Effect of media polarity on the photoisomerisation of substituted stilbene, azobenzene and imine chromophores

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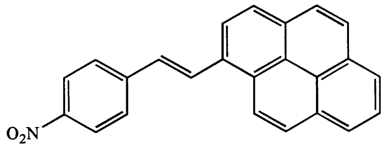
The influence of substituents and media polarity on the photoinduced $E \rightarrow Z$ geometrical isomerisation of the stilbene, azobenzene and *N*-benzylideneaniline chromophores has been compared and assessed. The efficiency of the process in all three systems is markedly dependent on the presence and characteristics of electron-donor and electron-acceptor substituents at the 4- and 4′-positions. The results are discussed in terms of relaxation of the *E*-excited singlet state. In the absence of a nitro substituent, relaxation to the S_1 orthogonal state competes effectively with non-productive intramolecular electron transfer; in the presence of a nitro substituent, the T_1 orthogonal state is formed from inter-system crossing. For systems with a 4-nitro and a 4′-electron-donor substituent, access to the triplet state is inhibited by polar solvents promoting formation of the inactive charge-transfer state from the S_1 state, and no isomerisation is observed. Similar effects are observed in both solution and polymer films. Such variations in behaviour have important implications for the utilisation of the chromophores in nonlinear optical phenomena including photorefractivity.

There is currently considerable interest in initiating and controlling changes in polymer properties by the use of photoinduced molecular rearrangements of chromophores which are incorporated either as tethered side chains or in a guest–host system.[1,2] The *E–Z* photointerconversions of aryl-substituted 2π systems has attracted particular attention for this application, and the volume of literature describing the use of azobenzene-based dyes and of arylpropenoates for this purpose is considerable.[2,3,4] The photoinduced geometrical changes of *N*-benzylideneanilines and stilbenes also have potential in this area. Azobenzene and stilbene and their derivatives have been extensively studied in the area of nonlinear optical properties, including second-order phenomena such as photoinduced poling[5] and frequency doubling[6] and in third-order phenomena such as degenerate four-wave mixing[7] and photorefractivity.[8] The trends found in these investigations may have important implications in the exploitation of stilbenes and azobenzenes in these emerging technologies.

