THE ABSORPTION SPECTRA AND THE SUBSTANTIVITY TO COTTON OF CONGO RED AND RELATED STRUCTURES

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The effects of substitution in the 3:3'- and in the 2:2'-positions in the diphenyl nucleus have been further investigated by means of measurements of the ultra-violet and visible absorption spectra (in solution) of Congo Red, its chlorine- and brominedisubstituted derivatives, and the corresponding monoazo half-structures. It is found, consistently with earlier work, that 2:2'-substitution weakens the molecular conjugation. The equilibrium dyeing of cotton at 90°C with these dyes and with methyl-disubstituted derivatives of Congo Red has been examined, and it is confirmed that the 2:2'-substituted derivatives. Thus the spectra and the substantivity are consistent with the view that 2:2'-substitution induces sterically a non-coplanarity of the two halves of the diphenyl nucleus.

Morris and Brode,¹ Standing and Stein,² and Krasovitskii and Pereyaslova ³ measured the ultra-violet and visible absorption spectra of symmetrical disazo dyes, derived from benzidine, in solution. They found, consistently with the results of many investigations of simpler substituted diphenyls, that substituents introduced in the 2 : 2'-positions in the diphenyl nucleus weakened the molecular conjugation by causing a partial insulation at the $C_{(1)}$ — $C_{(1')}$ bond. They interpreted this finding in terms of a sterically induced non-coplanarity of the two halves of the diphenyl nucleus, and showed ², ³ that this interpretation was consistent with the marked difference in dyeing properties ⁴ between 3 : 3'-substituted and 2 : 2'-substituted dyes.

Standing and Stein ² measured the ultra-violet and visible absorption spectra of *o*-Benzopurpurine 4B (C.I. Direct Red 2; structure I, having methyl groups in the 3:3'-positions in the diphenyl nucleus), *m*-Benzopurpurine (structure II, having methyl groups in the 2:2'-positions), and the monoazo half-structures corresponding essentially to the cutting of the $C_{(1)}$ — $C_{(1')}$ bond in structures I and II. The present paper extends the investigation to Congo Red (C.I. Direct Red 28; the parent, unsubstituted, compound), its chlorine-disubstituted and bromine-disubstituted derivatives of types I and II, and the corresponding monoazo half-structures.



 $\mathbf{R} = \mathbf{H}$ (in Congo Red), CH₃ (in the Benzopurpurines), Cl, or Br. 1166

I

F. H. HOLMES

Griffiths and Neale⁴ studied the relation between molecular structure and substantivity of some of these dyes. The present paper describes a more detailed study of the dyeing of cotton, under equilibrium conditions, with Congo Red, its methyl-, chlorine- and bromine-disubstituted derivatives, and its half-structure.

Nomenclature.—Disubstituted derivatives of Congo Red are, for brevity, referred to as (for example) " the 3: 3'-dibromo dye ", " the 2: 2'-dimethyl dye ".

EXPERIMENTAL

MATERIALS

Congo Red was purified by the method of Robinson and Mills.⁵ The dimethyl dyes and their half-structures were the samples prepared and purified by Standing and Stein. The dichloro and dibromo dyes, their half-structures, and the half-structure of Congo Red were prepared from the appropriate diamine or amine by tetrazotising or diazotising, and coupling with sodium naphthionate, as described by Standing and Stein, and were purified by repeated recrystallization from ethanol + water mixtures or water. For the measurement of absorption spectra, three of the dyes (the 3 : 3'-dichloro, the 3 : 3'-dibromo and the 2 : 2'dibromo dyes) were further purified in small amount by adsorption chromatography on filter-paper, with an 80/20 mixture (by vol.) of 2-methoxyethyl acetate and water as solvent and developer (as recommended by Venkataraman⁶). The other compounds, when examined chromatographically, were found to contain no significant amount of coloured impurity.

Details of the preparation and purification of the intermediates are as follows.

DIAMINES.—The appropriate halogen-substituted nitrobenzene was reduced in ethanolic NaOH with Zn powder to the substituted hydrazobenzene, which was converted by means of $SnCl_2$ and HCl to the substituted benzidine. This was recrystallized from ethanol, and the m.p. determined to verify the purity.

AMINES.—B.D.H. aniline and chloroanilines were used. The latter were further purified by the preparation and decomposition of the acetyl derivative or picrate. Bromoanilines were prepared by reducing B.D.H. bromonitrobenzenes with $SnCl_2$ and HCl. For all amines, purity was verified from the m.p. and b.p. of crystalline derivatives.

For the preparation of standard solutions the solid dyes were conditioned at 20° or 25°C in an atmosphere of 66 % or 65 % r.h. over saturated sodium nitrite; the moisture content of samples, not used for solutions, was determined by vacuum-drying at approx. 110°C to constant weight. For the measurement of absorption spectra the solvent was 94% ethanol (by wt.). For use in the ultra-violet, the ethanol was B.D.H. "special for spectroscopy". Sodium chloride, for use in the dyeings, was of Judex A.R. quality. The cotton (Egyptian, Giza 12), used in the dyeings in the form of a soft-twisted yarn, was mercerized, and was purified as described by Bilsbury, Martin and Standing.⁷ Its fluidity 8 (in 0.5 % solution in cuprammonium at 20°C) was 8.6, and its carboxyl content (determined by the Methylene Blue method 9) was 5.5 millimoles/kg.

