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Photochromism of the Azo Tautomer of 4-Phenylazo-1-Naphthol and its *O*-Methyl Ether in Solvents and Polymer Substrates

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SUMMARY

The trans ⇌ cis photoisomerism of 1-phenylazo-4-methoxynaphthalene and the azo tautomer of 4-phenylazo-1-naphthol was studied in liquid solvents (ethanol and cyclohexane) and polymer films (cellulose acetate and triacetate, and poly(methyl methacrylate)). In the solvents, first-order kinetics for thermal cis → trans reversion of the former compound were observed after overlap of the absorbance bands of each isomer had been taken into account. However, in polymer substrates, the heterogeneous environment and restricted molecular motion gave rise to more complicated kinetics. The cis isomer of the azo tautomer of 1-phenylazo-4-naphthol had too short a lifetime to be observed in solution, but in dry polymer substrates its lifetime was sufficiently prolonged to allow spectroscopic observation. Wetting the dyed polymer films with water greatly accelerated the rate of cis → trans reversion of the azo tautomer of 1-phenylazo-4-naphthol.

INTRODUCTION

Photochromism due to *trans* ⇌ *cis* isomerization is a phenomenon that has long been associated with azo compounds.[1] It is likely that a number

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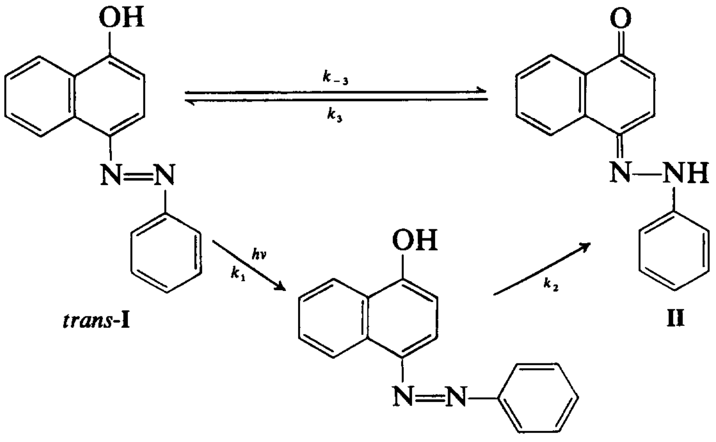
of mechanisms for this transformation are possible, depending on whether the reaction proceeds from a (π, π^*) or (η, π^*) excited state of singlet or triplet multiplicity.[2] Although photochromic azo compounds perform many useful functions,[3] severe photochromism is a disadvantage for azo compounds intended for use as colourants. Commercial azo dyes rarely exhibit noticeable photochromism for two possible reasons. First, aromatic azo compounds are able to undergo a thermal (dark) reaction from the higher energy *cis* isomer to the more stable *trans* isomer. The activation energy for this process is typically about 96 kJ mol^{-1} for azobenzenes,[4] but substitution such as is often found in commercial dye structures can substantially reduce this value. For example, the activation energy for the thermal *cis* → *trans* isomerization of 4-nitro-4-dimethylaminoazobenzene is 47·7 kJ mol^{-1}.[5] The mechanism for the thermal reversion has been debated in the literature for some time.[1] It now appears that most azobenzene derivatives undergo a 'rehybridization' or 'inversion' mechanism with the double bond between the nitrogen atoms remaining intact.[6]

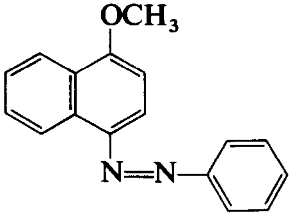
Second, many commercial azo dyes possess a hydroxy group in an *ortho-* or *para-* position relative to the azo group, and are therefore capable of azo–hydrazone tautomerism.[7] For such compounds, the thermal reversion (*cis* → *trans*) of the azo tautomer is usually a rapid process characterized by a low activation energy (for example, 35·6 kJ



cis-I

Scheme 1. Thermal reversion of the *cis* isomer of 4-phenylazo-1-naphthol to the *trans* isomer via the hydrazone tautomer **II**.