While photoinduced geometrical isomerisations can be useful to tailor polymer properties for specified purposes,[4,5] they can also be detrimental for other applications; for example isomerisation may lead to an undesirable reduction in the second-order nonlinear optical response of a material[5] or in photorefractivity, a feature which is particularly important with azobenzene-based chromophores.[8] Furthermore, the type of photoactivated devices for which these systems may find use is markedly dependent on the time response of the chromophores both in the forward photochemical process and in the back thermal relaxation.[9] It is therefore of importance to determine the features of the chromophore and the influence of the media which promote or inhibit the photoisomerisation and its thermal reversion.[10] We have observed with a number of these chromophores that their photoresponses and thermal relaxation depend markedly on the nature and position of substituents. Kikuchi *et al.* have recently described solvent-dependent anomalous photochemical behaviour of a nitrostyrylpyrene.[11] Thus the direct photoconversion of *trans*-1-[2-(4-nitrophenyl)ethenyl]pyrene **1** to the *cis* isomer observed in hexane solution with 436 nm light ($F = 0.11$), is reported to be completely suppressed in acetonitrile. A similar, although less marked, influence of solvent polarity is noted with the corresponding nitrostyrylnaphthalene derivative. The influence of solvent on the efficiency of photoisomerisation of the nitrostyrylarenes may be rationalised in terms of the increase in polarity enhancing the relaxation of the excited singlet state to a low-lying intramolecular charge-transfer state and/or promoting a higher degree of electron transfer in this state (as shown in Scheme 1). The resulting dipolar species **2** has low energy and undergoes neither intersystem crossing to the triplet state nor conversion to the orthogonal excited state from which either geometrical isomer may be formed. Thus no, or very inefficient, *E–Z* photoconversion is observed.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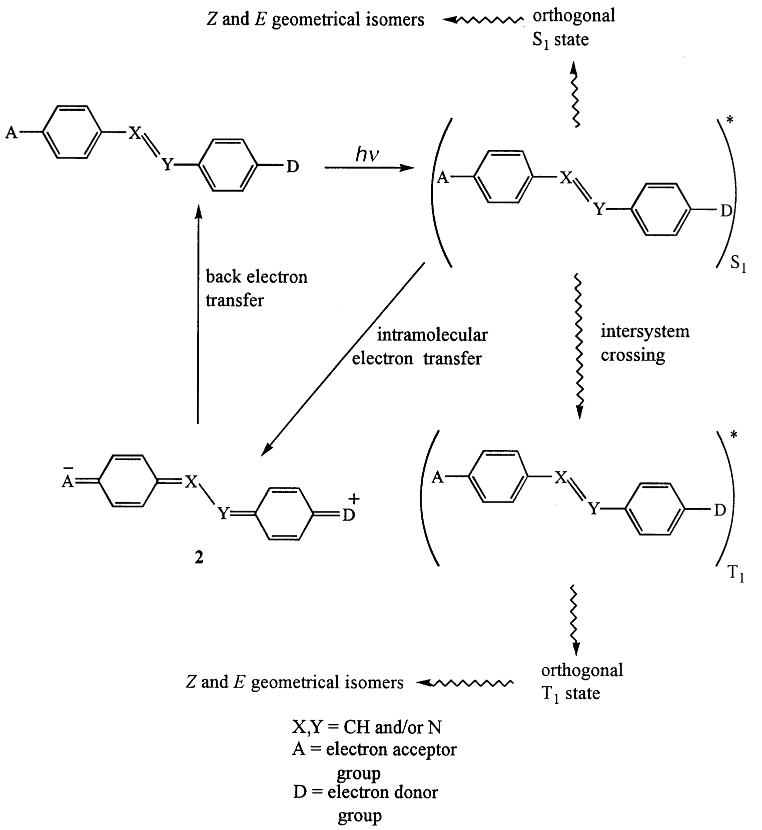
Here we evaluate the way in which substituents can influence the solvent polarity-sensitive photoisomerisation of stilbenes, and consider whether such sensitivity to the polarity of the media is relevant to the azobenzenes and to benzylideneaniline derivatives: the former chromophores are commonly used for nonlinear optical phenomena and as chromophores for inducing photochemical changes in polymer systems. Stilbenes and arylpropenoates isomerise by internal rotation about the ethene bond in the π,π^* excited state, but in contrast azobenzenes and benzylideneanilines may also undergo such geometrical change by a mechanism which involves a semi-linear excited transition state with inversion of the bond angle at one of the nitrogen atoms.[12]

Results and Discussion

The absorption data obtained from UV–VIS spectroscopy of selected stilbenes, azobenzenes and benzylidine anilines are summarised in Table 1. The long wavelength absorption maxima are given for both methylcyclohexane and acetonitrile solutions together with the absorbance observed before and after irradiation (to a steady-state absorbance) at the $\lambda_{\max}$. These data are discussed below.

Stilbenes

It has been known for many years that, upon direct irradiation, geometrical isomerisation of unsubstituted stilbene and the



Scheme 1 Decay of the S$_1$ state of 2π systems and the associated geometrical conversions for diaryl systems

4-cyanostilbenes occurs from the singlet excited state,[13,14,15] whereas nitrostilbenes undergo the conversion from the triplet excited state.[16,17] Increasing the solvent polarity lowers the efficiency of the *E* to *Z* photoconversion of 4-nitrostilbene ($\Phi = 0.5$ in benzene and 0.39 in methanol) but this effect is little different from that reported for 4,4′-dinitrostilbene.[16] However, in agreement with the above rationale for the influence of solvent polarity, an increase in the electron-donor properties of the 4′-substituent increases this effect and the quantum yield for the *E* to *Z* isomerisation for 4-nitro-4′-dimethylaminostilbene **3** decreases from 0.28 in cyclohexane[18] to essentially zero in acetonitrile.[19] Solvent effects on the photophysical behaviour of **3**[20] and of electron-rich stilbenes have been discussed in terms of a twisted intramolecular charge-transfer species.[21]

