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Author(s)	Lim, Yongjin; Komatsu, Kiroku; Katayama, Akira; Kuroki, Nobuhiko
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## Phototropism of Cationic Azo Dyes Containing 1,3-Dialkyl Imidazole Ring

Yongjin LIM\*, Kiroku KOMATSU\*, Akira KATAYAMA\* and Nobuhiko KUROKI\*

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Cationic azo dyes were synthesized by means of N-alkylation of azo dyes prepared by coupling diazotised aniline derivatives with substituted imidazoles. Dacron T 92 and Cashimilon F fabrics were dyed with the cationic azo dyes. A set of the dyed sample was exposed to light from a high-intensity carbon arc lamp. Most of the dyed samples exhibited a phototropic effect on irradiation. A relation between the degree of discoloration and the chemical constitution of the dyes in this series was examined. The phototropic effect on fabrics was assumed to be due to the cis-trans isomerism. The absorption isotherms of the cationic azo dyes on anionic modified polyester fiber were determined in the dark and when irradiated with light from four 40-W incandescent lamps. The absorption from the irradiated baths was less than that in the dark. The results seemed to support the cis-trans isomerism.

### 1. Introduction

In a previous paper<sup>1)</sup> cationic azo dyes were synthesized by means of N-alkylation of azo dyes prepared by coupling diazotised aniline derivatives with substituted imidazoles. During studying the fading of a set of the dyed sample, phototropic phenomena were encountered. The dyed sample was exposed to light from a high-intensity carbon arc lamp. Most of the dyed samples changed their color to deeper one on irradiation with the light. On storage at room temperature in the dark the sample recovered its original color.

Many studies have been done on the phototropy of azo dyes. In particular the phototropic behavior of some azo dyes in solution has been carefully investigated by Hartley<sup>2)</sup> and Brode et al<sup>3)</sup>, because of their wide use in industry. However, little is known concerning the phototropic phenomena of cationic dyes<sup>4)</sup>.

In an attempt to investigate further the reversible changes in color which were observed in the fading experiments it was thought worthwhile to examine a relation between the degree of discoloration and the chemical constitution of the dyes in this series.

### 2. Results and Discussion

Dacron T 92 and Cashimilon F fabrics were dyed with the cationic dyes in this series. A set of the dyed sample was exposed to light from a high-intensity carbon arc lamp. The

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\* Department of Applied Chemistry, College of Engineering.

Table 1. Phototropy of dyes on fabrics

Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Dacron T 92	Cashimilon F
1	H	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	++	++
2	H	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	++	++
3	H	H	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	+	+
4	<i>p</i> -CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	++	+
5	<i>p</i> -CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	++	++
6	<i>p</i> -CH <sub>3</sub>	H	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	+	+
7	<i>m</i> -CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	+	+
8	<i>m</i> -CH <sub>3</sub>	H	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+	+
9	<i>m</i> -CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	++	++
10	<i>m</i> -CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	++	++
11	<i>o</i> -CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	+	+
12	<i>o</i> -CH <sub>3</sub>	H	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+	+
13	<i>o</i> -CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	+	+
14	<i>o</i> -CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+	+
15	<i>o</i> -CH <sub>3</sub>	H	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	+	+
16	<i>p</i> -C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	+++	+++
17	<i>p</i> -C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+++	+++
18	<i>o</i> -C <sub>2</sub> H <sub>5</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	+	+
19	<i>o</i> -C <sub>2</sub> H <sub>5</sub>	H	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+	+
20	<i>o</i> -C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	+	+
21	<i>o</i> -C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+	+
22	<i>p</i> -OCH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	+++	+++
23	<i>p</i> -OCH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+++	+++
24	<i>m</i> -OCH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	++	++
25	<i>m</i> -OCH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	++	++
26	<i>o</i> -OCH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	+	+
27	<i>o</i> -CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+	+
28	<i>p</i> -Cl	H	CH <sub>3</sub>	CH <sub>3</sub>	+	+
29	<i>p</i> -Cl	H	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+	+
30	<i>p</i> -Cl	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	++	++
31	<i>p</i> -Cl	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	++	++
32	<i>p</i> -Cl	H	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	+	+
33	<i>m</i> -Cl	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	++	++
34	<i>m</i> -Cl	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	++	++
35	<i>o</i> -Cl	H	CH <sub>3</sub>	CH <sub>3</sub>	+	+
36	<i>o</i> -Cl	H	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+	+
37	<i>o</i> -Cl	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	+	+
38	<i>o</i> -Cl	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+	+
39	<i>o</i> -Cl	H	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	+	+
40	<i>p</i> -COOC <sub>2</sub> H <sub>5</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	+	+
41	<i>p</i> -COOC <sub>2</sub> H <sub>5</sub>	H	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+	+
42	<i>p</i> -COOC <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	+	+
43	<i>p</i> -COOC <sub>2</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	+	+
44	<i>p</i> -NO <sub>2</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	+	+
45	<i>p</i> -NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	+	+
46	<i>p</i> -NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	+	+
47	<i>p</i> -NO <sub>2</sub>	H	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	+	+
48	<i>p</i> -N <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	+	+

