[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Optically Active Dyes. V. Molecular Asymmetry in Dyes and Their Dyeing Properties

BY WALLACE R. BRODE AND RICHARD ENSIGN BROOKS

In the work directed by Adams and described in the earlier papers of this series[1,2,3,4] the use of dyes containing an asymmetric carbon atom failed to support a chemical theory of dyeing, since no partial resolution of the racemic dye resulted from the dyeing of wool and silk, nor was any difference shown in the dye absorption rates of the optically active forms. This work has been extended and again confirmed through the use of a new dye type in which the whole molecule is asymmetric.

According to present-day information, the dyeing of textile fibers occurs in three phases: (1) diffusion of the dye into the sub-microscopic voids of the fiber (2) adsorption of the dye (3) irreversible fixation of the dye. The nature of the union between the dye molecule and the fiber molecule has not been proven but the preponderance of evidence favors a physical, adsorptive phenomenon through hydrogen bonds and secondary valences in the dyeing of vegetable fibers and a chemical phenomenon such as salt-formation in the dyeing of animal fibers. But the distinction between these two types of combination is not altogether sharp and the process might conceivably be the result of both.

The chemical reactions of stereoisomers with the single optically active form of another substance to form a pair of diastereoisomers sometimes proceed at measurably different rates and reach different reaction equilibria. This is known as kinetic-resolution because the result is the formation of a larger proportion of one diastereoisomer.[5]

Because of the optically active structure of protein and cellulose fibers, it has been suggested that there might possibly be some difference in the dyeing of fibers with the two isomeric forms of an optically active dye, and that there should be a partial resolution of the dye in dyeing the fibers with the racemic modification,[6] if the dyeing process were chemical in character.

Only very slight evidence of optically selective adsorption of one form of a dye containing an asymmetric carbon atom has been obtained.[7] This claim could not be substantiated because the proof was of the same order of magnitude as the experimental error. The first dyes made expressly for this type of experiment were derivatives of diazotized *p*-aminodiphenylmethylcarbinol.[8] Qualitative experiments seemed to give positive indication of a partial resolution of the racemic dye by dyeing wool fibers. Later this work was extended using dyes prepared by coupling various intermediates to diazotized *m*-aminomandelic acid. At first quantitative evidence of a resolution was claimed,[9] but was soon refuted and shown to be due to experimental error.[4] Other dyes prepared by coupling β-naphthol or dimethylaniline to diazotized phenyl-(*p*-aminobenzoylamino)-acetic acid[1] were selected because of their suitability for experiments of this kind and used in careful quantitative dyeing experiments. The exhausted racemic dye liquors were examined polarimetrically and no rotation could be detected. Analysis of the dye liquors by titanous chloride titration showed that, within the experimental error, the same amounts by per cent. of both active forms were taken up, a slightly greater amount of the racemic form, by wool and silk fibers. This was confirmed by spectrophotometric examination of the dyed samples.[3] The conclusion is that the active isomers of optically active dyes have the same physical properties, including adsorption by inert and active materials, color, fastness to light, melting point, and absorption spectra.

In each previous attempt to test the proposition that there might possibly be selective adsorption of one form of an optically active dye by textile fibers, it must be noted that, within the dye-molecule, the origin of optical activity, an asymmetric carbon atom, has been well removed from the origin of color, *i. e.*, the chromophore and auxochrome groups. In the work described in this

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(1) Ingersoll with Adams, THIS JOURNAL, **44**, 2930 (1922).

(2) Brode with Adams, *ibid.*, **46**, 2032 (1924).

(3) Brode with Adams, *ibid.*, **48**, 2193 (1926).

(4) Brode with Adams, *ibid.*, **48**, 2202 (1926).

(5) Gilman, "Organic Chemistry," Vol. 1, John Wiley & Sons, Inc., New York, N. Y., 1938, Chapt. 3 (Shriner, Adams and Marvel), pp. 193–195.

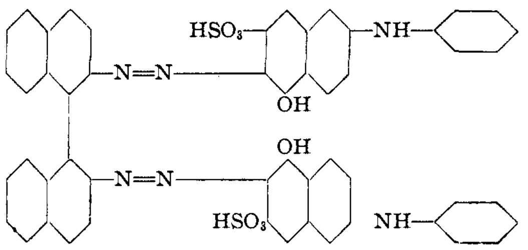
(6) Willstätter, *Ber.*, **37**, 3758 (1904).

(7) Morgan and Skinner, *J. Chem. Soc.*, **127**, 1731–1742 (1925).

(8) Porter and Hirst, THIS JOURNAL, **41**, 1264 (1919).

(9) Porter and Ihrig, *ibid.*, **45**, 1990–1993 (1923).

paper a dye has been synthesized in which the whole molecule is asymmetric and the chromophore and auxochrome groups are situated as nearly as possible to the seat of optical activity. The dye chosen was prepared from an asymmetric diphenyl intermediate which involved molecular rather than atomic asymmetry. For this purpose 2,2′-diamino-1,1′-binaphthyl was resolved and the active and racemic diamines tetrazotized and coupled to phenyl-J acid to yield the dyes indicated by the following formula.