We were interested in electron-donor–electron-acceptor 2π systems for their use in nonlinear optical applications and in photorefractive polymers, and have examined a number of stilbenes in this context. Essentially, the influence of solvent on the photoinduced *E*–*Z* isomerisation, as measured by absorption spectroscopy, was predictable and directly related to the potential for intramolecular electron-transfer in the excited state of the stilbene. For example, while the efficiency of geometrical isomerisation of 4-nitro-4′-alkoxystilbenes decreased markedly as the solvent polarity was increased, the results from irradiation of the more polar derivatives **3** and **4** were in agreement with literature reports.[11,18,19] Thus in cyclohexane, irradiation at the λ_{max} of 415 and 454 nm of **3** and **4**, respectively, induced *E* to *Z* isomerisation, but in acetonitrile neither stilbene showed any spectral change. Furthermore, while luminescence was observed in the non-polar solvent from both stilbenes, no emission was detected in either case in acetonitrile solution consistent with very rapid decay of the S$_1$ state to a non-emissive intramolecular charge transfer state.[20] 4-Cyanostilbene **5** produced no solvent-dependent photochemistry but it is to be noted that for cyanostilbenes the geometric isomerisation arises from the singlet rather than the triplet state.[15] These results are consistent with the proposal that while relaxation of the *E*-excited singlet state of the stilbene to the common orthogonal state can compete effectively with intramolecular electron-transfer, intersystem crossing and access to the triplet state is inhibited by polar solvents for systems having a 4-nitro and 4′-electron-donor substituents.

Azobenzenes

For azobenzenes, photoinduced *Z*–*E* isomerisation is a more complex process since there are two pathways of rotation involving an orthogonal p-state (as for stilbene) and inversion about the nitrogen.[12] Either mechanism may be operating, and which is favoured would seem to depend upon the character of the excited state (n,π* or π,π*); furthermore, it is likely that this is influenced by the nature and position of the substituents. Despite considerable interest in the photochemistry of azobenzenes, there is only scant information concerning the mechanism of the interconversion of derivatives having both electron-donor and electron-acceptor substituents in a conjugative relationship (frequently termed ‘pseudo stilbenes’). Since in the system the two excited states have similar energies, in such derivatives both inversion (n,π*) and rotation (π,π*) pathways are likely; furthermore, the *Z* to *E* thermal reversion, probably by an inversion process, may be expected to be very rapid.[12] From our studies, it is apparent that at room temperature azobenzene derivatives having either (i) a 4-nitro substituent but with a low potential for excited state intramolecular electron-transfer, as in **6**, or (ii) significant electron-donor–electron-acceptor properties but with a cyano in place of the 4-nitro group as the electron-acceptor moiety, as in **7**, undergo *E* to *Z* isomerisation in polar and non-polar solvents with closely similar efficiencies. Thus isomerisation, probably following intersystem crossing due to the presence of the nitro group in the former case, occurs in preference to relaxation to the intramolecular charge-transfer state. The situation can, however, be readily perturbed and azobenzenes such as Disperse

Table 1 UV–VIS spectra of chromophores **3**–**16** in methylcyclohexane and acetonitrile

