XXIII.—*Studies in Colour and Constitution. Part II. Further Observations on the Effect of Substituents on the Colour of Azo-dyes.*

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Azo-dyes with Schäffer's salt or R-salt as the second component have been prepared from the bases IX—XX named on p. 165 and have been included, together with those described in Part I (J., 1926, 542), in a scheme showing the effects of the substituents on the colour of the dyes.

By dyeings on wool and colorimetric estimations of the dye solutions with the Lovibond tintometer, the powerful bathochromic influence of a methylthiol group in the para-position with respect to the azo-group and the almost equally powerful influence of an *o*-methoxy-group have been further demonstrated, and a less powerful but still pronounced bathochromic influence has been established for chlorine in the para-position. In the ortho- or meta-position, especially in the latter, chlorine produces a hypsochromic effect, which is manifested in the colours of the dyes prepared from the bases containing 2 : 4- and 2 : 5-dichloro-, 2-chloro-

4-methoxy-, 5-chloro-2-methoxy-, and 5-chloro-2-methylthiol substituents.

The mass of the substituent appears to affect the colour developed by the dye in concentrated sulphuric acid solution.

EXPERIMENTAL.

Initial Materials.—By prolonging the time of nitration from 10 to 25 minutes 2 : 4-dichloronitrobenzene was prepared in 88% yield by Roberts and Turner's method (J., 1925, **127**, 2011). It was converted almost quantitatively into 2 : 4-dimethoxynitrobenzene, m. p. 74°, by the action of methyl-alcoholic sodium methoxide. Reduction of this (4 g.) with iron powder (8 g.), glacial acetic acid (5 c.c.), and water (20 c.c.) gave 2 : 4-dimethoxyaniline (2·4 g.), m. p. 39°. Reduction with tin (4 g.) and conhydrochloric acid (20 c.c.) gave an oily chlorinated product the acetyl derivative of which crystallised from alcohol or dilute acetic acid in colourless needles, m. p. 142° (Found : Cl, 15·5. Calc. for $C_{10}H_{12}O_3NCl$: Cl, 15·5%), and was probably 6-chloro-2 : 4-dimethoxyacetanilide.

4-*Chloro*-2-*thioanisidine.*—A solution of 3-chloro-6-nitrothioanisole (2·8 g.) (Hodgson and Handley, *J. Soc. Chem. Ind.*, 1927, **46**, 435T) in glacial acetic acid (10 c.c.) containing tin (4 g.) was cautiously heated while concentrated hydrochloric acid (10 c.c.) was being gradually added. After 30—45 minutes, the mixture was heated on a boiling water-bath for 10 minutes, and then steam-distilled after being made alkaline with sodium hydroxide; 4-chloro-2-thioanisidine (1·5 g.) was thus obtained as an oil in the distillate. Its aqueous solution gave an orange colour with bleaching powder and a bluish-green colour with ferric chloride. The *acetyl* derivative crystallised from water or dilute acetic acid in colourless needles, m. p. 110° (Found : N, 6·6; Cl, 16·3. $C_9H_{10}ONClS$ requires N, 6·5; Cl, 16·5%), and the *benzoyl* derivative from alcohol in colourless needles, m. p. 106° (Found : Cl, 12·7. $C_{14}H_{12}ONClS$ requires Cl, 12·8%).

4 : 4′-*Dinitro*-5 : 5′-*dimethylthioldiphenyl disulphide* was obtained by carefully adding aqueous sodium disulphide (crystallised sodium sulphide, 2·4 g.; sulphur, 0·32 g.; water, 5 c.c.) to a hot solution of 3-chloro-6-nitrothioanisole (4 g.) in alcohol (100 c.c.), boiling the mixture under reflux for 6 hours, and removing unchanged material by steam-distillation; the non-volatile product crystallised from glacial acetic acid, in which it was sparingly soluble, in pale yellow needles, m. p. 216—217° (Found : S, 31·8. $C_{14}H_{12}O_4N_2S_4$ requires S, 32·0%). It is insoluble in alcohol and very sparingly soluble in acetone.