mol^{-1} for *p*-hydroxyazobenzene[3]). This is thought to be due to the intermediacy of the hydrazone tautomer which allows a low-energy two-step process to occur as shown in Scheme 1 for 4-phenylazo-1-naphthol(I). The hydrazone tautomer does not appear to participate in direct photoisomerization.[8]



III

This study presents a comparison of the photochromism of the azo tautomer of 4-phenylazo-1-naphthol (I) and its *O*-methyl ether (III) which has no hydrazo form, in solution and in polymer substrates.

EXPERIMENTAL

Dyes

Dye I was synthesized by coupling benzene diazonium chloride with 1-naphthol. Its *O*-methyl ether (III) was prepared by treating a methanolic solution of **I** with a solution of diazomethane in ether. In each case, preparative column chromatography using silica gel and methylene chloride as eluent was used to purify the dyes.

Polymers

Purum grade cellulose acetate and cellulose triacetate were supplied in the form of small flakes by Fluka A.G. Monomeric methyl methacrylate (purum grade supplied by Fluka A.G.) was destabilized and dried, then polymerized in bulk by adding 0·05% benzoyl peroxide and treating at 40°C for 16 h. Residual traces of benzoyl peroxide initiator caused decolouration of **I**, so this polymer was used only in experiments involving **III**.

For cellulose triacetate and poly(methyl methacrylate), dyed films were formed by dissolving the polymer (0·9 g) and the required amount of dye in chloroform (50 g), then pouring the solution onto a level glass plate 145 mm square. Dyed cellulose acetate films were made in the same way, but acetone (30 g) was used instead of chloroform.

Irradiation

Broad band irradiation was carried out in a model PCR-128W irradiation chamber supplied by Oliphant Bros Pty Ltd. The chamber (25 cm diameter) contained 16 vertically mounted 8 W fluorescent tubes (Oliphant FL8E and Clemco 9008) with a maximum intensity at 310 nm. Solutions of **III** were placed in a stoppered 1·0 cm quartz cell and irradiated for 15 min at a temperature of 21 ± 2 °C. Samples of the polymer films were placed in a 1·0 mm quartz spectrophotometer cell and irradiated under the same conditions.

To excite selectively the azo tautomer of **I**, solutions and polymer films containing this dye were irradiated by a narrow radiation band, centred about 390 nm, with a bandwidth less than 40 nm at half peak height, obtained by passing light from a 150 W high-pressure xenon lamp through a Bausch and Lomb grating monochromator.

After irradiation, all samples were quickly transferred to a spectrophotometer (Cary model 210) for absorbance measurement. Between measurements, light from the spectrophotometer monochromator was blocked to prevent excitation of the dye.

RESULTS AND DISCUSSION

Photochromism in solvents

Figure 1 shows the spectral changes which resulted from irradiation of a solution of **III** in ethanol. The absorbance at 390 nm was reduced by about 40 % due to conversion of the *trans* to the *cis* isomer. However, with time, the spectrum recovered to its initial shape, thus confirming that *cis* → *trans* reversion had occurred. First-order behaviour for this reversion was expected, but a plot of $\log_e$(absorbance at 390 nm) versus time was not linear. Thus significant overlap of the *cis* and *trans* absorption bands at 390 nm was indicated. After assuming that the *cis* → *trans* conversion was first-order, this band overlap was taken into account in the following way.

