Photochemical Reactions of 1*H*-Pyrazolo[1,5-*b*][1,2,4]triazole Azomethine Dyes

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The photochemical reactions of 1*H*-pyrazolo[1,5-*b*][1,2,4]triazole azomethine dyes have been studied both in solution and in film. There are two different reaction pathways. (1) Under visible (VIS) light illumination, the reactive species are the lowest excited state of the dimer of the pyrazolotriazole dyes. The reaction proceeds by a one-photon process. (2) Under ultraviolet (UV) light illumination, the reactive species is the upper excited state of the monomeric pyrazolotriazole dye. The reaction may proceed by a step-by-step two-photon process.

A series of additives were tested to improve the light-fastness of pyrazolotriazole dyes. Of the various stabilizers, spiroindane derivatives quench the fluorescence of the dimeric pyrazolotriazole dyes with a maximum value of 1.1×10^2 dm^3 mol^{-1} for the product of $k_q\tau_0$. These compounds efficiently reduce the photochemical reactions of pyrazolotriazole dyes in film.

In colour photographic systems, yellow, magenta and cyan dyes are used to realize natural colours. Improvement of the light-fastness of these dyes, in particular for magenta dyes, is strongly desired in colour print systems. For this purpose, stabilizers to counteract light fading of magenta dyes are added in the magenta dye layer.

For magenta dye, a pyrazol-5-one skeleton has been used over a long period of time and the properties of excited states and the light-fading mechanism of this skeleton have been intensively studied by Herkstroeter and co-workers in the 1970s.[1-5]

In the 1980s, two kinds of pyrazolotriazole magenta dye were utilized in colour photographic materials. One is the 1*H*-pyrazolo[5,1-*c*][1,2,4]triazole skeleton[6] and the other is the 1*H*-pyrazolo[1,5-*b*][1,2,4]triazole skeleton.[7] Generally speaking, both pyrazolotriazole skeletons have two intrinsic advantages over the pyrazol-5-one skeleton as photographic magenta dyes. One advantage is the excellent magenta dye absorption. Fig. 1 shows the absorption spectra of 1*H*-pyrazolo[1,5-*b*][1,2,4]triazole azomethine dye and that of pyrazol-5-one in ethyl acetate. The most pronounced feature is that no side absorption appears at around 430 nm and that the long wavelength absorption is sharp, yielding vivid magenta and red colour reproduction in colour prints.

This report describes the photochemical reactions of 1*H*-pyrazolo[1,5-*b*][1,2,4] triazole azomethine dyes and the interaction between dyes and additives.

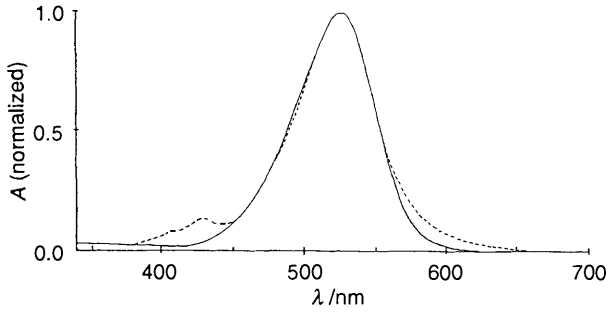
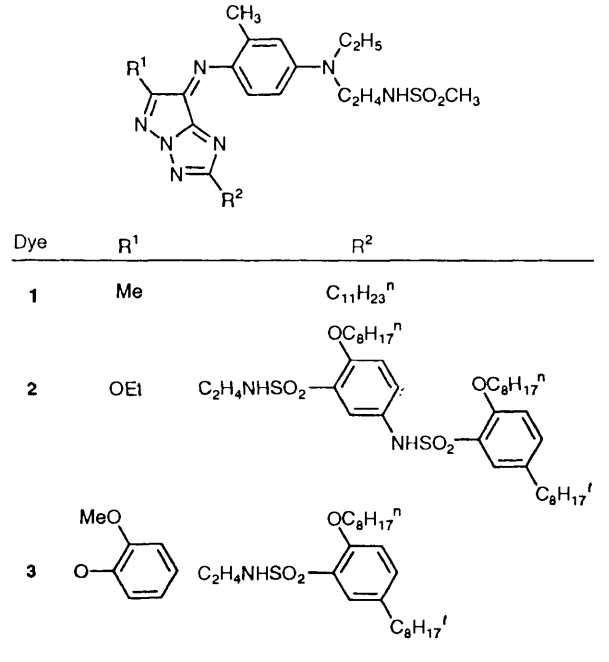