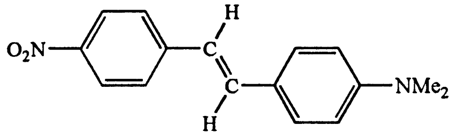
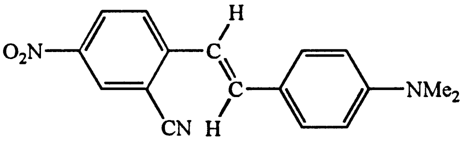
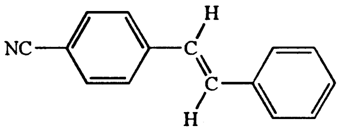
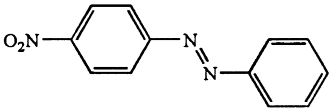
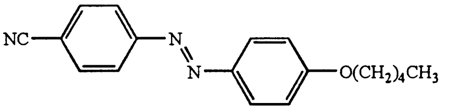
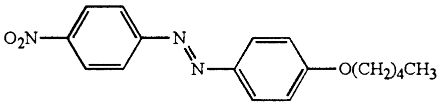
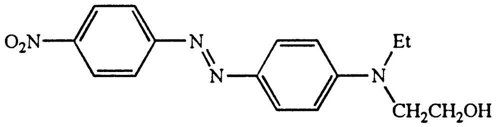
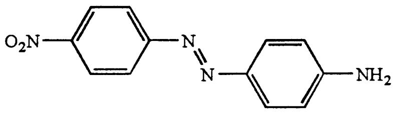
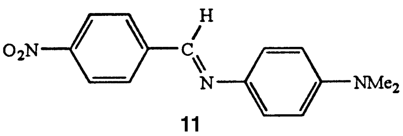
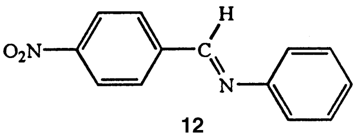
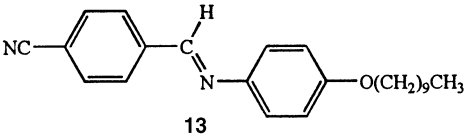
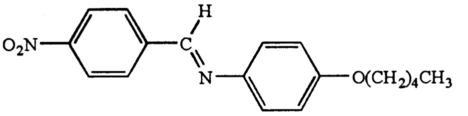
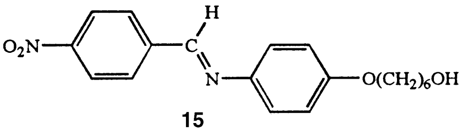
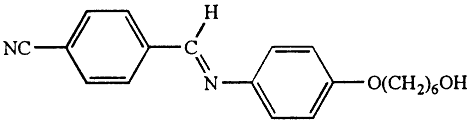
	methylcyclohexane				acetonitrile			
		effect of irradiation[a]				effect of irradiation[a]		
Chromophore	λ_{max}/nm	A_o	A_{ps}	% *cis*	λ_{max}/nm	A_o	A_{ps}	% *cis*
 **3**	415	1.14	0.68	$>40^b$	435	0.91	0.905	$\sim 0^b$
 **4**	454	1.20	0.74	$>38^b$	464	1.45	1.45	$\sim 0^b$
 **5**	315	1.17	0.58	$>56^b$	315	0.75	0.31	$>59^b$
 **6**	332	0.87	0.55	$>37^c$	335	0.54	0.36	$>33^c$
 **7**	364	1.83	0.23	$>88^b$	364	2.10	0.27	$>87^b$
 **8**	371	1.05	0.96	$>9^b$	375	1.05	0.93	$>13^b$
 **9**	450	0.39	0.27	$>31^b$	475	0.47	0.47	$\sim 0^b$
 **10**	410	0.54	0.45	$>17^b$	430	1.13	1.10	$\sim 0^b$
 **11**	436	1.29	1.16	$>10^d$	439	0.59	0.59	$\sim 0^d$
 **12**	340	0.95	0.84	$>11^e$	357	1.25	1.02	$>18^e$
 **13**	375	1.36	0.77	$>43^e$	374	1.31	0.76	$>43^e$

Table 1 (*continued*)

	methylcyclohexane				acetonitrile			
		effect of irradiation[a]				effect of irradiation[a]		
 **14**	380	1.24	0.98	>21[d]	380	0.82	0.66	>19[d]
 **15**	374	0.92	0.35	>62[f]	380	1.43	1.41	~0[f]
 **16**	355	0.36	0.28	>22[f]	359	0.47	0.36	>23[f]

[a] Reduction in A_{max} reflects minimum concentration of *cis* isomer at the photostationary state; a spectral subtraction procedure shows that the actual concentration of the unstable isomer is generally a few percent higher than this value. [b] At 298 K. [c] At 283 K. [d] At 238 K. [e] At 243 K. [f] At 248 K.

