CCXLV.—*Studies in Colour and Constitution. Part III. The Influence of the Methylthiol, Methoxy-, and Chlorine Groups on the Colours of the Nitrobenzaldehydephenylhydrazones.*

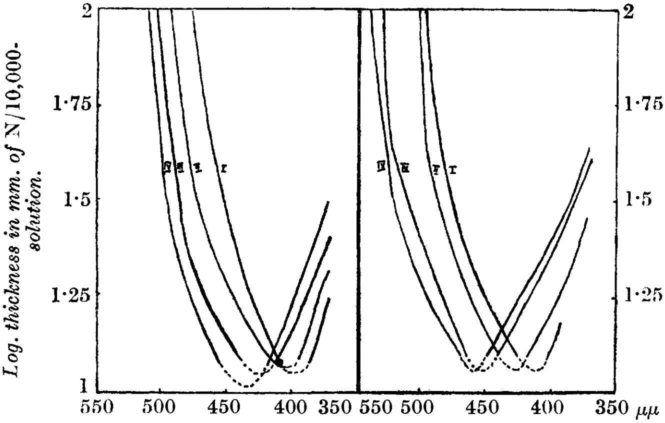
By Herbert Henry Hodgson and Frederick William Handley.

The study of the influence of the methylthiol, methoxy-, and chlorine groups on the colours of simple azo-dyes (this vol., p. 162) has been extended to certain nitrobenzaldehydephenylhydrazones containing these substituents in ortho- and para-positions in the benzaldehyde and phenylhydrazine residues, respectively. In addition to the visual observations, absorption spectra data are included; work in the latter field has been recorded by Baly and Tuck (J., 1906, **89**, 982), Hewitt, Johnson, and Pope (J., 1914, **105**, 364), and Ciusa and Rastelli (*Atti R. Accad. Lincei*, 1919, **28**, ii, 366; 1920, **29**, ii, 146; *Gazzetta*, 1922, **52**, ii, 121, 126).

Trustworthy conclusions could not be deduced from the colours of the solid hydrazones because of their wide variation with the mode of crystallisation, but equimolecular alcoholic solutions exhibited a well-defined order. The absorption spectra curves of the *p*-nitrobenzaldehydephenylhydrazones confirm the results of the visual observations, and the relative order of the effects of the substituents is the same whether these are present in the aldehyde or the hydrazine residue and is independent of the position of the nitro-group, *viz.*,

o-Cl, *o*-SMe, *p*-Cl, H, *o*-OMe, *p*-SMe, *p*-OMe.
Lemon-yellow $\xrightarrow[\text{Increasing depth}]{\qquad\qquad\qquad}$ Deep reddish-orange

The influence of the substituents is, in general, less marked than in the case of the azo-dyes; *e.g.*, (1) *o*-methoxyl is much less bathochromic; (2) *p*-methoxyl, which is only slightly bathochromic in the dyes, has a strong effect in the hydrazones, equalling or even exceeding that of *p*-methylthiol; (3) the feeble hypsochromic effect of *o*-chlorine in the dyes becomes most pronouncedly so in the hydrazones.



	Centre of band.		Centre of band.
I p-*Nitrobenzaldehyde*-o-*chlorophenylhydrazone*	395	I p-*Nitrobenzaldehyde*-p-*chlorophenylhydrazone*	413
II p-*Nitrobenzaldehyde*-o-*methylthiolphenylhydrazone*	405	II p-*Nitrobenzaldehydephenylhydrazone*	425
III p-*Nitrobenzaldehydephenylhydrazone*	425	III p-*Nitrobenzaldehyde*-p-*methylthiolphenylhydrazone*	455
IV p-*Nitrobenzaldehyde*-o-*methoxyphenylhydrazone*	433	IV p-*Nitrobenzaldehyde*-p-*methoxyphenylhydrazone*	465

The colours of the solutions in alcoholic potash of all the hydrazones studied were in accord with the generalisations of Chattaway and Clemo (J., 1923, **123**, 3041); as, however, the same marked differences in colour did not occur, no further conclusions have been drawn therefrom.