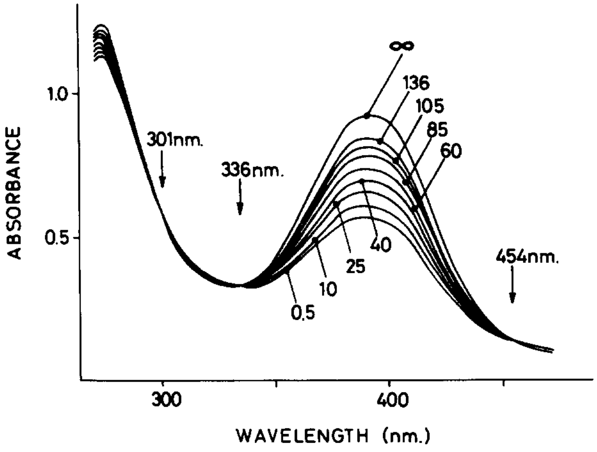


Fig. 1. Thermally reversible spectral changes following irradiation of III in ethanol ($6{\cdot}8 \times 10^{-5}$ M). Vertical arrows indicate isobestic points. Numbers indicate the time (min) after irradiation had ceased.

At time t after irradiation ceases, the absorbance of III at wavelength λ is given by:

$$A_t = A^{trans}_{t=0} + A^{cis}_{t=0} + \Delta A^{trans}_{t=0\to t} - \Delta A^{cis}_{t=0\to t} \qquad (1)$$

where $A^{trans}_{t=0}$ = absorbance of the *trans* isomer at $t=0$;

$A^{cis}_{t=0}$ = absorbance of the *cis* isomer at $t=0$;

$\Delta A^{trans}_{t=0\to t}$ = change in absorbance of *trans* isomer over the time interval $0\to t$ due to *cis*→*trans* isomerization;

$\Delta A^{cis}_{t=0\to t}$ = change in absorbance of *cis* isomer over the time interval $0\to t$ due to *cis*→*trans* isomerization. The decreasing nature of this absorbance change requires a negative coefficient.

Using the same super-/sub-script notation, but introducing the terms ε = molar absorbance at wavelength λ and C = concentration of absorbing species, eqn (1) may be rewritten as:

$$A_t = \varepsilon^{trans}C^{trans}_{t=0} + \varepsilon^{cis}C^{cis}_{t=0} + \varepsilon^{trans}(\Delta C^{trans}_{t=0\to t}) - \varepsilon^{cis}(\Delta C^{cis}_{t=0\to t}) \qquad (2)$$

The reaction of concern is:

cis isomer → *trans* isomer

Thus the amount of *trans* isomer formed equals the amount of *cis* isomer lost. Since first-order kinetics have been assumed,

$$C_t^{cis} = C_{t=0}^{cis}\,\mathrm{e}^{-kt}$$

where k = first-order rate constant for the thermal *cis*→*trans* isomerization.

Therefore, the amount of *cis* isomer lost at time t is given by:

$$C_{t=0}^{cis} - C_{t=0}^{cis}\,\mathrm{e}^{-kt} = C_{t=0}^{cis}(1-\mathrm{e}^{-kt}) \tag{3}$$

Thus:

$$\begin{aligned} A_t &= \varepsilon^{trans}C_{t=0}^{trans} + \varepsilon^{cis}C_{t=0}^{cis} + \varepsilon^{trans}C_{t=0}^{cis}(1-\mathrm{e}^{-kt}) - \varepsilon^{cis}C_{t=0}^{cis}(1-\mathrm{e}^{-kt}) \\ &= B + D(1-\mathrm{e}^{-kt}) \end{aligned}$$

where: $B = \varepsilon^{trans}C_{t=0}^{trans} + \varepsilon^{cis}C_{t=0}^{cis}$

= absorbance of isomeric mixture when irradiation ceases, i.e. $t = 0$;

$D = C_{t=0}^{cis}(\varepsilon^{trans} - \varepsilon^{cis})$

= (absorbance prior to irradiation, or at $t = \infty$) − B.