Red 1 **9** and Disperse Orange 3 **10**, having the potential both for significant intramolecular charge-transfer through the presence of donor and acceptor groups in a conjugative relationship and for reactivity from the triplet state by the mediation of the nitro group, again showed solvent polarity-dependent photochemistry. Thus, as with the stilbene systems, the presence of a 4′-alkoxy group on the 4-nitroazobenzene chromophore is sufficient to reduce markedly (*ca.* two-fold) the *E–Z* photoisomerisation efficiency on changing of the solvent from methylcyclohexane to acetonitrile. Furthermore, the magnitude of this influence is temperature-independent between room temperature and −35 °C indicating that the phenomenon does not arise from a rapid thermal relaxation of the *Z* isomer in the more polar solvent. In contrast, it is again evident that more powerful electron-donor 4′-substituents, as on the two Disperse dyes **9** and **10**, promote the intramolecular electron-transfer in acetonitrile solution to the exclusion of intersystem crossing as no photoisomerisation was observed in these systems down to −35 °C. Photoinduced *E–Z* isomerisation could be detected in both **9** and **10** at room temperature in methylcyclohexane by simultaneous monitoring of their absorption spectra during irradiation, but total reversion occurred rapidly in the dark. The half-lives of the *Z* isomers of **9** and **10** at 293 °C were determined as 0.65±0.05 and 1.00±0.07 s, respectively. The *Z* isomers of both dyes were stable at −35 °C and the spectra were fully restored to those of the *E* isomers on warming the solutions to room temperature. From these results, it is apparent that although the geometric conversion of azobenzenes may be accomplished by inversion at nitrogen and bond rotation, the influence of substituents and solvent polarity dominates the *E–Z* isomerisation process. Thus, as for the stilbenes, the efficiency of intramolecular electron-transfer compared to isomerisation in the *E*-azobenzenes is dependent upon the nature of the electron-acceptor group (cyano or nitro) at the 4-position and the strength of the 4′-donor substituent in conjunction with the polarity of the solvent.

Imines

The mechanism of *E–Z* photoisomerisation of the imino chromophore may again involve either or both bond rotation and linear inversion. There is an appreciable amount of literature on the photoinduced geometrical change of oximes and hydrazones,[22,23] but little interest seems to have been shown in the use of the conversions of the conjugated diarylazomethine systems for the manipulation of polymer properties, possibly because of their hydrolytic liability. However, since the thermal barrier between the two isomers is low, the relaxation from a photoinduced geometrical change in these imino compounds is extremely rapid and this feature may offer advantages for some light-driven devices. In 1977 Maeda and Fischer reported the photoinduced *E–Z* isomerisation of a number of *N*-benzylideneanilines and from experiments at −70 °C they were able to characterise the thermally labile *Z* isomers.[24] These authors also note that of the many derivatives of diarylazomethines studied, only the 4-nitro-4′-dimethylamino derivative **11** did not exhibit the photoinduced changes in non-polar solvents, but the reasons for this apparent anomaly were not discussed. In view of the results from the present and previous studies with the similarly substituted stilbenes and azobenzenes, this observation by Maeda and Fischer is unexpected and implies that even in aliphatic hydrocarbon solvents, photoinduced electron-transfer to yield the inactive intramolecular charge-transfer state can be exclusive for diarylazomethine systems substituted with both powerful electron-acceptor and -donor groups in a conjugative relationship. However, further investigations into the influence of electron-donor–electron-acceptor substituents to mediate either the *E* to *Z* isomer formation photochemically or the thermal retro-process appear to have attracted very limited attention.

