Pyrazolotriazole Azomethine Dyes Linked to Light Stabilizer: Conformational Analysis and Effect on Light Keeping Stability

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Abstract

We synthesized a series of new pyrazolo[5,1c]-1,2,4-triazole magenta couplers linked with a light stabilizer (an aminophenol derivative including a sulfonyl group) at 3-position of the coupler nucleus. We found that the light stability of the CD-3 azomethine dyes derived from these couplers appears to depend on an optimum length of the group linking the coupler nucleus and the stabilizer moiety, with a 5-atom-long linking group being most effective in achieving light stability. Molecular dynamic calculation and ^{1}HNMR studies suggested that the sulfonyl group (-SO_2-) of the light stabilizer moiety and the sulfonamide group (-$NHSO_2$-) of the CD-3 moiety form a macro-cyclic intra-molecular hydrogen bond in the dye when the number of atoms of the linking group is 4 or 5, which brings the light stabilizer moiety in close proximity to the dye nucleus. It appears that the high light stability of such dyes can be attributed to the distance between the dye nucleus and the light stabilizer moiety.

Introduction

It is well-known that the dye derived from a 1H-pyrazolo[5,1c]-1,2,4-triazole (PT) magenta coupler has poor light keeping stability. The PT magenta coupler is generally used with stabilizers[1], such as hindered phenol, hydroquinone, and aminophenol derivatives. In Konica QA Paper Type A6 (QA-A6), two types of light stabilizers, S-1 and S-2, are combined with a PT magenta coupler (M-1) seen in Fig.1, S-1 possesses both an aminophenol and a sulfonyl moiety and is a very efficient light stabilizer, although its mechanism is not entirely clear. In a study, reported elsewhere [2] , of the self association enthalpy of PT azomethine dye (M-1-CD-3 dye, i.e. the dye forming magenta color images in color paper QA-A6) produced by PT magenta coupler (M-1) and CD-3 through the HPLC technique, it was found that the sulfonamide moiety derived from CD-3 was the most effective unit with respect to this self association. We therefore suspected that one factor in S-1's light-keeping efficiency might be a conformation which brought the CD-3 moiety and the stabilizer moiety into close proximity. We further hypothesized that such a conformation might be characterized by a hydrogen bond between the sulfonyl group of S-1 (-SO_2-) and the sulfonamide group of M-1-CD-3 dye (-$NHSO_2$-). If such a hydrogen bond were formed, the functional unit of S-1 (aminophenol moiety) would be quite close to the dye nucleus, and the efficiency of S-1 as a light keeping agent could be expected to be higher.

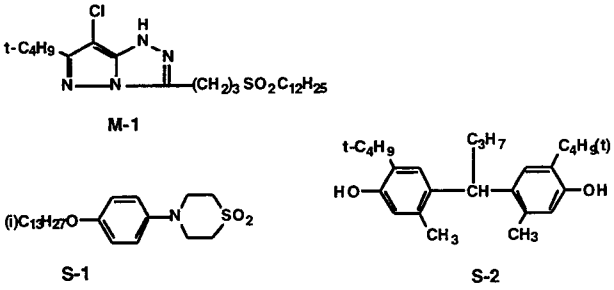
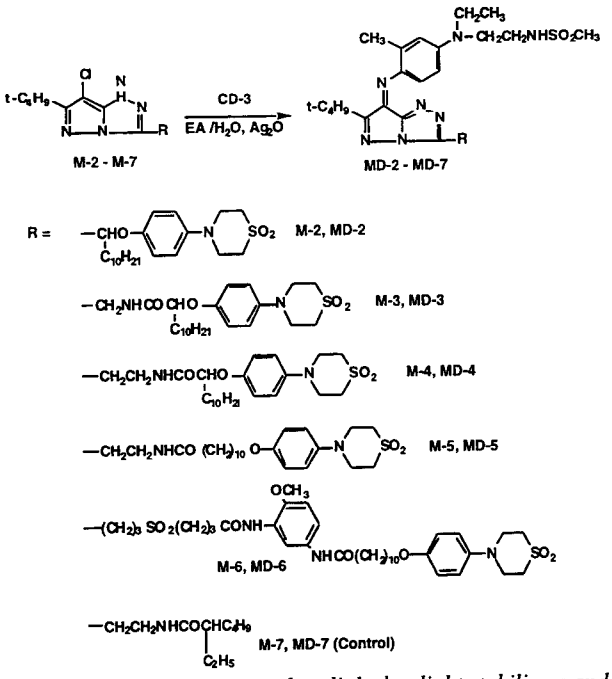


Fig.1 QA-A6 magenta coupler and light stabilizers

Results

In order to explore this hypothesis, we designed several varying placements of the functional unit S-1 in relation the PT magenta coupler. Several PT magenta couplers linked to light stabilizers were synthesized, and converted to CD-3 azomethine dyes, as seen in Scheme 1. These dyes were coated on a support (HBS=diisodecylphthalate[DIDP],HBS/Dye=2/1 [wt/wt]), and their light stabilities were then tested. The results are shown in Table 1.