Fig. 1 Absorption spectra of 1*H*-pyrazolo[1,5-*b*][1,2,4]triazole azomethine dye (—) and pyrazol-5-one azomethine dye (- - - -) in AcOEt



Experimental

Measurement of Excited States and Ground States.—A CRM-FA spectro-irradiator was used for the photoillumination experiment (light source: 5 kW Xe lamp, with a JASCO monochromator used to obtain *ca.* 23 nm band width monochromatic light). Light intensity was monitored by means of a silicon photodiode to compensate for intensity fluctuations during the experiments. The fluorescence of pyrazolotriazole dyes was measured using a M850 spectrofluorimeter (light source: 150 W Xe lamp, double monochromator for excitation, single monochromator for emission, R-928 photomultiplier for detection, Hitachi). A special mini cryostat was used for low-temperature measurement of fluorescence (liquid nitrogen was used to cool the sample, Unisoku).

Synthesis of Pyrazolotriazole Dyes and Additives.—The synthesis of 1*H*-pyrazolo[1,5-*b*][1,2,4]triazole azomethine dyes and additives are described elsewhere.[8] R^1 and R^2 groups were varied to evaluate the substituent effect on the light-fastness of pyrazolotriazole azomethine dyes in film. The model dye

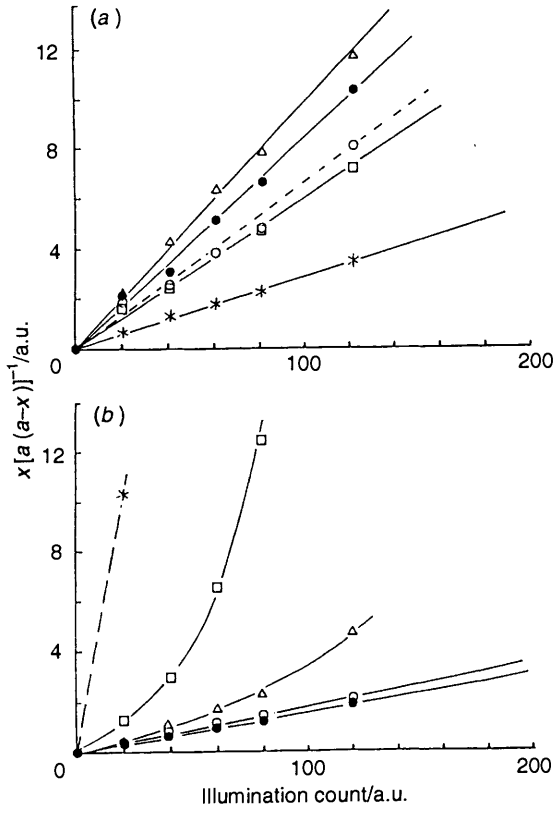


Fig. 2 The second-order plot of photochemical reaction of DYE-**1** in film illuminated at: (*a*) 532 nm (○); 506 nm (●); 479 nm (△); 453 nm (□); 426 nm (✱) and (*b*) 399 nm (○); 373 nm (●); 346 nm (△); 320 nm (□); 293 nm (✱); *a* initial quantity of dye and *x*, quantity of reacted dye

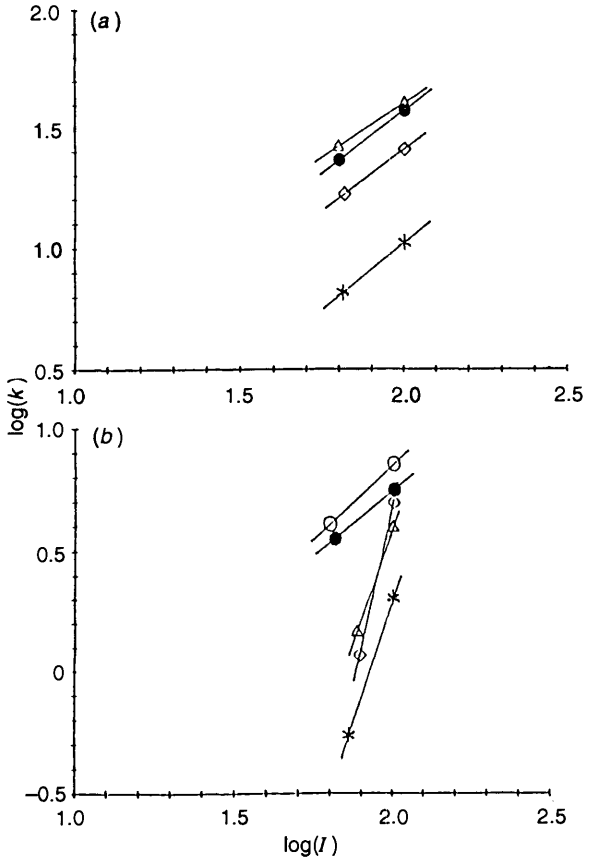


Fig. 3 Light-intensity dependence of the photochemical reaction rate of DYE-**1** in film at: (*a*) 506 nm (●); 479 nm (△); 453 nm (◇); 426 nm (✱) and (*b*) 399 nm (○), 373 nm (●), 346 nm (△), 320 nm (◇), 293 nm (✱); *I* light intensity (au) and *k* reaction rate (au)

(DYE-**1**) which has simple substituents was synthesized to investigate the reaction properties arising from the pyrazolo[1,5-*b*][1,2,4]triazole skeleton.