+++ marked    ++ a little    + little or none

degree of discoloration of the dyed sample on irradiation was judged visually. The observed phototropic effect of the cationic azo dyes on the fabrics are listed in Table 1. As can be seen in Table 1, the degree of discoloration on the dyed fabrics varies with the chemical constitution of the dyes. A series of the dyes containing an electron-donating group in *p*-position to the azo linkage in the benzene ring of the diazo component shows marked discoloration. On the other hand the following dyes show little or none discoloration: the dyes having a phenyl group in 2-position of the imidazole ring and the dyes having an electron-attracting group, a phenyl azo group or *o*-substituent to the azo linkage in the benzene ring of the diazo component.

For a large number of azo and stilbene dyes it is well known that their phototropic effects on fabrics and in solutions can be attributed to *cis-trans* isomerism<sup>2,3</sup>.

The reversible changes in color of the cationic azo dyes examined in this paper may be due to the transformation of the dye from the *trans* form to the *cis* form. This mechanism will be accordance with the results obtained in this paper. The fact that the dye having an *o*-substituent to the azo linkage in the benzene ring of the diazo component shown only little or none phototropy on fabrics supports the *cis-trans* isomerism of the dye. The formation of the *cis*-configuration would be hindered sterically by the *o*-substituent to the azo linkage.

The spectra of all the cationic azo dyes examined in this paper exhibit a phototropic effect on irradiation with scattered light in aqueous solutions. Fig. 1 shows phototropic changes of Dye No. 22, which exhibits marked phototropic effect on the fabrics and Fig. 2 those of Dye No. 45, which exhibits little or none phototropic effect. On irradiation with scattered light, the peak at 350 nm is reduced in intensity and shifted slightly toward shorter wavelength, and another peak appears at about 500 nm. The new peak in the region of 500 nm is easily recognized in Fig. 1, but scarcely in Fig. 2.

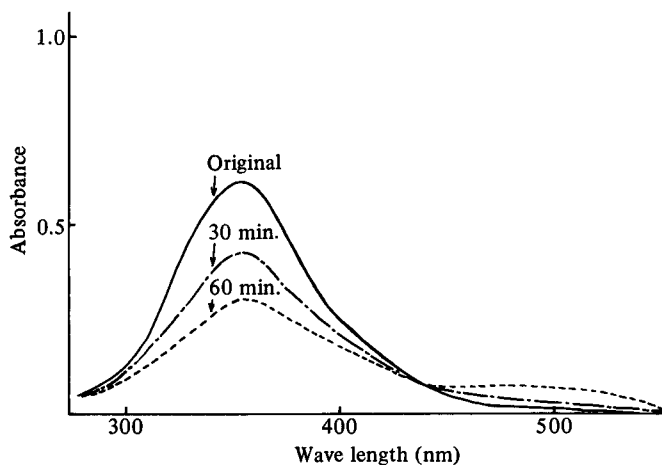


Fig. 1. The spectral change of Dye No. 22 with time on irradiation with the scattered light.

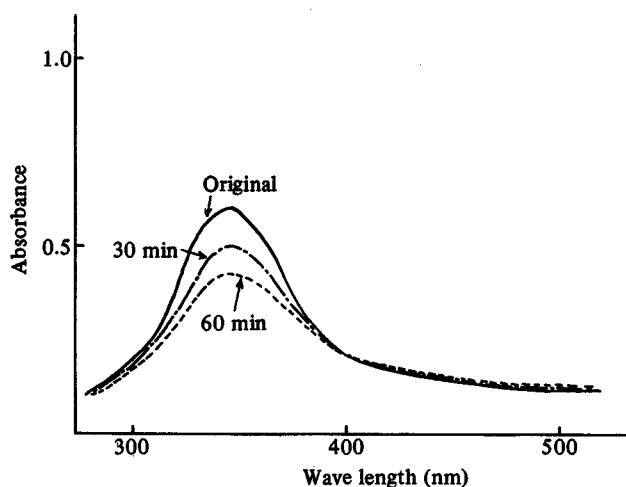


Fig. 2. The spectral change of Dye No. 45 with time on irradiation with the scattered light.

According to the idea that solutions of the cationic azo dyes contain the *cis* and *trans* forms in equilibrium with each other, the spectra of the solutions which have stood overnight in the dark (original curves) correspond to those of the *trans* form, since the *cis* isomer is present only in negligible amounts in the solution. The principal absorption band of the *cis* form should be at a shorter wavelength than that of the *trans* form. The new band which appears in the region of 500 nm on irradiation should be the secondary band of the *cis* form.

Hartley<sup>2)</sup> and Cook<sup>5)</sup> reported that solutions of 4-amino-, 4-acetyl-amino- and 4-hydroxyazobenzene exhibited considerable darkening in color upon irradiation. Brode et al<sup>3)</sup> examined the absorption spectra of derivatives of *p*-hydroxyazobenzene in benzene exposed to light and found that the principal absorption band was at a shorter wavelength, and that there was a weak, but distinct secondary band at the wavelength end of the spectrum of each dye of this type. The behavior of the cationic azo dyes toward irradiation agrees with earlier observations on the effect of light on azobenzene derivatives.

