UNIVERSITY OF ILLINOIS

January 15, 19 88.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

ANDREW JAMES PROCTOR

ENTITLED THE ADSORPTION OF CHIRAL METALLIZED AZO

DYES ON NATURAL FIBERS

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN

LIBERAL ARTS AND SCIENCES

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O-1364

THE ADSORPTION OF CHIRAL
METALLIZED AZO DYES ON
NATURAL FIBERS

BY

ANDREW JAMES PROCTOR

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THESIS

FOR THE
DEGREE OF BACHELOR OF SCIENCE
IN
LIBERAL ARTS AND SCIENCES

College of Liberal Arts and Sciences
University of Illinois
Urbana, Illinois

1988

ACKNOWLEDGEMENT

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# THE ADSORPTION OF CHIRAL METALLIZED AZO DYES ON NATURAL FIBERS

I. INTRODUCTION

Azo dyes torm the largest chemical class of dyestuffs. These dyes number in the thousands. Azo compounds as a class are strongly colored. They can be intensely yellow, orange, red, or even green, depending on the exact structure of the molecule. Because of their color, azo compounds are of tremendous importance as dyes; about half the dyes in industrial use today are azo dyes (1).

Azo dyes consist ot a diazotized amine coupled to an amine or a phenol and have one or more azo linkages. The characteristic azo group structure is R-N=N-R' (2). Many commercial azo dyes are metallized to increase their fastness to light and to extensive washing. In effect, the dye forms a coordination compound with the metal and this often results in a chiral compound. The metal atom thus serves as the center of asymmetry, and it creates an optically active molecule.

The dextro rotatory and levo rotatory forms of an optically active azo dye molecule often react differently with other chiral substances. Of course an active chiral azo dye will rotate the plane of polarization of light, but the two isomers of such a dye will react differently to other optically active compounds. Wool and silk are natural

fibers which owe their optical activity to asymmetric carbon atoms in the protein chain:

$$-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{C}}-\overset{\overset{}{}}{\underset{\underset{\displaystyle O}{\|}}{C}}-J$$
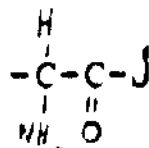
Cotton is a carbohydrate and is optically active because of the grouping:

$$-C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-$$
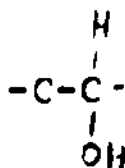
Both the dextro and levo forms of the dye are present at the start of the dyeing process, but one form may not adhere well to the material and thus be lost in the process or shortly thereafter.

The question of a physical or chemical phenomenon involved in the dyeing process has been debated for decades. The selectivity of one rotatory form over another provides the best evidence for a chemical mechanism involved in the dyeing phenomenon.

The goal of this paper is to provide additional experimental data which supports the chemical explanation of the dyeing phenomenon by causing a chiral metallized azo dye to react with cotton, wool, and silk. Specifically, this paper is a continuation of empirical research begun by Mark R. Hutchinson in 1983 at the University of Illinois,

Urbana. The same materials were used, with variations in procedure (3).

The nature of the action by which dyes are absorbed and
more or less permanently bonded to animal or vegetable
fibers has been the subject of many investigations.
Experiments in this field have been extensive and date back
to the eighteenth century. From all the results obtained so
far, no one can say with any certainty as to what type of
phenomenon is involved in the dyeing process. Is it a
chemical or physical reaction? Is it both? Many would say
it is chemical. Then again, many would say it is
physical. If the nature of the action were physical, it was
believed then the dextro rotatory and levo rotatory isomers
would attach themselves to the fibers in the same manner and
amounts. If the action were chemical, as is believed by the
author, then the two isomers would behave differently and
thus show selectivity for adherence to the fibers.

In 1904, Willstaetter carried out experiments upon
solutions of racemic alkaloids, but found no evidence of
selective absorption. However, Willstaetter made some
studies and discovered that wool could possibly serve as a
selective absorber (4). Using this discovery, Porter and
Hirst, in 1919, reported that they synthesized asymmetric
dyes, and selective absorption by wool was observed for one
of them (5). However, they could not get quantitative
confirmation of their results.