Film Sample.—Pyrazolotriazole azomethine dyes were dispersed in a mixture of alkyl phosphate and alkyl phthalate plasticizers in gelatin and coated on a cellulose triacetate film base. The mean size of the emulsion was about 1.5×10^{-7} m in the film. The dye concentration of the film samples was controlled by changing the volume of the plasticizers while the weight of the pyrazolotriazole dye was kept constant. For example, the notation 'oil : dye = 2 : 1' means that 1 g of dye was dissolved in 2 cm^3 of the plasticizer in oil droplets in the gelatin film.

Results and discussion

Photochemical Reactions in Film.—The wavelength dependence of photochemical reactions of DYE-**1** in film was studied from 293 nm (± 13 nm) to 532 nm (± 13 nm). Absorbance decreased rapidly under illumination at 293 nm which corresponds to the second absorption band of DYE-**1**. An isosbestic point at 440 nm was observed during the illumination experiment. Absorbance decreased under illumination at 532 nm which corresponds to the main absorption band of DYE-**1**, but the change of spectrum was small compared with that of UV illumination.

A second-order plot of absorption against illumination count successfully gave straight lines. From Fig. 2(*a*), it can be seen that DYE-**1** reacts with a second-order reaction rate under VIS light illumination. The results of illumination at 399 nm and 373 nm also gave straight lines [Fig. 2(*b*)], and the reaction path is the same as occurs in the VIS region. On the other hand, under UV illumination the curve is bent upward in the second-order plot [Fig. 2(*b*)] and downward both in the raw and the first-order plot. These plots suggest that the reaction involves accelerated processes caused by the reaction products and that the information concerning reaction order was not obtainable from UV light illumination of the dye. It is estimated that there are at least two reaction pathways available to DYE-**1**, which depend on the wavelength of the light.

The second-order plot of Fig. 2(*a*) could be a consequence of the formation of dimers of DYE-**1**. To determine the effect of substituents R^1 and R^2 on the pyrazolotriazole azomethine dyes, a series of experiments was carried out under the same conditions for DYE-**2** and DYE-**3**. Though the photochemical reaction rates of these dyes are different, the second-order plots of absorption against illumination count also successfully gave straight lines for VIS light illumination. The photochemical behaviour of these three dyes is essentially the same, and it is estimated that the pyrazolotriazole azomethine dyes react with a second-order reaction rate under VIS light illumination. The substituents R^1 and R^2 would influence the formation of such dimers and may vary the reaction rate.

To clarify the light-intensity dependence of photochemical reactions, a sharp cut-off filter or Nickel mesh filter was used to control the light intensity. Fig. 3 shows the results of the light-intensity dependence of DYE-**1** in film upon the reaction rate in the VIS and UV light regions. The slope of a log–log plot of reaction rate against light intensity is 1.0 for VIS and 2.0 for UV light illumination. This means that the usual one-photon process occurred under the former conditions, and a two-photon process occurred under the latter. The two-photon process is thought to be a step-by-step reaction because