ABSORPTION SPECTRA were measured at room temperature in a 0.5 cm cell with a Unicam SP 500 spectrophotometer. The concentration of the solutions was about 0.03 mM for the disazo dyes and 0.06 mM for the monoazo half-structures. By making measurements $2\frac{1}{2}$ h, one day, and one week after the preparation of the solutions it was verified that the dyes were stable in 94 % ethanol. The optical densities were reproducible to about 0.5 %. Special tests showed that none of the solutions was phototropic.

The accuracy of the optical density readings of the spectrophotometer was checked by means of a standard solution containing 0.005 % $K_2Cr_2O_7 + O\cdot 1 N H_2SO_4$. The values of " E (1 %, 1 cm)" at the maxima and minima of absorption in the ultra-violet (approx. 235, 257, 313 and 350 mµ) were 123.0, 143.0, 47.8 and 106.8. From a collaborative test ¹⁰ in which 72 instruments were compared, the mean values were 125.2, 145.6, 48.9 and 107.0, and had a coefficient of variation between instruments of 1.65 %. The present results deviate from the mean results of the collaborative test by 1.8, 1.8, 2.3 and 0.2 %.

EQUILIBRIUM DYEING

Sodium chloride was the inorganic electrolyte in the dyebaths, and the temperature was 90° C. The dyebaths were not buffered; their final pH, measured at room temperature, was usually between 5.5 and 7.5. The experimental methods were similar to those of Bilsbury, Martin and Standing.⁷ Preliminary measurements showed that equilibrium was attained within 6 h under the experimental conditions, and this duration was

adopted as standard. The dye concentration of the equilibrium dyebaths, and the amount of dye extracted from the dyed cotton, were both determined. Often it was found that after the 6 h dyeing the total amount of dye in the system (determined from its light absorption in the visible region) was significantly less than the initial amount. It is well known that many direct cotton dyes decompose in hot salt solutions,^{11, 12} giving relatively colourless products. The mean percentage loss of dye was: Congo Red, 1·3; 3:3'-dimethyl dye, 5·6, 3:3'-dichloro dye, 0·7; 3:3'-dibromo dye, negligible; 2:2'-dimethyl dye, 3·4; 2:2'-dichloro dye, 2·0; 2:2'-dibromo dye, 5·5; half-structure of Congo Red, 2·2. The products of decomposition are probably far less substantive than the dyes to cellulose, and are therefore unlikely to affect seriously the distribution of dye between cotton and dyebath.

RESULTS

ABSORPTION SPECTRA

Typical spectra, viz., those of the 3:3'-dichloro dye, the 2:2'-dichloro dye, and the half-structure of the latter, are shown in fig. 1. The wavelengths λ_{max} of maximum absorption and the corresponding molar extinction coefficients ϵ_{max} are stated in table 1. Results for the dimethyl dyes and their half-structures² are included for comparison. For disazo dyes, ϵ_{max} is quoted; for half-structures, $2\epsilon_{max}$.



FIG. 1.-Absorption spectra of chlorine-substituted derivatives of Congo Red.

Within each series (methyl, chlorine, or bromine) the spectra of the two monoazo half-structures are closely similar. For all series the same type of spectral change accompanies the sequence: half-structure, 2:2'-substituted disazo dye, 3:3'-substituted disazo dye. This change (indicative of a lengthening of the conjugated chain) consists in: (i) in the near ultra-violet, an increase in λ_{max} and a decrease in intensity of absorption (measured by ϵ_{max} for the disazo dyes and by $2\epsilon_{max}$ for the half-structures); (ii) in the visible, a greater increase in λ_{max} and an increase in intensity of absorption.

When corresponding structures having different substituents are compared, it is seen that Congo Red and the 3:3'-dimethyl dye have closely similar spectra. The 3:3'-dichloro and the 3:3'-dibromo dyes have spectra closely similar to each other, but distinctly different from that of Congo Red. The 2:2'-dichloro and the 2:2'-dibromo dyes have spectra closely similar to each other, but slightly different from that of the 2:2'-dimethyl dye.

F. H. HOLMES

The half-structures form two groups, each fairly uniform in spectrum : (i) the unsubstituted and the methyl-substituted, (ii) the chlorine- and the bromine-substituted. In general, the halogen-substituted structures (monoazo or disazo) have λ_{max} larger in the visible region than the corresponding unsubstituted or methyl-substituted structures.