This expression may be transformed to eqn (4) to enable calculation of k as the slope of a graph.

$$\log_{\mathrm{e}}\left\{\frac{D}{(B+D)-A_t}\right\} = kt \tag{4}$$

The linear plots in Fig. 2 demonstrate that once the overlap of the *cis* and *trans* absorption bands has been taken into account, first-order behaviour for the thermal *cis*→*trans* reaction may be observed. For the two solvents employed, a solvent dependence on the rate of reversion was indicated, with the more polar ethanol giving a slower rate of reversion ($k = 1{\cdot}37 \times 10^{-4}\,\mathrm{s}^{-1}$) than the less polar cyclohexane ($k = 2{\cdot}14 \times 10^{-4}\,\mathrm{s}^{-1}$). This solvent dependence is probably due to differences in the structure of the solvent molecules. The dipolar nature of ethanol would allow it to alter the form of its interaction with a dissolved molecule to accommodate changing solute polarity. This is not possible to the same extent for non-polar cyclohexane.

When solutions of I in cyclohexane and ethanol were irradiated by light of wavelength 390 nm (selective excitation of azo form), no spectral changes were observed. The extremely short lifetime of the *cis* isomer is due to its ability to convert thermally to the *trans* configuration via the

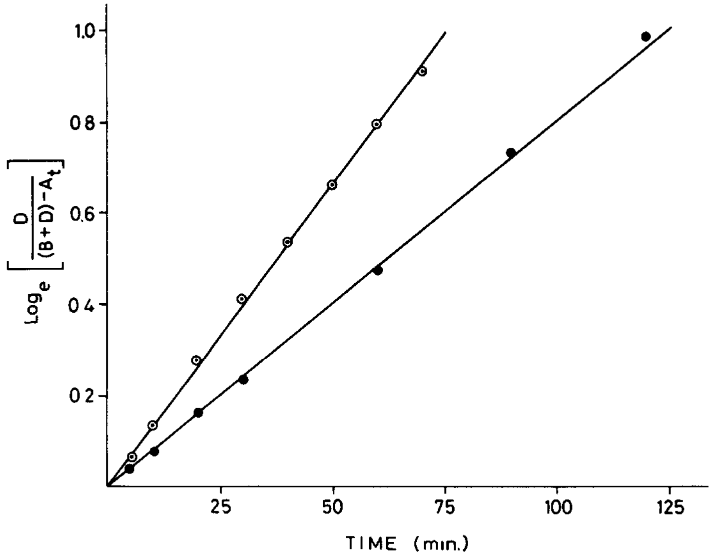


Fig. 2. Kinetics of thermal *cis*→*trans* reversion of **III** in solution ($4 \cdot 9 \times 10^{-5}$ M); ●, ethanol; ⊙, cyclohexane.

hydrazone tautomer **II** (see Scheme 1). Spectroscopic observation of the *cis* isomer of the azo tautomer of **I** in solution has not been achieved without recourse to low experimental temperatures,[8] or flash spectroscopy.[9] A study[9] of **I** in methanolic solution used the latter technique to determine the following rate constants for the reactions of Scheme 1.

$$k_1 > 10^5\,\text{s}^{-1} \qquad k_2 = 1{\cdot}5 \times 10^4\,\text{s}^{-1}$$
$$k_3 = 1{\cdot}0 \times 10^3\,\text{s}^{-1} \qquad k_{-3} = 3{\cdot}5 \times 10^2\,\text{s}^{-1}$$

A comparison of these rate constants with those obtained from Fig. 2 shows that the rate of thermal *cis*→*trans* isomerization in solution is seven orders of magnitude greater for the azo tautomer of **I** than for its *O*-methyl ether, **III**, which has no hydrazo form.

Photochromism in polymer substrates

In polymer substrates, the *cis*→*trans* isomerizations of **III** and **I** were more complex than those observed in solution. For **III**, plots of $\log_e [D/\{(B+D) - A_t\}]$ versus time gave the non-linear curves shown in Fig. 3. This is not an unprecedented result, since others (for example, refs.