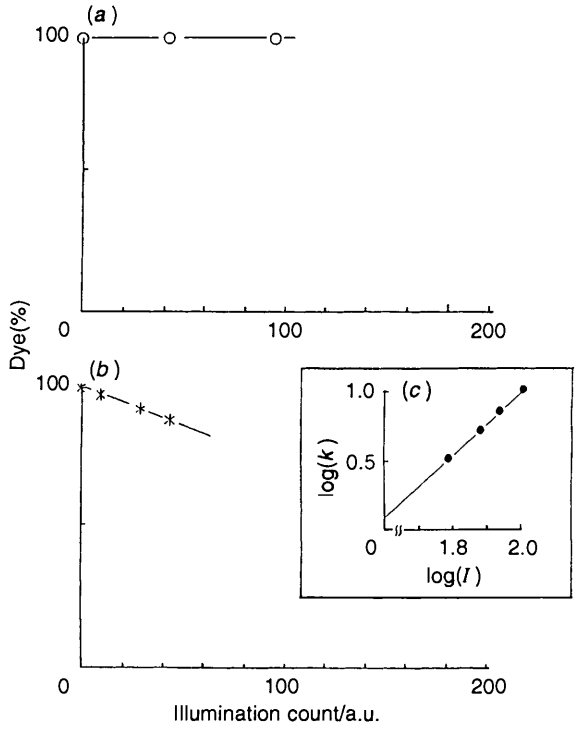


Fig. 4 Wavelength dependence of photochemical reactions of DYE-1 in MeCN (2×10^{-5} mol dm^{-3}) at (*a*) 532 nm (○) and (*b*) 293 nm (✱); *I* light intensity (au) and *k* reaction rate (au)

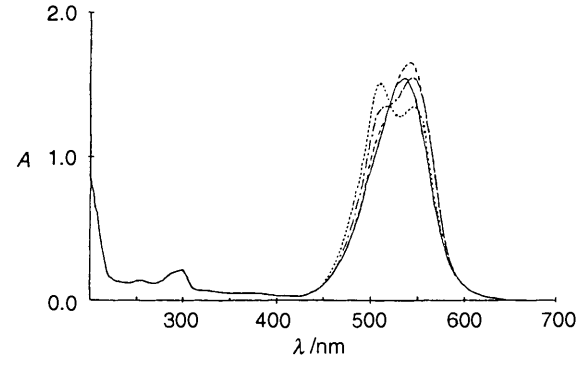


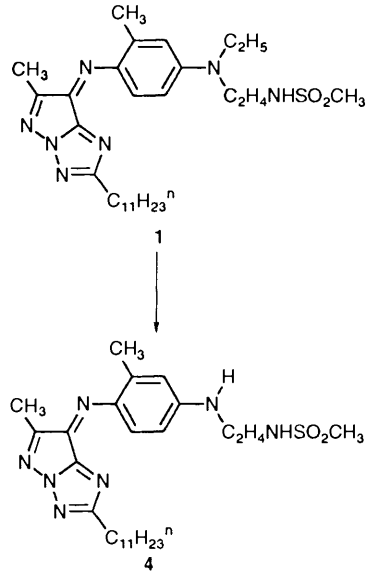
Fig. 5 Temperature effect on absorption spectrum of DYE-1 in EPA (5.0×10^{-4} mol dm^{-3}) at 263 K (—), 193 K (- - -), 173 K (-·-·-) and 123 K (····)

the flux of photons generated by the Xenon lamp used here is not particularly high when compared with that of lasers. A second possible explanation for the two-photon process is that the first photon slightly changes the structure of dye but the UV–VIS absorption spectrum remains almost the same; a second photon then decolourizes the sample (see later).

Photochemical Reactions in Dilute Solution.—To determine the concentration dependence of the photochemical reactions of the pyrazolotriazole azomethine dyes, the photochemical reaction in MeCN was tested at two different wavelengths (Fig. 4). While illumination in the 532 nm (± 13 nm) region did not cause a photochemical reaction, illumination in the 293 nm (± 13 nm) region caused a fast photochemical reaction. This result indicates that the photochemical reaction in the VIS region depends on the concentration of pyrazolotriazole dye. As we know that the photochemical reaction of these dyes in film obeys second-order kinetics, the excited dimer is the reactive species at high concentration. From the results of the light-intensity dependence in the UV region, one can easily see that the same two-photon process occurred in the dilute solutions as well as in the film under UV illumination.

The association of pyrazolotriazole dyes in the ground state was investigated by analysing the temperature effect on the absorption spectrum in dilute solution (Fig. 5). The spectrum of DYE-1 in an organic glass, EPA (ether–isopentane–ethanol 5:5:2) showed a clear change at low temperature. At a higher temperature, DYE-1 showed an absorption maximum at 540 nm, so we assigned this absorption band to that of the dye monomer. When the temperature was gradually lowered to 153 K, the second absorption appeared at a shorter wavelength (510 nm), and this new absorption band was tentatively assigned to the dimer band of pyrazolotriazole dyes.

Analysis of Photochemical Reaction Products.—To obtain more information about the photochemical reactions, the structure analysis of photochemical reaction products was studied both in film and in dilute solution. The samples were illuminated with VIS light until about 50% of the dye had faded, then the reaction products were separated from gelatin and other materials and purified by conventional methods. In the case of film samples, product 4 was identified by ^{1}H NMR and mass spectroscopy (Scheme 1). The ethyl group of DYE-1 was removed from the *N*,*N*-dialkylamino group upon VIS light illumination. Product **4** was also detected in MeCN. Attempts were made to produce a detailed analysis of other reaction products including colourless compounds; however, we could not obtain useful information about the photochemical reaction processes involved with the exception of the dealkylation reaction.