Following Porter and Hirst, Porter and Ihrig obtained selectivity using wool dyed in a racemic mixture of m-azo-β-naphthol mandelic acid. The residual portion, i.e. the dye not taken up by the wool, was levo rotatory. Thus the wool took up both the dextro and levo forms of the dye, but at different rates. The dextro isomer was held tighter by the wool than the levo isomer thus allowing the levo form to remain in the solution of dye. Porter and Ihrig used an excess of wool and extendended the time of contact to 72 hours. This method gave an almost pure levo rotatory residual dye (6). This would seem to be good evidence for a chemical explanation of the dyeing process. However, others would tend to disagree based on their observations.

Ingersoll & Adams (7) and Brode & Adams (8,9) disagreed with the above evidence for a chemical dyeing phenomenon. They made careful observations using many chiral azo dyes and found no significant difference in the behavior of the two isomers in any case. They concluded the optical isomers of any dye were adsorbed in the same way. Many of the experiments done at this time used non-metallized azo dyes, so it is quite possible that other dyes or other azo dyes might give different results.

The dye used by Hutchinson is the same one used here. It is alpha-pyridyl-azo-beta-naphthol (3). This substance was first prepared by Jennie Ching-I Liu at the University of Illinois by diazotizing alpha-aminopyridine and coupling

it with beta-naphthol (10). This dye is not used in the
treatment of fabrics, but is of the same type as many that
are. This dye is, however, used as an indicator in the
titration of metal ions and is sold commercially under the
name PAN. The structure of alpha-pyridyl-azo-beta-naphthol
can be seen in Figure 1.

The complexing metal is cobalt, which is from hexammine
cobalt (III) sulfate. A water molecule is also present.
The dye and the metal are coordinated together to obtain the
final complex. Since the metal ion, cobalt (III), shows a
coordination number of six, the final complex will be
octahedral in structure. This is logical because an azo dye
must have two or three points of attachment to the metal.
Thus, the final structure of the product is asymmetric. The
crystal structure can be either facial or meridonal, and
each structure can be either dextro or levo in rotation.
Each combination of structure and rotation can produce a
different color, as can be seen in the following
experiments. See Figure 2 for possible product structures.

In this study, PAN is a tridentate complexing agent.
This means it attaches itself to the metal ion through three
atoms--the pyridyl nitrogen, the azo nitrogen adjacent to
the naphthalene ring, and the naphthol oxygen. Upon
coordination with the metal, this oxygen atom loses the
proton so the metallized dye molecule has a charge of +1.
The complex formed is $[Co(dye)_2]^+$.

The author synthesized the cobalt complex using hexammine cobalt (III) sulfate, whereas Jennie Ching-I Liu and Mark Hutchinson both used hexammine cobalt (III) chloride (3,10). This difference aside, the initial procedures described by Jennie Ching-I Liu were followed. However, this produced low yield and low purity, so the author adopted some procedural modifications. The eventual final product was obtained by dissolving 0.6 grams of hexammine cobalt (III) sulfate and 1 gram of alpha-pyridyl-azo-beta-naphthol into 300 ml of 100 percent alcohol. This solution was refluxed for fifteen hours. Some decolorizing carbon was added at the beginning (about 1-2 grams) to act as a catalyst. After refluxing, the decolorizing carbon was hot filtered off. Once cooled, the remaining product was a dark orange-red precipitate. This was filtered, recrystallized from 100 percent alcohol, and dried in a dessicator. Upon analysis, the product was determined to be in high yield and purity.

Early experiments done in this field required the fibers to be imersed in a solution of the dye, and left to react over a period of time. Then the rotation was observed on the filtered solution of dye. But many inconclusive results were obtained by this method. As Hutchinson points out in his work, column chromatography provides good

selectivity and acceptable data (3). The same procedure and column dimensions are used here. The silk and cotton column were 26 cm x 0.5 cm. The wool column was 26 cm x 1 cm. Each column was packed with the fiber, and a solution of the metallized dye was allowed to slowly pass through.