By modifying the electron-donor–electron-acceptor properties of the substituents, we have been able to observe *E–Z* photoinduced isomerisation in a range of polarised *N*-benzylideneanilines, and, furthermore, with these systems, there appears to be the potential to tailor the photoresponse for particular applications. Thus irradiation at the wavelength maximum of solutions of *N*-(4-nitrobenzylidene)aniline **12**, and azomethine derivatives such as **13**, which have a cyano group as the 4-position electron-acceptor substituent and a weaker electron-donor group than amino in the 4′-position, produced the change in the absorption spectrum associated with *E–Z* isomerisation. As for the respective corresponding azo compounds **6** and **7**, the photoconversions of **12** and **13** occurred with approximately equal efficiencies in both polar and non-polar solvents. Combining the influences of the nitro group with the weaker alkoxy donor substituent did, however, have a considerable effect on the photochemistry of these diarylazomethines. Thus in marked contrast to the photoinactive derivative **11**,

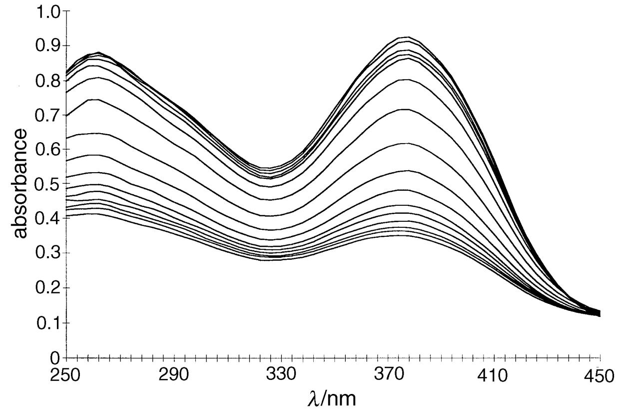


Fig. 1 UV Spectra obtained as a function of time on irradiation of *N*-(4-nitrobenzylidene)-4-(6-hydroxyhexyl)aniline **15** at −25 °C in methylcyclohexane (spectra recorded every 120 s)

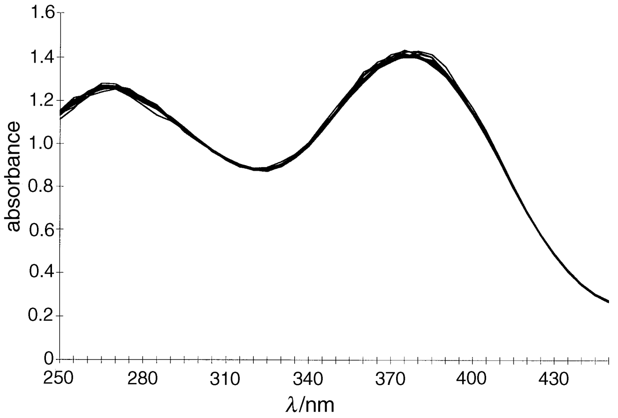


Fig. 2 UV Spectra obtained as a function of time on irradiation of *N*-(4-nitrobenzylidene)-4-(6-hydroxyhexyl)aniline **15** at −25 °C in acetonitrile (spectra recorded every 120 s)

14 underwent photoisomerisation at −10 °C in methylcyclohexane and at a rate three times faster than in acetonitrile. At this temperature, the *Z* isomer was stable but reverted rapidly to the *E* isomer on warming to 25 °C. As we wished to use such derivatives as **14** for pendent chromophores on polyacrylate backbones, the *N*-benzylideneaniline **15** was synthesised. This azomethine underwent a smooth *E* to *Z* isomer conversion at −25 °C in methylcyclohexane (Fig. 1), but under the same conditions in acetonitrile solution little change was observed in the absorption spectrum (Fig. 2) of **15**. Similar results were observed with **15** at 0 °C, but at this temperature the thermal reversion to the *E* isomer is rapid and there was less than 20% photoconversion in the stationary state from irradiation in the non-polar solvent.