Scheme 1

Fluorescence of Dyes in Solution.—The fluorescence of the pyrazolotriazole dyes was measured at various temperatures and concentrations. DYE-1 dissolved in EPA at 2×10^{-5} mol dm^{-3} shows fluorescence of emission maxima at 580 nm (the absorption maxima is 530 nm) at room temperature. When the sample was cooled to 173, 123 and 77 K, respectively, the full width at half maximum of emission was gradually reduced because of the decrease in vibrational contributions, but the emission maxima did not change. Under these experimental conditions, only the fluorescence of the monomer of DYE-1 was detected.

Fig. 6 shows the fluorescence spectra of DYE-1 in EPA at 2×10^{-4} mol dm^{-3} instead of 2×10^{-5} mol dm^{-3}. When the temperature was gradually lowered from 213 to 153 K, the

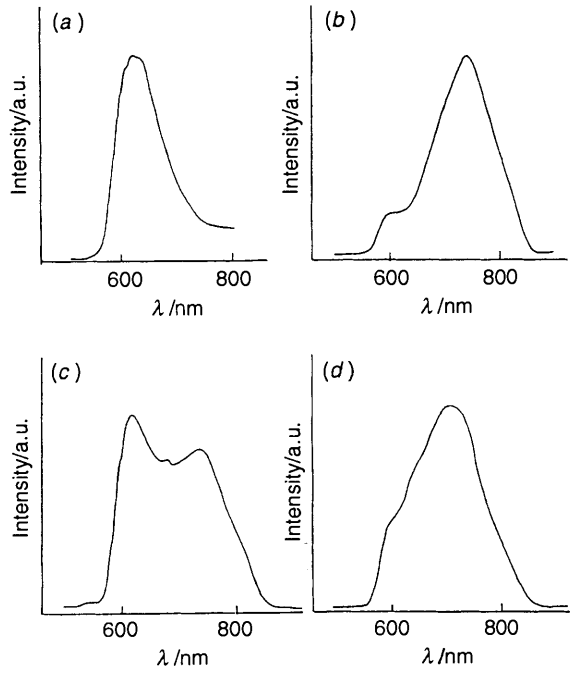


Fig. 6 Fluorescence spectra of DYE-1 in EPA (2×10^{-4} mol dm^3) at: room temperature (*a*), 173 K (*c*), 123 K (*b*) and 77 K (*d*)

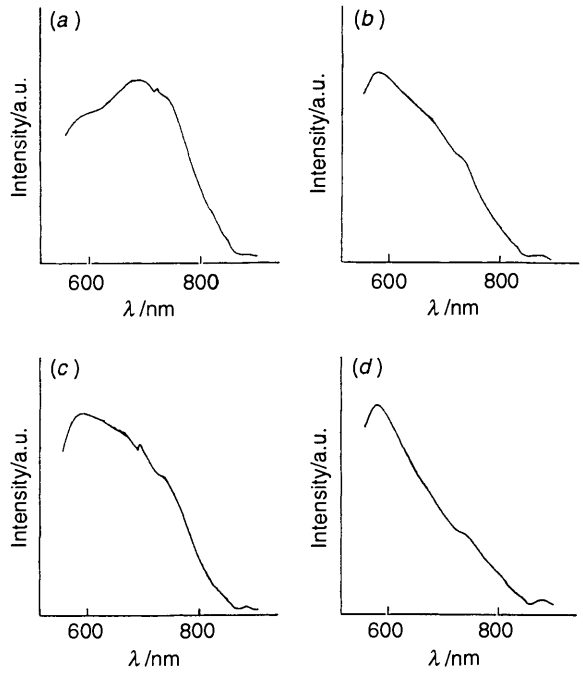


Fig. 7 Fluorescence spectra of DYE-1 in film at room temperature, oil:dye ratio 2:1 (*a*); 4:1 (*c*); 8:1 (*b*) and 16:1 (*d*)

Table 1 Quenching efficiencies ($k_q\tau_0$) of some additives for fluorescence of the dimer of DYE-1

Additive	$k_q\tau_0$
SI-5	110
SI-6	60
HQ-7	6
SC-8	3

fluorescence of the monomer of DYE-1 decreased (shifted from 580 nm to 610 nm because of self-absorption of fluorescence at higher concentration) and in addition the new fluorescence band at 740 nm increased. This new fluorescence at 740 nm was assigned to that of the excited dimer of DYE-1. The fluorescence at 77 K showed a third emission band at 700 nm which is thought to be the fluorescence of the highly associated states of DYE-1.