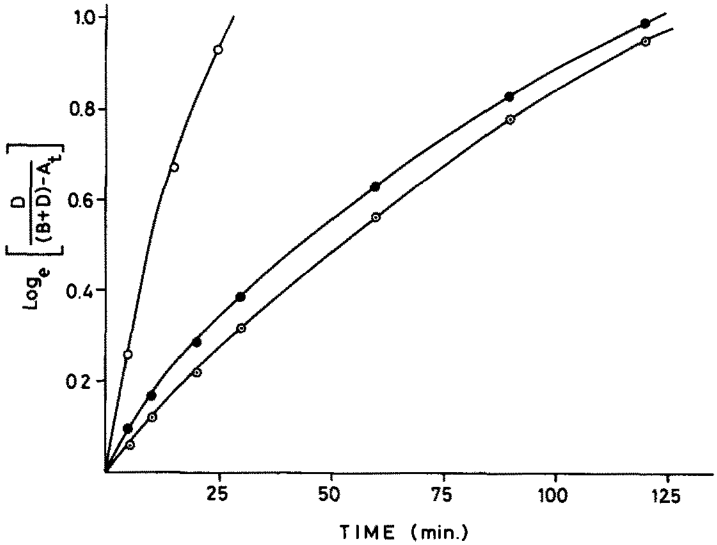


Fig. 3. Kinetics of thermal *cis*→*trans* reversion of **III** in polymers ($1{\cdot}2 \times 10^{-5}$ mol g polymer); ○, poly(methyl methacrylate); ●, cellulose acetate; ⊙, cellulose triacetate.

3, 10, 11) have reported non-first-order kinetics for thermal *cis*→*trans* isomerization of aromatic azo compounds incorporated in polymers at temperatures below T_g. A possible reason for this behaviour is that the restricted segmental motion of polymer chains at temperatures below T_g gives rise to heterogeneity in terms of free volume and specific intermolecular interactions. This, in turn, would result in a range of rates for thermal *cis*→*trans* reversion, because the isomerization cannot occur if there is insufficient free volume for the molecular movement required, or if a specific interaction stabilizes one isomer preferentially (note the solvent effect shown in Fig. 2).

To carry this further, molecules of **III** may be considered to be situated in a range of locations, 1, 2, . . ., n within the polymer. Depending on the local environment, each of these locations will have its own particular rate constant k_i ($i = 1, 2, \ldots, n$) for the thermal *cis*→*trans* reaction. Thus, the amount of *cis* isomer lost at time t after irradiation ceases is given by eqn (5) rather than by eqn (3).

$$\text{Amount of } cis \text{ isomer lost at time } t = \sum_{i=1}^{n} \left[(C^{cis}_{t=0})^i - C^{cis}_{t=0}\, \mathrm{e}^{-k_i t}\right] \qquad (5)$$

Following the previous derivation, it can be shown that in this case,

$$A_t = B + E\left[C_{t=0}^{cis} - \sum_{i=1}^{n} (C_{t=0}^{cis})^i e^{-k_i t}\right] \tag{6}$$

where $E = (\varepsilon^{trans} - \varepsilon^{cis})$ at the wavelength being monitored and

$$C_{t=0}^{cis} = \sum_{i=1}^{n} (C_{t=0}^{cis})^i$$

= total concentration of *cis* isomer in all locations at time $t = 0$.

Other symbols are as defined previously.

Equation (6) cannot be transformed to give a linear relationship between time and a function of absorbance unless $n = 1$, i.e. the case for solutions. As the gradients of the curves in Fig. 3 show, the rate 'constant', k_i, for the *cis* → *trans* isomerization of **III** in the polymers decreased with time. This is in keeping with the hypothesis that a range of environments is present. Immediately after irradiation ceases, the rate will be rapid (steep slope in Fig. 3) due to isomerization of molecules in locations conducive to the *cis* → *trans* conversion. As time progresses, the observed rate will decrease as it is dominated by molecules in locations which do not facilitate *cis* → *trans* isomerization. On the other hand, the fluid environment of a liquid solvent permits relatively unhindered molecular motion and is thus a homogeneous medium which is capable of giving a uniform rate of *cis* → *trans* isomerization. A previous spectroscopic study[12] of the photochromism of **III** and a number of its substituted derivatives in nylon film reported first-order kinetics for the *cis* → *trans* reversion following irradiation in a xenotest apparatus. However, these results must be viewed sceptically since overlap of the absorption bands of the *cis* and *trans* isomers was not taken into account.