Polymer matricies

We have carried out a preliminary assessment of the influence of a polymer matrix on the photochemistry of selected examples of the three types of chromphores. Thin films of poly(methyl methacrylate), polystyrene or polyacrylonitrile (glass transition temperatures well in excess of room temperature) incorporating 5% w/w of the stilbene **3**, the azobenzenes **6**, **7** and **9**, or the *N*-benzylideneanilines **12** and **13** were prepared by dip coating. In most cases, the films had poor optical characteristics when measured at low temperature; as a consequence, the occurrence of photoinduced *E* to *Z* isomerisations was assessed from birefringence measurements of the 18 samples before and after their irradiation with plane polarised light at the wavelength maximum of the chromophores. This technique relies on the biasing of the optical axis of the chromophores in a direction perpendicular to the plane of polarisation of the light source.[2] With the exception of the stilbene, all chromophores in poly(methyl methacrylate) and polystyrene displayed birefringence changes, although the magnitude of the effect was variable between samples. Chromophores **3**, **6** and **9** showed no change in polyacrylonitrile and the effect of radiation on the other four samples was only small. Not surprisingly, it appears that the environment in the polymer matrix has a similar effect to a change in the solvent polarity on the photochemistry of the chromophores.

Conclusion

In summary, the present study shows that the tendency for *E* to *Z* photoisomerisation in stilbene, azobenzene and diarylazomethine chromophores is markedly influenced by the electron-acceptor–electron-donor characteristics of the 4- and 4′-substituents, and yet further mediation of the process results from a change in the polarity of the media. The stilbenes and azobenzenes exhibit closely parallel behaviour which may be rationalised by isomerisation from the excited singlet state for those derivatives having a cyano group as the electron-acceptor substituent, but for systems having a 4-nitro group a competition occurs between intersystem crossing to the reactive excited triplet state and intramolecular electron transfer in the S_1 state to the inactive charge-transfer state. For the latter type of chromophores, the competition is markedly influenced by the power of the electron-donor substituent at the 4′-position and the polarity of the solvent or polymer matrix. For azobenzene systems it is also possible that the low yields of the *Z* isomer on irradiation can be attributed to a rapid thermal back-reaction; indeed the rate of this process appears to increase markedly with increasing solvent polarity.[9,25,26] Clearly, such a mechanism could not apply to stilbene systems. Overall, although the photochemical behaviour of the diarylazomethine system is similar to that of the other two chromophores, the asymmetry in the 2π unit appears to facilitate the intramolecular electron-transfer and this evidently occurs for the 4-nitro-4′-dimethylamino derivative even in a non-polar solvent.

Experimental

Photochemical measurements

The photochemical *E*–*Z* geometric isomerisation and the thermal back reaction were measured by absorption spectroscopy supported by HPLC analysis for systems showing change at room temperature. Fig. 3 depicts a schematic diagram of the UV–VIS spectrometer arrangement used for the measurement of the change in UV–VIS absorption spectra of the chromophores whilst simultaneously being irradiated.

A 1024 pixel photodiode array (Jobin Yvon) coupled with a monochromator allowed for rapid accumulation of spectra (with a minimum interval of 14 ms). The data described in this presentation used an acquisition time of 250 ms and the absorption spectra were recorded every 20 s. Typically, the absorption spectra were obtained while the sample under investigation was simultaneously irradiated by a 150 W xenon arc lamp, the light from which passed through a monochromator set at a wavelength close to the absorption maximum of the chromophore. A purpose-built sample chamber allowed the temperature to be kept constant within the range 173–473 K.

The apparatus for monitoring changes in the birefringence of thin polymer films is described elsewhere.[27] Polymer films of thickness *ca.* 1.5 μm were prepared by dip-coating.[28]

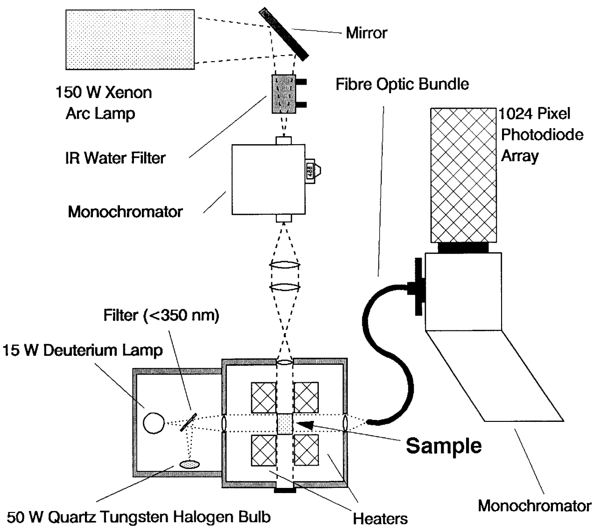


Fig. 3 Schematic of the apparatus used for simultaneous irradiation and monitoring of stilbene, imine and azo chromophores at variable temperatures