Fluorescence of Dyes in Film.—Because it was found that the excited singlet states of the monomer, dimer and highly associated states of DYE-1 fluoresce at different wavelengths, we measured the fluorescence spectra of the film sample at various dye concentrations.

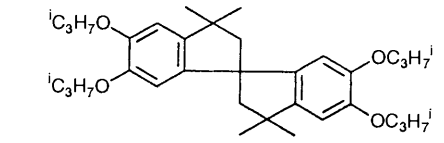
When the concentration of DYE-1 was high (oil:dye ratio 2:1) the fluorescence spectrum at room temperature showed at least three components (Fig. 7). By comparison with the fluorescence spectra measured at low temperature in EPA, each of the emission peaks can easily be assigned: the 590 nm emission band is the fluorescence of the monomer of DYE-1, the 740 nm emission band is that of the dimer of DYE-1, and the 700 nm emission band is that of the highly associated states of DYE-1. The intensities of the 700 nm band (associated states) and the 740 nm band (dimer) were stronger than that of the 590 nm band (monomer). When the concentration was lowered (oil:dye ratio 2:1 to 16:1) the fluorescence spectra at room temperature decreased the peaks of the 700 nm and 740 nm emission bands which were related to the associated states of DYE-1.

Additives for Pyrazolotriazole Azomethine Dyes.—Many different compounds have been synthesized and tested as stabilizers for pyrazolotriazole azomethine dyes. Of these stabilizers, spiroindane (SI) derivatives were revealed to have high efficiency in reducing the photochemical reactions associated with these dyes. On the other hand, hydroquinone (HQ) and spirochroman (SC) compounds showed negligible effects on the light-fading reactions.

The effects of the stabilizer SI-5 on the photochemical reaction of DYE-2 in film are shown in Fig. 8. For example, under VIS light illumination at 532 nm, compound SI-5 showed a large stabilizing effect on the photochemical reaction of DYE-2. When the concentration of SI-5 in the oil droplets was increased in the film, SI-5 showed a greater inhibition of the photochemical reaction of DYE-2. In contrast, under UV illumination at 293 nm, SI-5 did not show any stabilizing effect on the photochemical reaction of DYE-2. These data imply that SI-5 stops the first pathway where the lowest excited state of dimer of DYE-2 is the reactive species, but is not able to stop the second pathway where the upper excited state of monomeric DYE-2 is the reactive species.

Quenching of Fluorescence of Dyes by Additives.—To analyse the interaction between the pyrazolotriazole azomethine dye and a number of additives, we compared the fluorescence spectra of the dyes both in the presence and in the absence of additives both in film and in solution (Fig. 9). The fluorescence of dimeric DYE-1 at 740 nm seemed to decrease upon addition of SI-5 to the dye at room temperature; however, the magnitude of the change was not particularly remarkable. Consequently, the sample was cooled to 173 K, and under these conditions the fluorescence of DYE-1 dimer clearly decreased. The same kind of experiment was carried out for 2×10^{-4} mol dm^{-3} DYE-1 in EPA. The fluorescence at 740 nm (DYE-1 dimer) clearly decreased upon addition of SI-5 (2×10^{-2} mol dm^{-3}). Under these conditions the absorption spectrum was not changed by the addition of SI-5 at all, so the excited state of dimeric DYE-1 must have been quenched by SI-5.

Fig. 10 shows a Stern–Volmer plot of the fluorescence of DYE-1 in the presence of SI-5. The Stern–Volmer plot gave a straight line, and from whose slope, a value of 1.1×10^2 was evaluated as the product of the quenching rate constant (k_q) and the lifetime of the lowest excited singlet state of the dimer of



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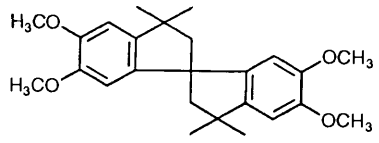

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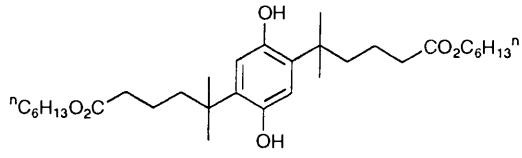

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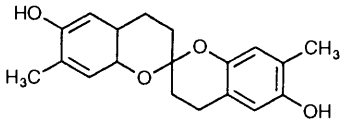