The Chromoisomerism of p-*Nitrobenzaldehydephenylhydrazone.*—Ciusa and Vecciotti (*Atti R. Accad. Lincei*, 1911, **20**, i, 803) recorded the existence of two polymorphic forms of *p*-nitrobenzaldehydephenylhydrazone, and the following related phenomena have now been observed: (1) The hydrazone crystallises from glacial acetic acid in yellow needles, m. p. 194°, which slowly become pale orange without alteration of m. p. (2) Exposure to ultra-violet light for some hours or to sunlight for some weeks failed to bring about any such change as that noted by Chattaway (J., 1906, **89**, 462) for benzaldehydephenylhydrazone. (3) Addition of water to a solution of *p*-nitrobenzaldehydephenylhydrazone in glacial acetic acid precipitated a yellow variety which changed in a few seconds into the red form of Ciusa and Vecciotti, a transformation which occurs in the absence of sunlight.

Attempts to prepare *o*-methylthiolbenzaldehyde were unsuccessful.

EXPERIMENTAL.

4-*Methylthiolphenylhydrazine*, which could not be prepared satisfactorily by the methods of Hodgson and Beard (*J. Soc. Chem. Ind.*, 1926, **45**, 56T) and Thompson (*J. Soc. Dyers and Col.*, 1921, **31**, 7), was obtained as follows: The diazonium compound obtained from 4-thioanisidine hydrochloride (8 g.), concentrated hydrochloric acid (40 c.c.), and 20% aqueous sodium nitrite (18 c.c.) at 0° was reduced at 0° with stannous chloride (24 g.) and hydrochloric acid (24 c.c.), and the *hydrochloride* produced was collected after 1 hour, washed with a little concentrated hydrochloric acid, and recrystallised from hot water, separating in colourless, glistening plates (Found: N, 15·0; Cl, 18·45. $C_7H_{10}N_2S,HCl$ requires N, 14·8; Cl, 18·6%).

4-*Methylthiolphenylhydrazine*, liberated from a hot aqueous solution of the hydrochloride by alkali or sodium acetate, crystallised from water in colourless plates, m. p. 60° (Found: S, 20·8. $C_7H_{10}N_2S$ requires S, 20·65%).

2-*Methylthiolphenylhydrazine*.—The reaction product obtained by the above method from 2-thioanisidine hydrochloride consisted of a mixture of a pale brown, amorphous substance A (1·1 g.) and a colourless, crystalline substance B (7 g.). A melted below 100°, was insoluble in cold and decomposed by boiling water, and was probably analogous to certain compounds described by Thompson (*loc. cit.*), who suggested a diazo-hydrazide structure for them (compare Bamberger, *Ber.*, 1895, **28**, 840); it has not been studied further. B contained tin, which was removed from an aqueous solution of the substance by hydrogen sulphide; addition of alkali or sodium acetate then gave 2-*methylthiolhydrazine*, which crystallised from water in colourless needles, m. p. 40° (Found: S, 20·6. $C_7H_{10}N_2S$ requires S, 20·65%). Both 2- and 4-methylthiolphenylhydrazine reduce Fehling's solution and ammoniacal silver nitrate in the cold, and decompose on keeping.

4-Methylthiolbenzaldehyde (phenylhydrazone, m. p. 138°) was obtained by Friedländer and Lenk's method (*Ber.*, 1912, **45**, 2084).

Preparation of the Hydrazones.—A mixture of the aldehyde in glacial acetic acid and of a slight excess of the hydrazine hydrochloride in aqueous solution was warmed gently for 5 minutes. The hydrazone separated on cooling and was recrystallised from dilute acetic acid.

Comparison of the Colours of 0·001N-*Alcoholic Solutions.*

Aldehyde.	Substituents in the hydrazine.
	Order of increasing redness ⟶
o-Nitrobenzaldehyde.	*o*-Cl, *o*-SMe, *p*-Cl, H, *o*-OMe, *p*-SMe, *p*-OMe
	Lemon-yellow ⟵orange—deep orange⟶red orange
m-Nitrobenzaldehyde.	Pale yellow⟵yellow⟶ ⟵orange ⟶
p-Nitrobenzaldehyde.	Yellow⟵orange—reddish-orange ⟶

Hydrazine.	Substituents in the benzaldehyde.
o-Nitrophenylhydrazine.	*o*-Cl, *p*-Cl, H, *o*-OMe, *p*-SMe, *p*-OMe
	⟵Yellow⟶ ⟵orange ⟵reddish-orange⟶
m-Nitrophenylhydrazine.	⟵Yellow⟶ ⟵orange—deep orange⟶
p-Nitrophenylhydrazine.	⟵Yellow⟶ ⟵orange—reddish-orange⟶