2 : 4-Dimethylthiolnitrobenzene was prepared by heating together a suspension of the above disulphide (2 g.) in alcohol (10 c.c.) and a solution of crystallised sodium sulphide (1 g.) and sodium hydroxide (2·4 g.) in water (12 c.c.) for 10 minutes and then cooling the deep brown solution, diluting it with water (30 c.c.) and treating it with methyl sulphate (2·5 c.c.), whereupon the thioether (1·9 g.) separated immediately. It crystallised from alcohol, acetone, or acetic acid in yellow, curved needles, m. p. 113° (Zincke and Krüger, *Ber.*, 1912, **45**, 3474, give m. p. 114° for a product obtained by the nitration of *m*-dimethylthiolbenzene) (Found : N, 6·5. Calc. : N, 6·5%). It was also obtained in a similar manner but in poorer yield from 1 : 1′-dinitrodiphenyl 2 : 2′ : 4 : 4′-tetrasulphide (Hodgson and Handley, *loc. cit.*).

2 : 4-*Dimethylthiolaniline* was obtained from 2 : 4-dimethylthiolnitrobenzene by reduction with tin and hydrochloric and acetic acids. It is a colourless oil with a geranium-like odour and is readily volatile in steam. The *hydrochloride* crystallises from water in colourless needles which rapidly turn blue on exposure to light (Found : N, 6·5. $C_8H_{11}NS_2,HCl$ requires N, 6·3%), and give a deep blue colour with ferric chloride. The *acetyl* derivative crystallises from alcohol or dilute acetic acid in silky needles, m. p. 114° (Found : S, 28·2. $C_{10}H_{13}ONS_2$ requires S, 28·1%), and the *benzoyl* derivative from alcohol in colourless needles, m. p. 125° (Found : S, 22·2. $C_{15}H_{15}ONS_2$ requires S, 22·1%).

3 : 3′-*Diacetamido*-4 : 4′-*dinitrodiphenyl Disulphide.*—3-Chloro-6-nitroaniline was first prepared by heating (6—7 hours) 2 : 4-dichloronitrobenzene (8 g.) with alcohol (10 c.c.) and aqueous ammonia (35 c.c.; *d* 0·880) in a sealed tube at 160—165°; the mixture was then diluted with water and the product (7 g.) filtered off. The chlorine in 3-chloro-6-nitroaniline is very stable towards alcoholic sodium disulphide, whereas in 3-chloro-6-nitroacetanilide, obtained by acetylation with a mixture of acetic anhydride (which alone only partly acetylates the base) and acetyl chloride, the chlorine is again labile and readily reacts with sodium disulphide to form 3 : 3′-*diacetamido*-4 : 4′-*dinitrodiphenyl disulphide*; this crystallises from glacial acetic acid in pale yellow needles, m. p. 192—193° (Found : N, 13·1; S, 15·3. $C_{16}H_{14}O_6N_4S_2$ requires N, 13·3; S, 15·2%), and is insoluble in alcohol and benzene and only slightly soluble in acetone.

6-*Nitro*-3-*thioanisidine* was obtained from the corresponding disulphide (above) by the method described for the preparation of 2 : 4-dimethylthiolnitrobenzene, and crystallised from alcohol in deep yellow needles, m. p. 116° (Found : S, 17·7. $C_7H_8O_2N_2S$ requires S, 17·4%).

Results.

The order of increasing redness is from left to right. Brackets indicate almost identical shades.