With regard to the materials used, the alpha-pyridyl-azo-beta-na ıthol was purchased from Aldrich Chemical Co. and was used as received. The hexammine cobalt (III) sulfate was a student preparation and was received from Dr. Bailar. The wool was raw, just as when it was sheared, except that it was washed with warm water and soap, rinsed and dried. The cotton was absorbent cotton as is usually obtained from drug stores. The silk was in the form of silk cocoons which had received no treatment of any sort. A colleague of Dr. Bailar, Dr. Isao Mochida, sent the cocoons from Japan. Each material was cut into small bits and fibers before use.

The first column run was with silk. A 26 cm x 0.5 cm column was packed with silk fiber using 100 percent alcohol as the solvent. The flow rate was adjusted to be around 0.7 to 1 ml per minute. The metallized dye solution was prepared by dissolving .01 grams of the complex in 50 ml of 95 percent alcohol. This procedure differs from Hutchinson's work in that he used distilled water for his samples and preparations (3). The next column run was with cotton. The same dimensions and flow rate as the silk

column were used, except a higher concentration of metallized dye was used; .025 grams in 50 ml of alcohol.

The final column run was the 26 cm x 1 cm column packed with wool. This experiment with wool is unique in that it has two parts. The first part was completed just as the silk and cotton columns were. A concentration of .025 grams of dye in 50 ml of alcohol was passed through the column at a slow flow rate. The second part of the wool experiment included a drying time for the column. Ten days elapsed after the 50 ml was put through the column. This allowed the wool to dry with color from the dye still evident. The silk and wool columns were washed free of the color by a steady flow of alcohol solvent. After ten days, the wool column was filled with alcohol and more cold samples taken. The first sample taken off at this time was a distinctive light yellow-brown solution. The immediate second sample taken was a distinctive light pink solution. Several other samples were taken off the column, each one becoming lighter and lighter pink. At this point the wool column was wrapped with a heating strip and heated up to try to remove the dye still adhering to the wool. These "hot" samples collected were becoming darker pink, but they also contained a white suspension of increasing density. This suspension was suspected to be particles of wool, and after a filtered sample of this suspension was completely burned away, this conclusion was substantiated.

With each column run, the samples collected were the same color as the initial preparation. Each 50 ml preparation was a dark orange-red color. Each sample taken from the columns was the same color, with the exception of the second run made with the wool. Each sample was then measured, to observe the rotation, with a JASCO D.I.P. 360 Polarimeter. A 10 cm cell was used, with a 1 dm. path length for the beam. Each sample was measured with a sodium filter, at the 5890 Angstrom level.

IV.   RESULTS

The modified procedure used to prepare the metallized complex afforded one striking result. Hutchinson obtained a dark purple precipitate, whereas here, a dark orange-red precipitate was obtained. This difference can be attributed to a difference in structure of the metallized complex. It is not possible to determine the exact structure without the use of expensive x-ray crystallography. A color difference is enough to determine that two different structures were obtained by the two different procedures.

The rotation results of the silk column are listed in Table 1. Fraction 1 was the first sample of eluted dye taken off the column. This means it was the least absorbed by the fibers. Fraction 10 was the most absorbed.

TABLE 1

Fraction	Alpha rotation ($\pm$ .003)
1	- .0023
2	+ .00186
3	+ .00187
4	+ .00026
5	- .0008
6	+ .00053
7	+ .00026
8	+ .00043
9	- .00095
10	+ .00129

This date for the silk column can be interpreted as
mostly positive rotations. A major portion of the levo
rotatory isomer is retained on the fiber. A small portion
of the levo rotatory isomer probably has come off, or these
negative readings can be said to be erroneous. Hutchinson's
work obtained all dextro for the first half, then all levo
for the second half of the samples (3). In effect, the
results here are similar. The half and half split is more
spread out though, but a definite selectivity can be seen.

Results of the cotton column are listed in Table 2.

Table 2

Fraction	Alpha rotation ($\pm$ .003)
1	- .0016
2	- .0018
3	- .0038
4	- .0037
5	- .0116
6	- .0103
7	- .0102
8	- .0078

The results for the cotton column are all negative
which indicates a high selectivity for the dextro isomer.
No dextro (positive rotations) forms came off the column.
Hutchinson, however, obtained a similar dextro-levo split as
with the silk experiment (3).