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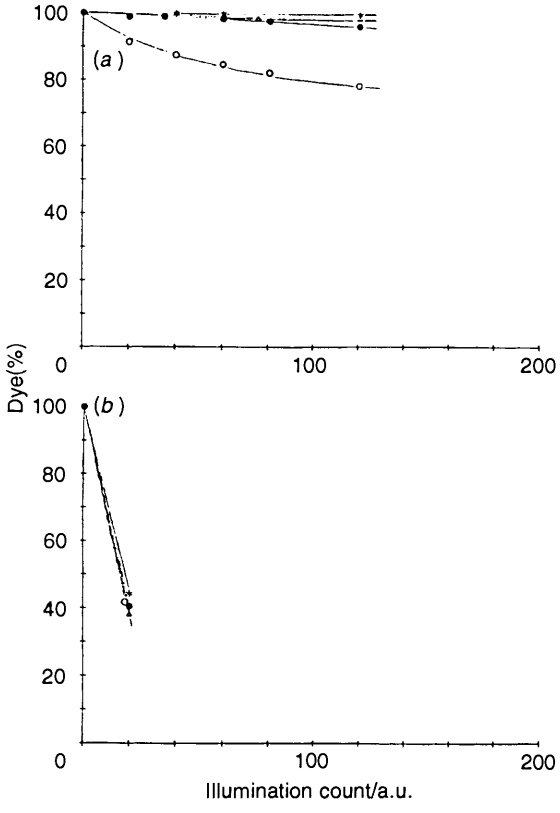

Fig. 8 Effect of stabilizer SI-5 on photochemical reactions of DYE-2 in film at 532 nm (*a*) and at 293 nm (*b*); [SI-5] : [DYE-2] = 0 : 1 (○); 0.2 : 1 (●); 0.5 : 1 (△) and 1 : 1 (✱)

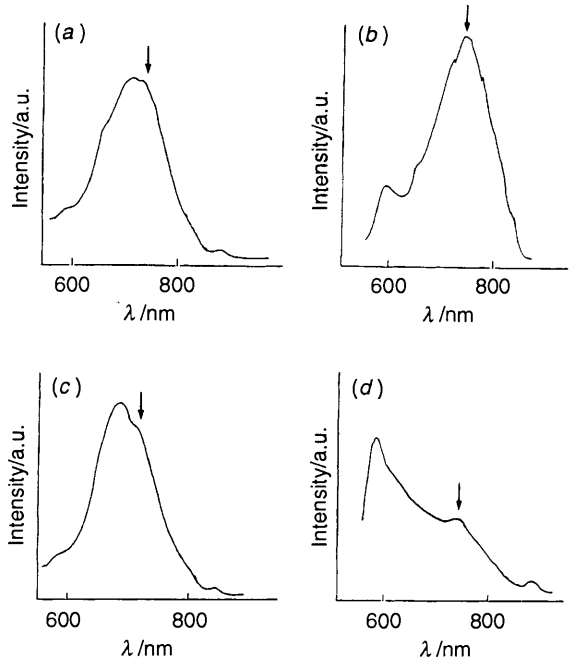

Fig. 9 Quenching of fluorescence of DYE-1 by stabilizer SI-5 at 173 K (*a*) without SI-5 in film; (*c*) with SI-5 ([SI-5] : [DYE-2] = 1 : 1) in film; (*b*) without SI-5 in EPA (2×10^{-4} mol dm^{-3}); (*d*) with SI-5 (2×10^{-2} mol dm^{-3}) in EPA (2×10^{-4} mol dm^{-3})

DYE-1 (τ_0). To date, we have not been able to determine the lifetime of the fluorescence of the DYE-1 dimer. On the assumption that the lifetime (τ_0) is of the order of 10^{-8}–10^{-9} s, the quenching rate constant (k_q) should be of the order of 10^{10}–10^{11} dm^3 mol^{-1} s^{-1}, which means that SI-5 may quench the fluorescence of dimeric DYE-1 at a nearly diffusion-controlled rate.

Other additives were tested to determine the fluorescence quenching efficiency with regard to DYE-1 dimer. The quenching efficiencies ($k_q\tau_0$) of a number of additives for DYE-1 are listed in Table 1; spiroindane derivatives have the highest quenching efficiency which was observed to be subject to substituent effects. The quenching efficiency of the hydroquinone derivative and that of the spirochroman derivative is relatively low compared with the quenching efficiency of spiroindane compounds.