Dye.	Experiment.	Order.																			
From Schäffer's salt.	Wool dyeing.	V	XV	XIV	VIII	XVIII	III	I	XIX	XVI	VII	XVII	VI	II	IV	XI	XII	XX	IX	X	XIII
		(Reddish-violet)	Bluish-red)	(	Red	)				Scarlet to reddish-orange					)	(	Orange to orange-yellow				)
,, ,, ,,	Lovibond.	V	XIV	XV	VIII	XVIII	VI	III	I	IV	XIX	VII	II	XVI	XVII	XII	XI	XX	IX	XIII	X
,, ,, ,	Sulphuric acid.	XIV	XVIII	VIII	V	XVI	VI	XIX	XVII	VII	XV	IV	II	III	I	XII	XI	XIII	IX	XX	X
		(	Blue		)	(			Violet			)	(		Crimson			)	(Scarlet)	(Reddish-orange)	(Orange)
From R-salt	Wool dyeing.	V	XIV	XV	VIII	XVIII	III	I	XIX	VI	II	VII	XVI	IV	XVII	XI	XII	XX	IX	X	XIII
		(Violet)	(Reddish-violet)		(Bluish-red)		(		Red with gradual increase of yellow							)(	Orange with increase of yellow				)
,, ,,	Lovibond.	V	XV	XIV	XVIII	VIII	III	I	VI	XIX	IV	II	VII	XVI	XII	XVII	XI	XX	IX	XIII	X
,, ,,	Sulphuric acid.	XIV	XVIII	VIII	V	VII	VI	XVI	XIX	XVII	IV	XV	II	III	I	XII	XIII	XI	IX	XX	X
			Blue		)				Violet			)	(			Crimson			)	(Reddish-orange)	

Combined Effects of the Substituents deduced from the Dyeing Results.

A denotes a resultant additive effect, S a resultant subtractive effect.

Groups in the basic component.	Effect on depth of shade.	
	Dye from Schäffer's salt.	Dye from R-salt.
2-Chloro-4-methoxy	2-Cl, no effect	S
4- ,, -2- ,, ...	A	4-Cl, no effect
5- ,, -2- ,, ...	S	S
2- ,, -4-methylthiol	S (slightly)	S (slightly)
4- ,, -2- ,, ...	4-Cl, no effect	A
5- ,, -2-	S	S

Groups in the basic component.	Effect on depth of shade.	
	Dye from Schäffer's salt.	Dye from R-salt.
2-Methoxy-4-methylthiol	A (optimum effect)	A (optimum effect)
4- ,, -2- ,, ...	A	A
2 : 4-Dimethoxy	A	A
2 : 4-Dimethylthiol	A	A
2 : 4-Dichloro	S	S
2 : 5- ,, ...	A (hypsochromic)	A (hypsochromic)

3-*Chloro*-4-*nitrothioanisole*, prepared by the Sandmeyer method from 6-nitro-3-thioanisidine, is slowly volatile in steam and crystallises from alcohol in pale yellow needles, m. p. 61° (Found : Cl, 17·2. $C_7H_6O_2NClS$ requires Cl, 17·4%).

2-*Chloro*-4-*thioanisidine*, prepared by reduction of the preceding nitro-compound with tin and hydrochloric acid, is an oil. The *hydrochloride* crystallises from water in long needles, m. p. 217—218°, and gives a reddish-purple colour with ferric chloride. The *acetyl* derivative separates from dilute acetic acid in long needles, m. p. 129° (Found : Cl, 16·3; S, 15·2. $C_9H_{10}ONClS$ requires Cl, 16·5; S, 14·8%).

The Dyes, Dyeing Trials, and Dye Solutions.—These were made by the methods described in the previous paper (*loc. cit.*). For convenience, each dye is referred to by the attached numeral, which indicates the amine employed in its preparation : 2-anisidine (I), 4-anisidine (II), 4-chloro-2-anisidine (III), 2-chloro-4-anisidine (IV), 2-anisidine-4-methyl thioether (V), 4-anisidine-2-methyl thioether (VI), 2-thioanisidine (VII), 4-thioanisidine (VIII), 2-chloroaniline (IX), 3-chloroaniline (X), 4-chloroaniline (XI), 2 : 4-dichloroaniline (XII), 2 : 5-dichloroaniline (XIII), 2 : 4-dimethylthiolaniline (XIV), 2 : 4-dimethoxyaniline (XV), 4-chloro-2-thioanisidine (XVI), 5-chloro-2-thioanisidine (XVII), 2-chloro-4-thioanisidine (XVIII), 5-chloro-2-anisidine (XIX), aniline (XX).

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