Lastly, the wool results are listed in Table 3.

TABLE 3

Fraction	Alpha rotation (± .003)
1	− .00016
2	− .00015
3	− .0013
4	− .0022
5	− .00025
6	− .00048
7	+ .00103
8	− .00003
9	− .0010
10	− .0009
After 10 day drying period....	
1	− .0011
2	+ .0012
3	+ .0010
4	+ .0008
5	suspension (burned off)

The results for wool are similar to the results for cotton. A strong specificity for the dextro isomer is seen. After the ten day drying period, one levo then all dextro results were obtained. After the heated, eluted samples were taken, the column still retained some color. This color was a light-dark purple shade. Hutchinson's data revealed all positive rotations for the wool column. The data here reveal the opposite. But remember a different

structure was obtained. Hutchinson may have had either[14] a facial or a meridonal crystal structure. The same applies to the work here. The color change and rotation switch evident after the ten day period probably separated out the same structure Hutchinson had.

V.   CONCLUSION

By using the technique of column chromotography, it can be shown that different fibers do indeed show preferential adsorption for alpha-pyridyl-azo-beta-naphthol. Different structures of the same compound can produce different results, as can be seen with a comparison to Hutchinson's data. However, the same conclusion is reached. That is, the selective adherence of one isomer over another.

In this study, cotton gave the best results. The dextro isomer was held by the fiber and the levo was not. For the silk and wool fibers, a mix did occur, but it can be concluded that silk held the levo isomer and wool held the dextro isomer. Also, upon drying, the wool gave up much of its dextro isomer.

These results, taken together, provide qualitative support for the chemical explanation of the dyeing process. The early techniques used by past researchers only scratched the surface compared to the results possible with column chromotagraphy. Dye manufacturers and the textile industry could easily use these findings some day. From a financial point of view, using one isomer over another for dyeing purposes would be ideal, since much of what you buy will end up on your sweater and not go down the drain.
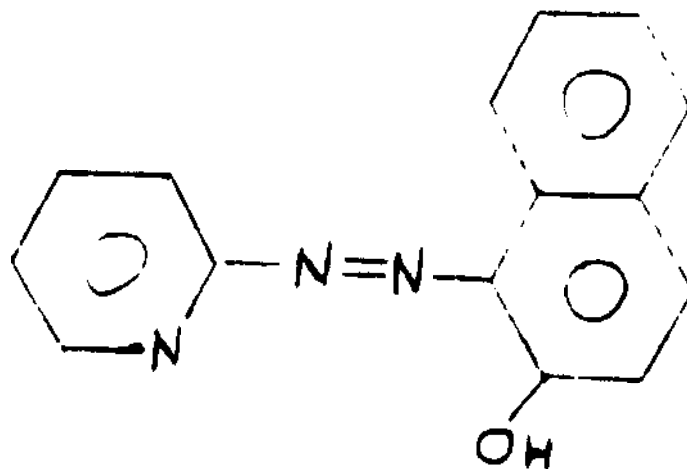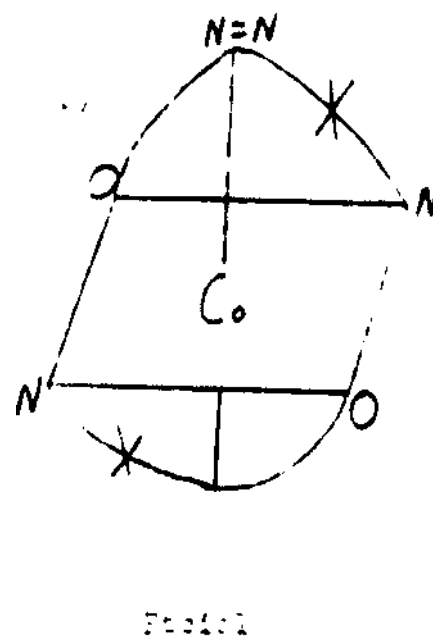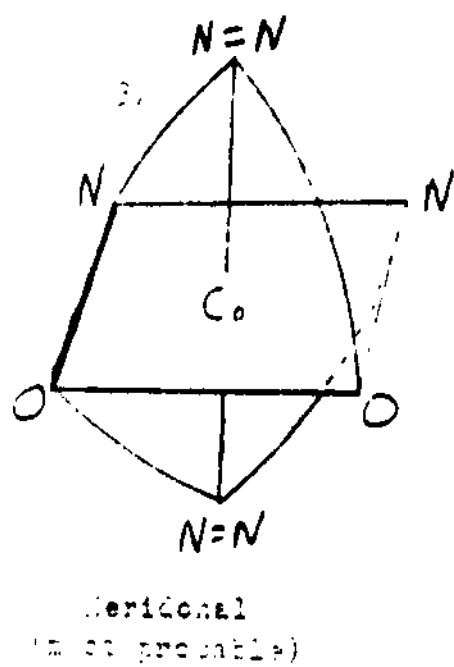
Alpha-pyridyl-azo-beta-naphthol