Materials

4′-(*N*,*N*-Dimethylamino)-4-nitrostilbene was obtained commercially and used without further purification. Cyanostilbene was prepared according to a literature procedure; mp 117–118 °C (lit.,[29] 115 °C). The procedure for the preparation of 4-nitro-2-cyano-4′-(*N*,*N*-dimethylamino)stilbene **4** is described below. 4-Nitroazobenzene **6**, Disperse Red 1 **9** and Disperse Orange 3 **10** (Aldrich) were used as supplied, following chromatographic assurance of purity. 4-Cyano-4′-hydroxyazobenzene and 4-nitro-4′-hydroxyazobenzene were prepared from cyanoaniline and nitroaniline by diazotisation followed by coupling with phenol in the usual way;[30] both compounds gave satisfactory analytical data. The pentyloxy-substituted azobenzenes **7** and **8** were prepared from these compounds *via* their reaction with bromopentane in DMF containing sufficient (>1 equiv.) potassium carbonate to ionize the phenol. Subsequent purification using column chromatography and recrystallisation gave the desired compounds in yields of 50% or greater.

The imine chromophores were prepared using standard procedures. Alkoxy and ω-hydroxy alkoxy imines were prepared from the corresponding hydroxy-terminated imine by reaction with the appropriate alkyl halide. The imine precursor was added to a solution of sodium methoxide (formed *in situ* from Na and methanol); this was stirred for approximately 20 min before dry toluene was added. The solvent was then removed by vacuum distillation. Dimethylformamide and the appropriate alkylhalide were then added and the solution was heated at 110 °C for at least 12 h. The solution was added to water and the organics separated by washing with diethyl ether. The diethyl ether was then dried using $MgSO_4$. The solvent was removed by rotary evaporation leaving an oil. This was purified by column chromatography (silica using 1 : 1 diethyl ether–CH_2Cl_2 as the eluent).

4-Nitro-2-cyano-4′-(*N*,*N*-dimethylamino)stilbene 4. A mixture of 2-methyl-5-nitrobenzonitrile (40 mmol, 6.5 g) and 4-(*N*,*N*-dimethylamino)benzaldehyde (50 mmol, 5.5 g) with 10 drops of piperidine was heated for 2 h at 140 °C. A red solid cake formed during the reaction. The solid product was dissolved in 30 ml of hot ethanol and the solution was refrigerated. Red crystals formed over 12 h, which were removed by filtration and then recrystallised from dioxane; mp 218 °C; ν_{max}/cm^{-1} 2224; ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 [1H (H_3), d, J_{5-3} 2.2], 8.31 [1H (H_5), dd, J_{3-5} 2.0, J_{6-5} 9.0], 7.91 [1H (H_6), d, J_{5-6} 9.2], 7.49 [2H ($H_{2',6'}$) d, $J_{3'2'}=J_{5'6'}=9.0$], 7.42 [1H (H_α), d, $J_{\beta-\alpha}$ 15.8], 7.21 [1H (H_β), d, $J_{\alpha-\beta}$ 16], 6.69 [2H ($H_{3',5'}$) d, $J_{2'-3'}=J_{6'-5'}=9.0$], 3.10 [6H (NMe_2), s]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.55, 147.42, 144.62, 138.51, 129.42 ($C_{2',6'}$), 128.62, 127.14, 124.85, 122.88, 116.50, 116.42, 111.89 ($C_{3',5'}$), 110.30, 40.09 (NMe_2).

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