Figure 3 also reveals a large discrepancy between the rate of *cis* → *trans* isomerization of **III** in poly(methyl methacrylate) and the cellulose acetates. Each of the acetates has an initial *cis* → *trans* rate 'constant' of a similar magnitude to those found in solution. However, poly(methyl methacrylate) has a very rapid rate of recovery. This may be due to a higher proportion of disordered regions in poly(methyl methacrylate) relative to cellulose secondary and tri-acetates, which could result in less steric hindrance to the *cis* → *trans* reversion in the case of the former substrate. In addition, the lack of segmental chain motion (temperature of irradiation = 21 ± 2 °C, cf. T_g of poly(methyl methacrylate) = 124 °C[10]) would inhibit a rearrangement of the polymer chains surrounding the dye molecule, and thus prevent stabilization of the *cis* isomer by 'resolvation'.

The time required to establish the photostationary states in the polymer films was not more than one minute in all cases. The exact proportions of *cis* and *trans* isomers in the photostationary state cannot be determined without a knowledge of the molar absorbances of each isomer at the wavelength being monitored. Since the absorbance of the *cis* isomer at approximately 400 nm is buried beneath that of the *trans* isomer, its molar absorbance cannot be readily measured. However, an idea of the proportions of *cis* and *trans* isomers in the photostationary state can be obtained by assuming negligible absorbance of the *cis* isomer at the wavelength being monitored. If this is done, the isomer proportions are given by the decrease in absorbance caused by irradiation according to eqns (7) and (8).

$$\text{Proportion of } \textit{trans} \text{ isomer} = \frac{\text{photostationary absorbance}}{\text{initial absorbance}} \tag{7}$$

$$\text{Proportion of } \textit{cis} \text{ isomer} = 1{\cdot}0 - (\text{proportion of } \textit{trans} \text{ isomer}) \tag{8}$$

Substituting absorbance values into eqn (7) gave the isomer proportions of **III** in the photostationary states shown in Table 1. However, since these values have been calculated by assuming negligible *cis* isomer absorbance, they represent upper and lower limits for the proportion of *trans* and *cis* isomers respectively.

TABLE 1
Limits of *trans* and *cis* Isomer Proportions of 1-Methoxy-4-Phenylazonaphthalene in the Photostationary State (310 nm) in Polymer Substrates

Polymer	*Proportion trans (upper limit)*	*Proportion cis (lower limit)*
Poly(methyl methacrylate)	0·85	0·15
Cellulose acetate	0·82	0·18
Cellulose triacetate	0·72	0·28

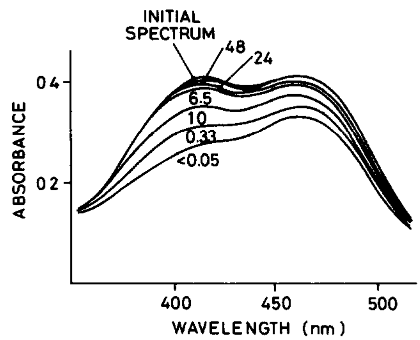


Fig. 4. Spectral changes in cellulose triacetate film containing **I** (R = H) following irradiation for 16 h at 390 nm. Numbers indicate the time (h) after irradiation had ceased.