FIGURE 2

N

1)

Co

N=N   N=N

N

Meridonal

2)

Co

N

N

Facial

N=N

3)

N   N

Co

O   O

N=N

Meridonal
(not probable)

N=N

4)

O   N

Co

N   O

Facial
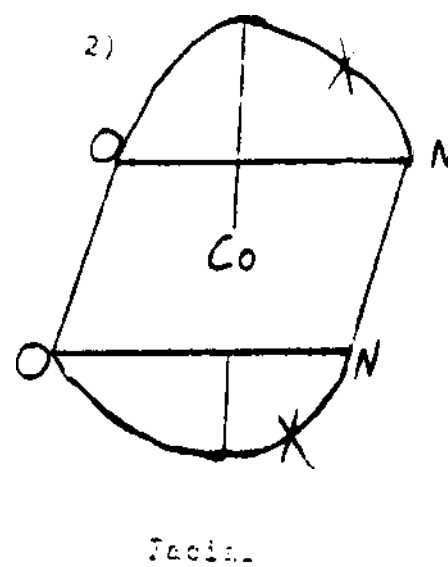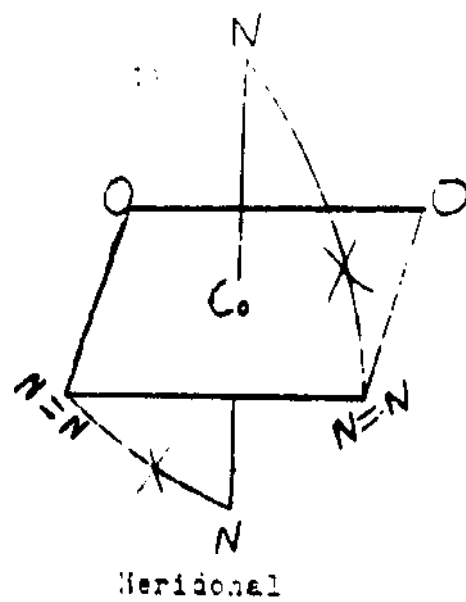
LITERATURE CITED

1. Morrison, Boyd Organic Chemistry Allyn & Bacon Pub. 4th
    Ed. 1983, pp. 942-943.

2. Streitwiesser, Heathcock Intro. to Organic Chemistry
    Macmillan Pub. Co. 3rd Ed. 1985, p. 1101.

3. Hutchinson, M. R. Bachelor's Thesis, University of
    Illinois, 1983.

4. Wilstaetter, Ber, 1904, 37, p. 3758.

5. Porter, C. W., and Hirst. J. Am. Chem. Soc. 1919, 41,
    p. 1264.

6. Porter, C. W. and Ihrig, H. K. J. Am. Chem. Soc. 1923,
    45, pp. 1990-1993.

7. Ingersoll, A. W. and Adams. J. Am. Chem. Soc. 1922,
    44, pp. 2930-2937.

8. Brode, W. R. and Adams, J. Am. Chem. Soc. 1926, 48, pp.
    2193-2201.

9. Brode, W. R. and Adams, J. Am. Chem. Soc., 1926, 48, p.
    2202.

10. Ching-I Liu, Jennie. Ph.D. Thesis, University of
    Illinois, 1951.