LXXIII.—*Studies in Colour and Constitution. Part I. The Influence of the Methylthiol Group, alone and in Conjunction with the Methoxy-group.*

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THE superior bathochromic influence of the methylthiol group in comparison with the methoxy-group was discovered by Brand (*Ber.*, 1909, **42**, 3463). The work of Waldron and Reid (*J. Amer. Chem. Soc.*, 1923, **45**, 2399) and of Foster and Reid (*ibid.*, 1924, **46**, 1936), however, indicated this influence was stronger or weaker than that of the methoxy-group according as the methylthiol group was in the para- or ortho-position with respect to it.

Dyes were prepared from 2- and 4-thioanisidines by one of the authors (H. H. H.) in 1918 (Brit. Pat. 235334 of 1924), and his study of meta-halogenated phenols has afforded the opportunity of comparing the bathochromic effects of the methylthiol and methoxy-groups in ortho- and para-positions, and vice versa, in the same amine.

For this purpose, the action of sodium disulphide on 3-chloro-2-, -4-, and -6-nitrophenols (Hodgson and Moore, J., 1925, **127**, 1925) has been investigated. No replacement of chlorine in the free phenols and in 3-chloro-2-nitroanisole took place, but the methyl ethers of 3-chloro-4- and -6-nitrophenols were readily converted into disulphides. These ethers were prepared in good yield by Haworth and Lapworth's method (J., 1923, **123**, 2986) and have been described by Hodgson and Moore (this vol., p. 157). Conversion of the disulphides into thioethers and subsequent reduction produce respectively 4-anisidine-2- and 2-anisidine-4-methyl thioethers, in which the positions of the methoxy- and methylthiol groups are interchanged.

Azo-dyes were prepared from the above amines with Schäffer salt, R-salt, and H-acid (in alkaline solution) as second components, and also, for comparison purposes, from 2- and 4-anisidines and 2- and 4-thioanisidines. From the dyeings on wool, the colorimetric estimation of the dye solutions by the Lovibond tintometer, and the colours given by the solid dyes with concentrated sulphuric acid, the superiority of the bathochromic influence of the methylthiol group in the para-position was found to be most pronounced. The methoxy-group in the Schäffer and R-salt dyes, however, exhibited the converse influence, *i.e.*, it produced the optimum effect when it was in the ortho-position. The *o*-methylthiol and *p*-methoxy-groups appear to produce the same effect. The maximum effect was obtained with the *p*-methylthiol group in conjunction with an *o*-methoxy-group, *viz.*, very pronounced violet colour with the Schäffer and R-salt dyes and an almost indigo-blue colour with the H-acid dye. Chlorine exerts the same influence as the methylthiol group, but to a less degree; the shades, however, are brighter. In all cases the dyes from 4-thioanisidine are the strongest in tinctorial power.

EXPERIMENTAL.

3-*Chloro*-4- *and* -6-*nitroanisoles*.—The respective chloronitrophenols (8 g.) dissolved in xylene (40 c.c.) were heated under reflux on the water-bath for 8 hours in presence of potassium carbonate (10 g.), and methyl sulphate (10 c.c.) was gradually added. The mixture was rendered strongly alkaline and steam-distilled; xylene and a little ether passed over first and were followed by the main bulk (yield 7 g.; 81%).

4-*Chloro*-2- *and* 2-*Chloro*-4-*anisidines*.—The above ethers (1 g.) were each heated under reflux on the water-bath with concentrated hydrochloric acid (5 c.c.) and water (15 c.c.), with gradual addition of granulated tin (3 g.). After the ether had dissolved, the mixture was made alkaline and the products were removed by steam distillation. For convenience, the hydrochlorides were prepared (yield 0·8 g.). They formed long needles, m. p. 238° and 228°, respectively (Found: Cl, 36·4 and 36·5. C_7H_8ONCl,HCl requires Cl, 36·6%).

2 : 2′-*Dinitro*- *and* 4 : 4′-*Dinitro*- 5 : 5′-*dimethoxydiphenyl Disulphides*.—3-Chloro-4- and -6-nitroanisoles (8 g.) were each dissolved in alcohol (50 c.c.) and gently boiled under reflux during the cautious addition of aqueous sodium disulphide (crystallised sodium sulphide, 6 g.; sulphur, 0·8 g.; water, 40 c.c.); heating was then continued for 4—5 hours. The respective disulphides separated and the contents were filtered hot, unchanged nitroanisole being removed by warm alcohol (yield 6·5—7 g.; 88—90%).

2 : 2′-*Dinitro*-5 : 5′-*dimethoxydiphenyl disulphide* is insoluble in water, alcohol, or benzene, but soluble in carbon disulphide or glacial acetic acid, from which it crystallises in white needles, m. p. 152° (uncorr.); these rapidly turn yellow in sunlight (Found: N, 7·4; S, 18·0. $C_{14}H_{12}O_6N_2S_2$ requires N, 7·6; S, 17·4%). The last trace of free sulphur was retained even after repeated crystallisation. Concentrated aqueous or alcoholic alkali hydroxides give violet-red solutions. Concentrated sulphuric acid gives a pale yellow solution in the cold, unchanged by moderate heating or dilution. Chlorosulphonic acid gives a crimson solution in the cold, which becomes yellow on heating and remains so on dilution, whilst oleum (23% SO_3) produces a brownish-yellow colour, which

changes to yellow on heating and lemon-yellow on subsequent dilution.