TABLE 1.—ABSORPTION MAXIMA

 λ_{max} is in m μ . ϵ_{max} is in l./mole cm. Bracketed figures refer to inflections.

dye	¹ max	ε_{max} (or $2\varepsilon_{max}$)×10 ⁻⁴	λ _{max}	[€] max (or 2εmax)×10 ⁻⁴	λ _{max}	ε_{max} (or $2\varepsilon_{max}$) $ imes$ 10 ⁻⁴
Congo Red	237	4·3	340	3·8	510	5·4
half-structure of Congo Red	235	4·8	312	5·7	460	2·9
3 : 3'-dimethyl 2 : 2'-dimethyl half-structure of 3 : 3'-dimethyl half-structure of 2 : 2'-dimethyl	235 235 235 235 235	4·2 4·8 4·7 4·7	340 325 315 315	3·5 5·4 5·5 5·3	510 485 460 450	5·5 4·2 2·9 2·8
3 : 3'-dichloro	(235)	(4·0)	325	3·7	532	5·5
2 : 2'-dichloro	235	4·4	322	4·8	498	4·0
half-structure of 3 : 3'-dichloro	233	4·5	315	6·1	478	3·2
half-structure of 2 : 2'-dichloro	232	4·7	315	5·5	472	3·1
3 : 3'-dibromo	(240)	(3·7)	325	3·5	532	5·3
2 : 2'-dibromo	235	4·2	320	4·6	495	3·7
half-structure of 3 : 3'-dibromo	235	4·6	315	6·0	475	3·2
half-structure of 2 : 2'-dibromo	235	5·0	315	5·6	472	3·2

EQUILIBRIUM DYEING

Definitions

 $[Cl]_s$ and $[D]_s$ are the sodium chloride and the dye concentrations (in millimoles/l.) in the dyebath, in equilibrium with the cotton, at 90°C.

[D]_A is the uptake of dye by the cotton at equilibrium (in millimoles dye/kg dry cellulose.)

The salt/dye ratio $p \equiv [Cl]_s/r[D]_s$, where r is the valency of the dye anion (2 for the disazo dyes, 1 for the half-structures).

The substantivity ratio $q \equiv [D]_A/[D]_s$ (in l./kg).

For each dye, several fixed salt concentrations were used in turn. At each salt concentration, the dye concentration in the initial dyebath was so chosen that p, at equilibrium, came close to 200. Dyeings were done in duplicate, and usually two or three sets of duplicates were done, with initial dye concentrations made slightly different, so that the range of p included the value 200. From the results at each salt concentration, a plot of q against p was drawn, and by interpolation or very short extrapolation q corresponding to p = 200 was evaluated. The experimental values of q had a coefficient of variation, between duplicates, of about 1.7 % for six of the dyes, and about 4.7 % for the other two (the 2: 2'-dimethyl dye, and the half-structure of Congo Red).

The essential results are shown in fig. 2 and 3, where q (at p = 200) is plotted against $[D]_s$ over a 16-fold range of concentration. Congo Red and the 3:3'-substituted dyes are similar in behaviour. They have large values of q, which decrease considerably as the dye and salt concentrations in the dyebath are increased in the same proportion. The 2:2'-substituted dyes have a much smaller, but still considerable, substantivity, and q tends to increase with concentration. (We may note that the literature often states that 2:2'-substituted dyes have no substantivity to cellulose.) The half-structure of Congo Red has a small but real substantivity; over the range of $[D]_s$ from 0.2 to 1.6, $q = 4.6 \pm 0.2$.

Griffiths and Neale⁴ measured, at a single dyebath concentration, the equilibrium dyeing of cotton at 90°C with Congo Red, the 3:3'-dimethyl dye, the 3:3'-dichloro dye, and the 2:2'-dimethyl dye. The present results agree qualitatively with theirs, but cannot be compared quantitatively on account of a different pre-treatment of the cotton (mercerization, giving a greater accessibility to dye) and a different value of p in the dyebaths (200; Griffiths and Neale's value was about 600).



FIG. 2 and 3.—Variation of q with [D]_s, at p = 200, for Congo Red, its 3:3'-substituted derivatives, its 2:2'-substituted derivatives, and its half-structure.

F. H. HOLMES

DISCUSSION

Beaven and Hall¹³ found that in the 2: 2'-dihalogenodiphenyls the spectroscopic indications of conjugation varied continuously from the slightly hindered difluoro compound to the severely hindered di-iodo compound. In the present, more complex, structures, chlorine and bromine behave almost identically.

It is clear that the disazo dyes are classified consistently by molecular structure, by absorption spectrum, by the magnitude of the substantivity ratio, and by the nature of the variation of the substantivity ratio with concentration at a fixed salt-dye ratio. In the first three properties the results agree qualitatively with those of previous workers 1 , 3 , 4 and lead to the same conclusion of a non-coplanarity induced sterically by 2:2'-substitution. The fourth property will be discussed in the following paper 14 in relation to the theory of dyeing.

Mr. C. V. Caine prepared and purified the halogenated dyes. Mrs. J. Colling did much of the experimental work on equilibrium dyeing.

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