Quenching of Fluorescence and Stabilizing Effect on Photochemical Reactions.—Fig. 11 shows the relationship between the fluorescence quenching efficiencies of SI-5 for dimeric DYE-1

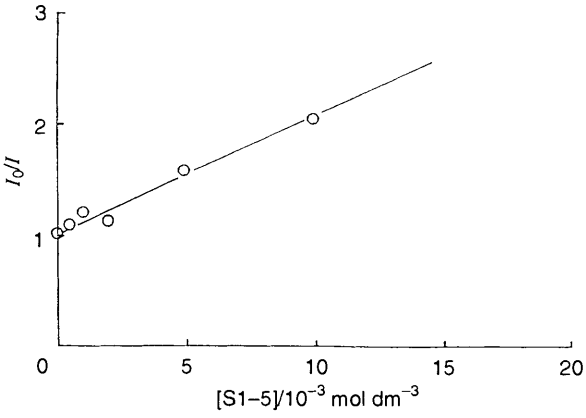

Fig. 10 Stern–Volmer plot of fluorescence of DYE-1 in EPA (2×10^{-4} mol dm^{-3}) by stabilizer SI-5 at 173 K: I_0, fluorescence intensity of DYE-1 without SI-5; I, fluorescence intensity of DYE-1 with SI-5

and the stabilizing effect of SI-5 on the photochemical reaction of DYE-1 in film. Using the value of 1.1×10^2 dm^3 mol^{-1} as the product of $k_q\tau_0$ and 4.6×10^{-2} mol dm^{-3} as the concentration of SI-5, a value of 6 : 1 was deduced for the equation, $1 + k_q\tau_0$

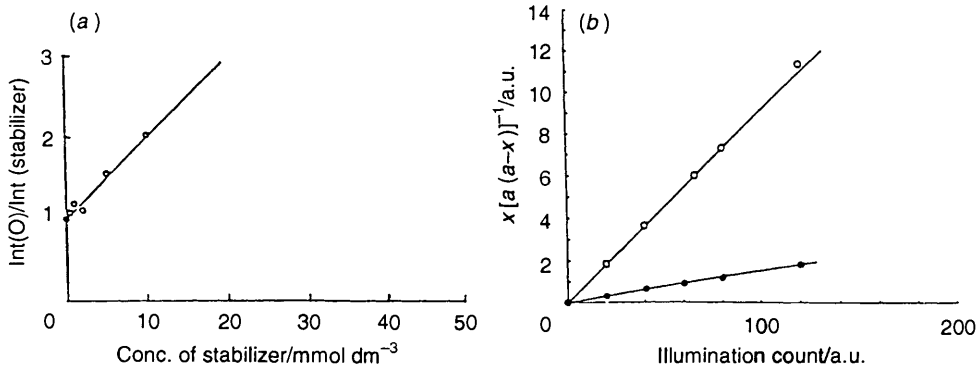

Fig. 11 Relationship between the fluorescence quenching and the stabilizing effect of photochemical reaction by stabilizer SI-**5**; (*b*) without SI-**5** (○) and with SI-**5** (●)

[SI-**5**]. This successfully explains the stabilizing effect of SI-**5** on the photochemical reaction of DYE-**1** in film [reaction rate, $k(0):k$(SI-**5**) = 6:1]. It also was found that the stabilizing effect for the photochemical reaction of pyrazolotriazole dye by hydroquinone derivatives and by spirochroman derivatives is not as high as that of spiroindane compounds.

Conclusions

The photo-fading mechanisms of 1*H*-pyrazolo[1,5-*b*][1,2,4]-triazole azomethine dyes were studied. Two types of photochemical reaction process were found in film. The reaction related to the self-association of the pyrazolotriazole dye, occurs under VIS light illumination, and this reaction path is efficiently reduced by the addition of spiroindane derivatives. The quenching of the fluorescence of pyrazolotriazole dye dimers by spiroindane derivatives quantitatively correlates with the stabilizing effect on the photochemical reaction of pyrazolotriazole dyes in film.

Acknowledgements

The authors wish to thank Mrs Yayoi Hashimoto, Mrs Atsuko Suzuki and Miss Kimiyo Ohta for their assistance in performing various experiments.

References

1 W. G. Herkstroeter, *Mol. Photochem.*, 1971, **3**, 181.
2 W. G. Herkstroeter, *J. Am. Chem. Soc.*, 1973, **95**, 8686.
3 W. G. Herkstroeter, *J. Am. Chem. Soc.*, 1976, **98**, 330.
4 W. G. Herkstroeter, *J. Am. Chem. Soc.*, 1976, **98**, 6210.
5 W. F. Smith, Jr., W. G. Herkstroeter and K. L. Eddy, *Photogr. Sci. Eng.*, 1976, **20**, 140.
6 J. Bailey, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2047.
7 T. Sato, T. Kawagishi and N. Furutachi, JAP, 59-171, 956.
8 T. Sato, T. Kawagishi and N. Furutachi, *J. Synth. Org. Chem.* (*Jpn*), 1991, **49**, 541.

Paper 3/05518C
Received 14*th September* 1993
Accepted 25*th November* 1993