Scheme 1 PT magenta couplers linked to light stabilizers and resultant CD-3 azomethine dyes

Table 1 Light stabilities of PT-CD-3 dyes linked to light stabilizer

No.	PT-CD-3 dye	Length of linking group (Number of atoms)**	$T_{0.3}$ (hr)*
1	MD-7(Control)	---	64
2	MD-7+S-1***(Control)	---	106
3	MD-2	1	87
4	MD-3	4	113
5	MD-4	5	143
6	MD-5	14	75
7	MD-6	24	36

*The value shows the time (hr) needed to lose 30% of the initial dye densities. Xe-Fade-O-Meter (70klux) was used as light fading test equipment.

**Length of linking group is the number of linking atoms between the 3-position of PT coupler nucleus and oxygen atom of phenoxy group.

***S-1 and MD-7 had the same molar.

In order to determine the conformation of the PT-CD-3 dye linked to the light stabilizer, we performed the molecular dynamic calculations for these dyes. The most stable conformation of MD-4 estimated from our calculations is shown in Fig.2. Here, the sulfonyl group of the light stabilizer unit (-SO_2-) and the sulfonamide group derived from CD-3 (-$NHSO_2$-) appear to be in very close proximity. Similar results were obtained with MD-3, but in other cases, this conformation was not observed.

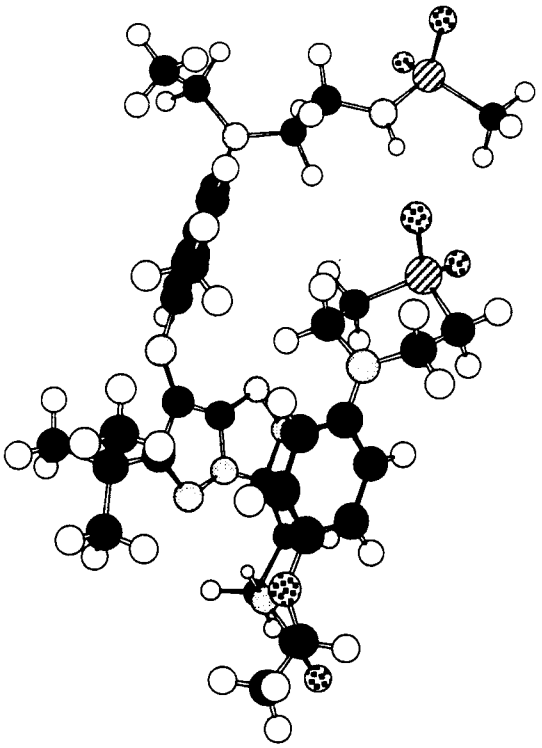


Fig.2 The most stable conformation of MD-4 estimated from molecular dynamic calculation

We measured the ^{1}HNMR spectra in chloroform-d ($CDCl_3$) of all seven couplers and three concentrations of CD-3 dyes (3.5M, 14.0M, 28.0M) . The chemical shifts of ^{1}HNMR spectra were assigned from ^{1}H-^{1}H cosy NMR spectra. The ^{1}HNMR data of MD-5, MD-4, and MD-7 are shown in Tables 2,3, and 4 respectively.

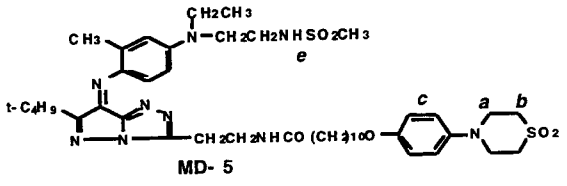


Table 2 ^{1}HNMR Data of M-5 and MD-5

No.		*a* (ppm)	*b* (ppm)	*c* (ppm)	*e* (ppm)
1	M-5(14mM, Coupler)	3.67	3.16	6.86	-
2	MD-5(3.5mM, Dye)	3.65	3.14	6.86	4.78
3	MD-5(14mM,Dye)	3.66	3.14	6.86	5.27
4	MD-5(28mM, Dye)	3.67	3.14	6.86	5.48
5	No.1 minus No.3	0.01	0.02	0.00	-
6	No.4 minus No.2	0.02	0.00	0.00	0.70

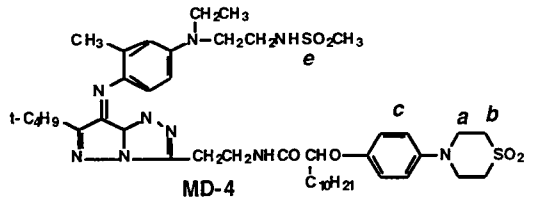


Table 3 ^{1}HNMR Data of M-4 and MD-4

No.		*a* (ppm)	*b* (ppm)	*c* (ppm)	*e* (ppm)
1	M-4(14mM, Coupler)	3.72	3.12	6.72	-
2	MD-4(3.5mM, Dye)	3.37	2.90	6.54	5.35
3	MD-4(14mM, Dye)	3.37	2.90	6.54	5.42
4	MD-4(28mM, Dye)	3.38	2.90	6.55	5.52
5	No.1 minus No.3	0.34	0.24	0.18	-
6	No.4 minus No.2	0.01	0.00	0.01	0.17