In view of the large and varied amount of evidence in support of a chemical theory of the dyeing of fiber proteins, it seems probable that the conditions chosen for these experiments were not ideal for revealing differences in the dyeing of wool by stereoisomeric dyes. In order that the dye and fiber come to an equilibrium adsorption, it is necessary that the dye be molecularly dispersed.[10] Furthermore, the very symmetry of the dye prepared could not be conducive to a steric effect which would lead to different rates of reaction or reaction equilibria of the stereoisomeric forms. Other purely physical attributes of the dye were not obtained in the optimum kind; that is, the color of the dye was such that visual examinations were necessarily made at such great dilutions and long wave lengths that they were not of the greatest possible accuracy.

With a more satisfactory dye the dyeing experiment should afford a fundamental method of determining the nature of the union of a dye molecule with a fiber molecule and is worthy of more elaborate and extended study. In order to magnify any partial optical resolution of an optically active dye, further work is contemplated employing the principles of chromatographic analysis: by pouring a solution of the racemic dye over one or more columns of fiber flock, an appreciable magnification of the effect might be obtained.

Experimental

Preparation of 2,2′-Diamino-1,1′-binaphthyl.[11,12]—2-Aminonaphthalene (140 g.) was purified by recrystallization from petroleum ether–benzene and dissolved in one liter of water containing 90 ml. of concentrated hydrochloric acid and 77 ml. of concentrated sulfuric acid. This was diazotized in the cold with 70 g. of sodium nitrite in 200 ml. of water. The diazonium compound was reduced by adding 155 g. of sodium sulfite in one liter of water. The precipitated 2-azo-naphthalene was filtered off and recrystallized from petroleum ether–benzene, yielding about 100 g. This was reduced by adding 50 g., in small portions, to 125 g. of stannous chloride in 200 ml. of cold absolute alcohol saturated with anhydrous hydrogen chloride. The 93 g. of tin double salt was filtered off and decomposed by digesting in 500 ml. of 10% sodium hydroxide. The free 2,2′-diamino-1,1′-binaphthyl which floats to the surface was filtered off, reprecipitated from dilute acid with dilute alkali and recrystallized from 50% acetone (m. p. 191–192° cor.). This modified procedure of converting 2-azo-naphthalene into 2,2′-diamino-1,1′-binaphthyl resulted in an increase of the yield from $36^1/_2$[2] to 87%.

Resolution of 2,2-Diamino-1,1′-binaphthyl.—The resolution was accomplished by adding 42 g. of *d*-camphor-β-sulfonic acid in 300 ml. of alcohol to 52 g. of the racemic diamine in 2 liters of chlorobenzene at 100°. The reaction mixture was kept at this temperature until the salt of the *d*-form completely precipitated out. The salt of the *l*-form was obtained by evaporating the mother liquors to a small volume. The salts, on dissolving in pyridine, were decomposed and the free diamines thrown out on diluting with large volumes of water. They were purified as before by reprecipitation from dilute acid with dilute alkali and recrystallization from acetone–water and alcohol–water to a melting point of 246–247°, cor. As thus obtained, using pyridine as a solvent, the *d*-form showed a specific rotation of $[\alpha]^{20}\text{D}$ +154.1°, the *l*-form $[\alpha]^{20}\text{D}$ −157.8°.

Preparation of Asymmetric Dyes.—The dyes were prepared by tetrazotizing the optically active and the racemic modifications of 2,2′-diamino-1,1′-binaphthyl in the exact molecular proportion of dilute acid and coupling to phenyl-J-acid in a mildly alkaline solution containing enough sodium carbonate to just neutralize all the aforementioned acid. A derivative of J-acid was chosen as the second component to increase the substantivity of the dye toward cotton. The dye produced was deep-red in color. It was, however, of such a molecular size that its colloidal properties were enhanced and it was not easily titrated with titanous chloride. The dyes were partially purified by dissolving in large volumes of water, treating with carboraffin, then precipitating from acid solution by adding sodium acetate in the hot and cooling. $TiCl_3$ analysis indicated a purity of from 94 to 96% in the three dyes.

$$\frac{[\alpha]^{25\,°}_{660\ \text{m}\mu}}{1000};\ (d) = +1.04 \pm 0.5;\ \ (l) = -1.17 \pm 0.5$$

Data on the visual absorption spectra of these dyes are give in Brode's "Chemical Spectroscopy."[13]

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[10] Goodall, *J. Soc. Dyers Colourists*, **54**, 45 (1938).

[11] Jacobson, *Ann.*, **427**, 195 (1922).

[12] Kuhn and Goldfinger, *ibid.*, **470**, 190 (1929).

[13] Brode, "Chemical Spectroscopy," John Wiley and Sons Inc., New York, N. Y., 1939, p. 132.