4 : 4′-*Dinitro*-5 : 5′-*dimethoxydiphenyl disulphide* resembles the preceding isomeride in solubility. It crystallises from glacial acetic acid in white, glistening micro-plates, m. p. 194° (uncorr.) (Found : N, 7·6; S, 17·9%). The solutions in alkalis are deep red. Concentrated sulphuric acid produces an orange-yellow colour in the cold, which becomes successively red, brown, and green on heating, and brownish-purple on subsequent dilution. Chlorosulphonic acid or oleum (23%) produces a green colour in the cold, which changes to reddish-brown on heating; a reddish-brown precipitate forms on dilution.

2-*Nitro- and* 4-*Nitro*-5-*methoxythioanisoles*.—The above disulphides (2 g.) were each heated on the water-bath for 15 minutes with alcohol (10 c.c.), crystallised sodium sulphide (1 g.), sodium hydroxide (2·4 g.), and water (10 c.c.). The mixture was then stirred into water (35 c.c.), filtered if necessary, and warmed with methyl sulphate (2—2·5 c.c.), when the thioanisole separated (yield 2 g.; 92%).

2-*Nitro*-5-*methoxythioanisole* is insoluble in cold but slightly soluble in hot water and is very slowly volatile in steam. It crystallises from alcohol in yellow needles, m. p. 112—113° (uncorr.), and is very slowly decomposed by nitric acid (Found : N, 7·2. $C_8H_9O_3NS$ requires N, 7·0%). The crimson solution in concentrated sulphuric acid becomes violet on heating and thereafter yellow on dilution. The corresponding colorations produced by oleum (23%) and chlorosulphonic acid are blood-red, reddish-brown and yellow, and blue, violet and yellow, respectively.

4-*Nitro*-5-*methoxythioanisole* resembles the preceding isomeride in solubility and volatility in steam, but crystallises from alcohol in paler yellow needles, m. p. 79—80° (uncorr.) (Found : N, 6·9%). The colorations produced by solution, heating, and subsequent dilution are : for concentrated sulphuric acid, scarlet, blood-red to reddish-violet, blood-red; for oleum, chocolate-brown, blood-red, yellow; for chlorosulphonic acid, red, orange, yellow.

2-*Anisidine*-4-*methyl- and* 4-*Anisidine*-2-*methyl Thioethers*.—The respective nitro-compounds (2 g.) were heated under reflux with granulated tin (4 g.), concentrated hydrochloric acid (10 c.c.), and water (10 c.c.) until all had dissolved. The solution was made distinctly alkaline with sodium hydroxide and steam-distilled. In both cases, the bases passed over as oils, but only 2-anisidine-4-methyl thioether crystallised on standing. The 4-anisidine isomeride was converted into the hydrochloride.

2-*Anisidine*-4-*methyl thioether* is very soluble in alcohol and crystallises from water in white, feathery needles, m. p. 44° (uncorr.), which become discoloured in air (yield 1·3 g.; 77%) (Found: N, 8·5; S, 19·1. $C_8H_{11}ONS$ requires N, 8·3; S, 18·9%). Concentrated sulphuric acid gives a yellow solution which remains unchanged on heating or dilution. The pale violet solution in oleum changes to deep violet on warming, but becomes colourless on prolonged heating.

The *hydrochloride* crystallises from hydrochloric acid in colourless needles which turn pink in air; m. p. 235° (approx.) (Found: Cl, 17·5; S, 15·2. $C_8H_{11}ONS,HCl$ requires Cl, 17·3; S, 15·6%).

4-*Anisidine*-2-*methyl thioether* is an oil which is very soluble in alcohol, but only slightly so in water. Concentrated sulphuric acid gives a violet solution in the cold, which becomes reddish-violet on heating. The corresponding colorations with oleum and chlorosulphonic acid are blue-violet and reddish-purple and purple and reddish-purple, respectively.

The *hydrochloride* forms white needles, m. p. 210—211°, which become steel-grey on exposure to light (Found: N, 7·4; Cl, 17·25; S, 15·3. $C_8H_{11}ONS,HCl$ requires N, 7·0; Cl, 17·3; S, 15·6%).

The Dyes.—These were prepared in the usual way and sodium chloride was removed as completely as possible.

Dyeing trials. Wet strips of wool (2·5 g.) were introduced into a bath of water (250 c.c.) containing the dyes (0·025 g.), sodium sulphate (0·25 g.), and sulphuric acid (0·05 g.). The solution was gradually heated to the boiling point and there maintained until the dyeing was complete.

Dye solutions. These were evaluated in terms of red, yellow, and blue components by means of the Lovibond tintometer.

The colours produced by sulphuric acid on the dry dye powders were also examined.

For convenience, the dyes are referred to by the attached numerals, which indicate the particular amine employed: 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).

The order of increasing redness is from left to right.

Results.

Dye.	Experiment.	Order.
From Schäffer Salt.	Wool dyeing.	V, VIII, I, III, VII, IV, II, VI. (Red-violet) (Red) (Scarlet to orange)
,, ,, ,,	Lovibond.	V, VIII, VI, III, I, IV, VII, II.
,, ,, ,,	Sulphuric acid.	VIII, V, VII, VI, IV, II, III, I. (Blue) (Violet) (Crimson)
,, R-Salt.	Wool dyeing.	V, VIII, III, I, VI, II, VII, IV. (Violet) (Bluish-red) (Red with gradual increase of yellow)

Dye.	Experiment.	Order.
From R-Salt.	Lovibond.	V, VIII, III, I, VI, IV, II, VII.
,, ,,	Sulphuric acid.	VIII, V, VII, VI, IV, II, III, I. (Blue) (Violet) (Crimson)
,, H-Acid.	Wool dyeing.	V, VIII, VI, II, VII, III, IV, I. (Indigo-blue) (Red-violet) (Violet-red)
,, ,,	Lovibond.	V, VI, VII, VIII, IV, I, II, III.
,, ,,	Sulphuric acid.	VIII, V, IV, VI, II, III, I, VII. (Blue) (Violet)

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