Colours with Alcoholic Potash.—A concentrated alcoholic solution of potassium hydroxide was added to a portion of each of the above solutions until no further change in colour occurred. The final colour is recorded below after the m. p. and is followed by the change on heating.

o-*Chlorobenzaldehyde*-o-*nitrophenylhydrazone*, orange needles, m. p. 178° (Found : Cl, 12·7. $C_{13}H_{10}O_2N_3Cl$ requires Cl, 12·9%). Deep blue. Unchanged.

p-*Chlorobenzaldehyde*-o-*nitrophenylhydrazone*, scarlet needles, m. p. 203—204° (Found : Cl, 12·9%). Blue. Unchanged.

o-*Methoxybenzaldehyde*-o-*nitrophenylhydrazone*, bright red needles, m. p. 176—177° (Found : N, 15·7. $C_{14}H_{13}O_3N_3$ requires N, 15·5%). Violet-blue. Unchanged.

p-*Methoxybenzaldehyde*-o-*nitrophenylhydrazone*, scarlet needles, m. p. 204° (Found : N, 15·8%). Blue-violet. Unchanged.

p-*Methylthiolbenzaldehyde*-o-*nitrophenylhydrazone*, scarlet needles, m. p. 225—226° (Found : S, 11·3. $C_{14}H_{13}O_2N_3S$ requires S, 11·1%). Blue-violet. Unchanged.

o-*Chlorobenzaldehyde*-m-*nitrophenylhydrazone*, pale orange needles, m. p. 171° (Found : Cl, 12·8%). Brownish-yellow. Deeper.

p-*Chlorobenzaldehyde*-m-*nitrophenylhydrazone*, orange-red plates, m. p. 172° (Found : Cl, 12·6%). Brownish-yellow. Deeper.

o-*Methoxybenzaldehyde*-m-*nitrophenylhydrazone*, reddish-orange plates, m. p. 176° (Found: N, 15·8%). Orange. Brownish-orange.

p-*Methoxybenzaldehyde*-m-*nitrophenylhydrazone*, orange-yellow plates, m. p. 156° (Found : N, 15·6%). Brownish-yellow. Deeper.

p-*Methylthiolbenzaldehyde*-m-*nitrophenylhydrazone*, old-gold prisms, m. p. 146° (Found : S, 11·4%). Brownish-yellow. Deeper.

p-*Chlorobenzaldehyde*-p-*nitrophenylhydrazone*, deep orange spears, m. p. 224° (Found : Cl, 12·7%). Violet. Deeper.

o-*Methoxybenzaldehyde*-p-*nitrophenylhydrazone*, brick-red needles, m. p. 204—205° (Found : N, 15·3%). Violet. Deeper.

p-*Methylthiolbenzaldehyde*-p-*nitrophenylhydrazone*, deep orange needles, m. p. 183° but turns yellow at 140—145° (Found : S, 11·3%). Violet. Deeper.

o-*Nitrobenzaldehyde*-o-*methylthiolphenylhydrazone*, deep orange needles, m. p. 87—88° (Found: S, 10·8%). Yellowish-green. Olive-green.

o-*Nitrobenzaldehyde*-p-*methylthiolphenylhydrazone*, brownish-red prisms, m. p. 204° (Found : S, 11·3%). Olive-green. Bluer.

m-*Nitrobenzaldehyde*-o-*methylthiolphenylhydrazone*, orange prisms, m. p. 118° (Found : S, 11·5%). Yellow. Brownish-yellow.

m-*Nitrobenzaldehyde*-p-*methylthiolphenylhydrazone*, orange-red plates, m. p. 152° (Found : S, 11·4%). Brown. Deeper.

p-*Nitrobenzaldehyde*-o-*methylthiolphenylhydrazone*, red needles, m. p. 147° (Found : S, 10·9%). Olive-green. Bluish-green.

p-*Nitrobenzaldehyde*-p-*methylthiolphenylhydrazone*, scarlet plates, m. p. 179° (Found : S, 11·3%). Olive-green. Bluish-green.

Benzaldehyde-p-*methylthiolphenylhydrazone*, colourless plates, m. p. 93° (Found: S, 13·5. $C_{14}H_{14}N_2S$ requires S, 13·2%). Yellow. Deeper.

p-*Methylthiolbenzaldehydephenylhydrazone*, m. p. 138° (Found : S, 13·4%). Yellow. Deeper.

Absorption Spectra.—These were obtained by means of a glass spectrograph, the source of light being an iron arc, and are shown in the figure.

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