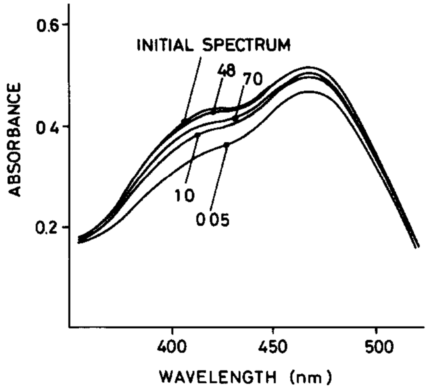


Fig. 5. As for Fig. 4 with cellulose acetate.

In contrast to the solution studies, selective excitation (390 nm) of **I** incorporated in polymer substrates induced thermally reversible spectral changes such as those depicted in Figs 4 and 5. It can be seen that the spectral changes caused by 390 nm irradiation were less pronounced for cellulose acetate than for cellulose triacetate. This agrees with the findings obtained using **III**, for which cellulose triacetate supported nearly twice as much *cis* isomer as cellulose acetate (see Table 1). The rate of recovery of the original spectrum was greatly increased by immersing the irradiated film in water, as depicted in Fig. 6. It is likely that the water

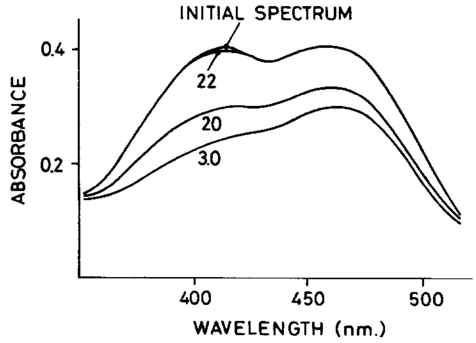


Fig. 6. Spectral changes in cellulose triacetate film containing **I** (R = H) following irradiation for 4 h at 390 nm. Numbers indicate the time (min) after irradiation had ceased. After 21 min the film was immersed in water.

penetrates the polymer and disrupts stabilizing hydrogen bonds between the solute molecules and the host polymer.

Selective irradiation of **I** caused non-uniform alterations to the spectrum of the dye (see Figs 4 and 5). Although the *trans* azo absorbance was reduced, the hydrazone absorbance was not reduced to the same extent. This indicates that the azo $\rightleftharpoons$ hydrazone tautomeric equilibrium does not maintain itself in polymer environments as it does in solutions. In solution, thermal rearrangements of the solvent constantly induce tautomeric interchange of the solute dye molecules in order to maintain a minimum free energy. It appears that in cellulose secondary and triacetates, restricted motion of the dye molecules allows specific interactions to be established which preferentially stabilize a particular tautomer at a given location within the polymer matrix.

CONCLUSION

Thermal *cis* → *trans* reversion of **III** is a first-order process in solution, but overlap of the *cis* and *trans* absorption bands must be taken into account before spectral changes can be used to monitor the kinetics of the transformation. First-order kinetics were not observed for this process in polymers, and this is likely to be due to a heterogeneous environment within the polymers, consisting of locations varying in such characteristics as the presence or absence of polar or non-polar groups, available free volume, and constraint of surrounding polymer chain segments.

The *cis* isomer of the azo tautomer of 4-phenylazo-1-naphthol (**I**) could not be spectroscopically observed in ethanol or cyclohexane at room temperature. Its very short lifetime was probably due to facile thermal reversion to the *trans* configuration via the two-step process shown in Scheme 1. However, when **I** was incorporated in cellulose acetate and triacetate, the lifetime of the *cis* isomer was prolonged. It would appear that incorporating the dye in the polymers resulted in specific interactions becoming established so that, at a given location, one particular tautomer was preferentially stabilized and tautomeric interchange was inhibited, thus interrupting the two-step reversion mechanism shown in Scheme 1. Thermal *cis* → *trans* isomerization of the azo tautomer of 4-phenylazo-1-naphthol in polymers could be accelerated by introducing water. This probably had the effect of breaking down stabilizing interactions by disrupting hydrogen bonds between dye molecules and the host polymer.

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