S, 17.2%. IR(Nujol) : 3150w, 3080w, 1620s, 1570w, 1521w, 1410w, 1317m, 1235m, 1200w, 1110m, 1025m, 978m, 850m, 817m, 790m, 748m and 682m cm<sup>-1</sup>; M<sup>+</sup> : m/e 190 (100%).

**Diazotization of the amine (IV)**—2-Amino-8H-pyrazolo (4.5-g) benzothiazole (1.90 g, 0.01 mol) was dissolved in orthophosphoric acid (87%, 30 ml) with warming. The solution was cooled to 0°C and sodium nitrite (0.7 g, 0.01 mol) was added. The diazo mixture was stirred for 1 hr at 0-5°C. It was used without dilution for the coupling reaction.

**Coupling**—The coupling component (from D1 to D7 in Table 1) (0.01 mol) was dissolved in a mixture of

acetic acid and ethanol (20 ml and 10 ml respectively). The diazo mixture was added to cooled (10°C) coupling solution over a period of 20 min. The reaction mixture was stirred for 1 hr at 10-15°C and then for 6 hr at room temperature. The pH was adjusted to 5-5.5 with saturated sodium acetate solution, when the dye separated out. The dye was isolated by filtration, washed with water (100 ml) and dried. The details of the dyes are given in Table 1.

**Dyeing trials**—Polyester was dyed by the high temperature, high pressure method and polyamide was dyed at 95°C in open dyebath.

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