Dye Adsorption.—The dyes prepared from both stereoisomers and the racemic modification of 2,2′-diamino-1,1′-binaphthyl were used in a series of dyeing experiments to attempt to detect an optically selective adsorption according to the methods of Brode.[8]

Samples of 7.000 g. of purified, desulfurized viscose rayon were dyed in 200 ml. (the volume of the bath in ml. was "29 times" the weight of the fiber sample in g.) dye-baths containing about 0.18 g. of the dye (the weight of the dye was "2.7%" of the weight of the fiber sample) and 0.03 g. of sodium acetate. The dyeings were commenced at 49°, taken to 100° in forty-five minutes and maintained at that temperature for one and one-half hours. The samples were then removed, thoroughly washed and freed of the dye liquors. The dye liquors were next analyzed by titrating with excess titanous chloride and back-titrating with standard ferric alum solution. Portions of the dye liquors were also diluted to equal strengths, about 0.043 g. per liter, and examined polarimetrically and spectrophotometrically. In a similar manner, 4.000 g. samples of purified, unbleached and unspun wool were dyed in dye-baths of the same strength (equivalent to 50 times and 4.7% of the weight of the fiber sample), but maintained at 100° for only forty-five minutes. The results were compared to blank experiments, the per cent. of dye taken up by the fibers calculated and the results set forth in the table.

Solution	Dye in liquors, g.	Dye taken up, g.	Dyeing, %	$[\alpha]^{25°C.}_{6600 Å.}$ (±500)
l-blank	0.1776			+1044
d & *l*-blank	.1888			+ 464
d-blank	.1964			−1177
l-rayon	.1641	0.0135	7.64±0.6	+1508
d & *l*-rayon	.1743	.0145	7.53±1.0	− 116
d-rayon	.1816	.0148	7.56±1.1	−1177
l-wool	.1091	.0685	38.6±1.5	+ 928
d & *l*-wool	.1107	.0781	41.3±0.8	+ 232
d-wool	.1187	.0777	37.4±1.1	−1161

Within the experimental error, the spectrophotometric observations confirmed the titanous chloride analyses. Together, they show that under the conditions of the experiments no optically selective adsorption of the stereoisomeric forms of 2,2′-di-(1-hydroxy-2-azo-3-sulfonic acid-6-anilino-naphthalene)-1,1′-binaphthyl occurred. This is substantiated by the polarimetric observations.

Summary

Optically active and racemic dyes have been prepared through the tetrazotization of the active and racemic forms of 2,2′-diamino-1,1′-binaphthyl and coupling to phenyl-J-acid. Dyeing tests with these active and racemic dyes failed to show any selective absorption by wool or rayon fibers and thus confirm previous experimental work. The data support a physical rather than a chemical combination between fiber and dyestuff.

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The Acetone Derivatives of the Mercaptals of Some Monosaccharides. VI. Crystalline 2-Monomethyl *d*-Mannose and its *alpha*-Methylglycofuranoside, Dimethyl Acetal and Dibenzyl Mercaptal

BY EUGENE PACSU AND S. M. TRISTER[1]

In 1931 Levene and co-workers[2] definitely established that Pacsu's supposed 4-methyl glucose[3] was identical with the true 2-methyl glucose,[4] the structure of which was proved by Brigl and Schinle.[5] Subsequently, Levene's conclusion was confirmed by Pacsu,[6] who also pointed out that in all probability the 4-methyl mannose of Pacsu and v. Kary[7] likewise represented a 2-methyl derivative, since the osazones derived from the two methyl hexoses were identical. Brigl and Schinle[5d] had previously found that under the standard conditions of osazone formation 2-methyl glucose gave rise to phenylglucosazone with the loss of the methyl group. In 1936 Munro and Percival[8] undertook "A Revision of the Constitution of the Supposed 4-Methyl Galactose and 4-Methyl Mannose of Pacsu. . . " and found that close agreement exists between the physical constants of the supposed 4-methyl galactose[9] as well as its osazone and phenylhy-

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[1] Research Assistant on Special Funds from the Rockefeller Foundation.

[2] (a) Levene, Meyer and Raymond, *Science*, **73**, 291 (1931); *J. Biol. Chem.*, **91**, 497 (1931); *cf.* (b) Schinle, *Ber.*, **64**, 2361 (1931).

[3] (a) Pacsu, *ibid.*, **58**, 1455 (1925); *cf.* (b) Part I, *ibid.*, **57**, 849 (1924).

[4] The similarly named sirupy products described both by Pictet [Pictet and Castan, *Helv. Chim. Acta*, **3**, 645 (1920)] and by Irvine [Irvine, *J. Chem. Soc.*, **125**, 1 (1924)] cannot any longer be regarded as the true representatives of 2-methyl glucose.

[5] (a) Brigl and Schinle, *Ber.*, **63**, 2884 (1930); *cf.* (b) Hickinbottom, *J. Chem. Soc.*, 3140 (1928); (c) Lieser, *Ann.*, **470**, 110 (1929); (d) Brigl and Schinle, *Ber.*, **62**, 1716 (1929).

[6] Pacsu, *ibid.*, **65**, 51 (1932); (b) THIS JOURNAL, **58**, 2076 (1936).

[7] Part II, Pacsu and v. Kary, *Ber.*, **62**, 2811 (1929).

[8] Munro and Percival, *J. Chem. Soc.*, 640 (1936).

[9] Part III, Pacsu and Löb, *Ber.*, **62**, 3104 (1929).