The rate of change of absorption maximum of several cationic azo dyes in this series is demonstrated graphically in Fig. 3.

In order to check an idea of *cis-trans* isomerism, the absorption isotherms of the cationic azo dyes on anionic modified polyester fiber were determined (a) in the dark and (b) when irradiated with light from four 40-W tungsten lamps. The results are given in Fig. 4, where it is seen that the absorption from the irradiated baths is less than that in the dark. When the *cis* form is produced on irradiation, the molecule loses its linear and planar character and is unable to interact effectively with polymer chains of the fiber. In this case electrostatic interactions between dye cations and negative charges on polymer

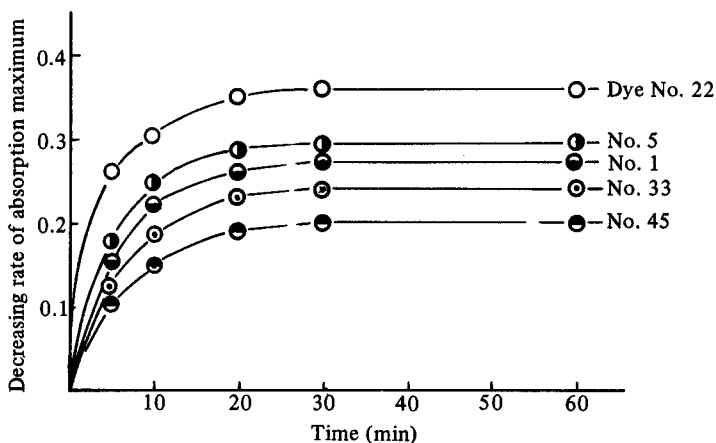


Fig. 3. The rate of change of absorption maximum of several cationic azo dyes on irradiation with the scattered light.

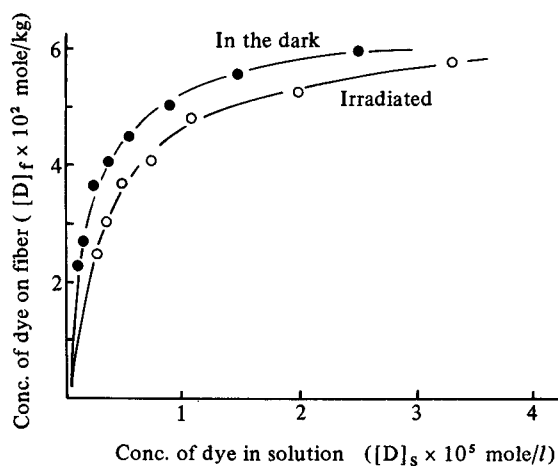


Fig. 4. The absorption isotherms of Dye No. 22 on Dacron T 92 in the dark and when irradiated with tungsten lamps.

chain should be a main factor to determine the affinity of the dyes to the fiber. However, short-range non-polar Van der Waals interactions between hydrophobic portions of the dye and polymer chain probably play an important role. Therefore, it could be expected that the *cis* form would have less affinity than the *trans* form.

Under dyeing condition the establishment of a true photostationary state may be extremely difficult. The results in Fig. 4, however, supports the *cis-trans* isomerism of the azo group of the cationic azo dyes.

### 3. Experimental

#### Preparation of cationic dye

The cationic azo dyes were synthesized by means of N-alkylation (methylation or ethylation) of azo dyes prepared by coupling diazotised aniline derivatives (*p*-toluidine, *m*-toluidine, *o*-toluidine, *p*-ethylaniline, *o*-ethylaniline, *p*-anisidine, *m*-anisidine, *o*-anisidine, *p*-chloroaniline, *m*-chloroaniline, *o*-chloroaniline, ethyl-*p*-aminobenzoate, *p*-nitroaniline and *p*-aminoazobenzene) with substituted imidazoles (2-methylimidazole, 2, 4-dimethylimidazole and 2-phenylimidazole).

#### Dyeing

Dacron T92 and Cashimilon F fabrics pre-scoured in the usual way were dyed with the cationic dyes for 60 mins at 100°C under the following dyeing condition: concentration 5 %, liquor ratio 50: 1, sodium sulfate 6 g/l, pH 4.4. In the case of Dacron T 92, 5 g/l of carrier (Tanatex, Carolid ELF-C) was used. The absorption isotherms were determined without any use of dyeing assistant, and if necessary, the dye-bath was irradiated with four 40-W incandescent lamps.

#### Discoloration test

Discoloration of the dyed fabrics was tested by means of a Model FA-1 Fadeometer and the results were judged visually.

#### Spectra

The absorption spectra of the cationic dyes were measured by means of a Hitachi Model 124 Spectrophotometer after keeping aqueous dye solutions over night in the dark. On exposing the solutions to the scattered light, the spectral changes with time were measured.

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