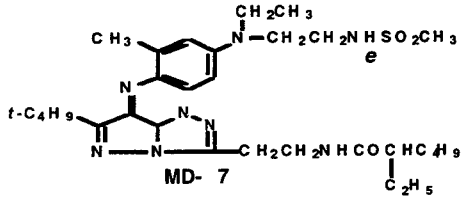


Table 4 ^{1}HNMR Data of M-7 and MD-7

No.		*a*(ppm)	*b*(ppm)	*c*(ppm)	*e*(ppm)
1	M-7(14mM, Coupler)	-	-	-	-
2	MD-7(3.5mM)	-	-	-	4.78
3	MD-7(14mM)	-	-	-	5.33
4	MD-7(28mM)	-	-	-	5.62
5	No.1 minus No.3	-	-	-	-
6	No.4 minus No.2	-	-	-	0.84

The values in row No.5 are differences of chemical shift of the proton a, b, and c values of rows No.1 (chemical shifts of the coupler) and No.3 (chemical shifts of corresponding CD-3 dye), all having the same concentration. The values of row No.6 are differences of chemical shifts of proton e values of those when the dye concentration equals 28mM (No.4) and the values when the concentration equals 3.5mM (No.2). Table 4 shows the chemical shift data of MD-7 (without light stabilizer unit) as a control. It is apparent that the chemical shift derived from the sulfonamide (-NHSO2-) of the usual PT-CD-3 dye (Table 4) is very variable with respect to the concentration of the solution.

Discussion

Fig.3 shows the relation between the light keeping stabilities and the lengths of the linking group of the CD-3 dyes derived from PT magenta couplers linked with a light stabilizer. We found that the light stability of the CD-3 azomethine dyes derived from these couplers appears to depend on an optimum length of the group linking the coupler nucleus and the stabilizer moiety, with a 5-atom-long linking group being most effective in achieving light stability.

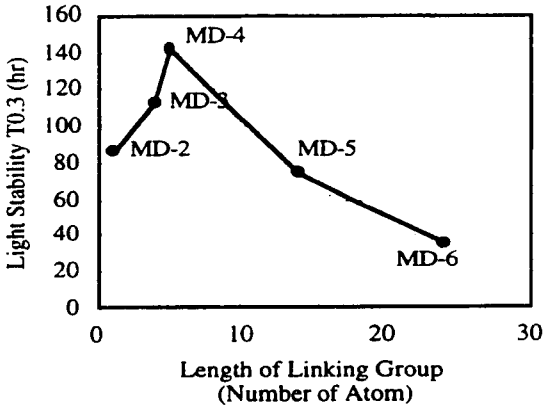


Fig.3 Optimum linking group length

The most stable conformation of MD-4 estimated from our calculations is shown in Fig. 2. Because of the proximity shown, it is assumed that an intra-molecular hydrogen bond was formed between the sulfonyl group of the light stabilizer unit (-SO_2-) and the sulfonamide group derived from CD-3 (-N$\underline{H}SO_2$-). Similar results were obtained with MD-3, but this conformation was not observed with other dyes.

The values listed in row No.5 in Table 2 show that the chemical shift changes of the light stabilizer unit between M-5 (coupler) and MD-5 (corresponding CD-3 dye) are about zero, while the corresponding values of M-4 and MD-4 (Table 3) are 0.18 to 0.34. These variances can be attributed to the ring current effect, and we assume that the stabilizer moiety of MD-4 is quite close to the CD-3 moiety. The lower magnetic fields of the chemical shifts of acidic protons such as -OH and -NH- can generally be attributed to hydrogen bond formation. It can be seen that the magnitude of value listed in Rows No.6 relate to the difference of the hydrogen bond forming probability of the sulfonamide protons (-N$\underline{H}SO_2$-) when the solution is diluted (3.5mM) and concentrated (28mM). The Row 6 value of MD-4 is much smaller than those of MD-5 and MD-7. This variance results from the formation of the inter-molecular hydrogen bond. Therefore, we believe that MD-4 very likely forms an intra-molecular hydrogen bond between the CD-3 moiety and the stabilizer moiety in $CDCl_3$.

However, when dimethylsulfoxide-d6 (DMSO-d6) was used instead of $CDCl_3$ as a solvent with MD-4, we were not able to observe ^{1}HNMR behavior similar to that observed when MD-4 was dissolved in $CDCl_3$. We believe that the intra-molecular hydrogen bond of MD-4 was easily cleft because DMSO is strong hydrogen

bond acceptor, resulting in the light stabilizer unit of MD-4 detaching from the dye nucleus.

We examined the light stabilities of MD-4 in several solvents (HBSs). The dielectric constants of the HBSs were used instead of hydrogen bond acceptive parameters, because few HBS hydrogen bonding parameters exist. The relation between the dielectric constant of several HBSs and the light stabilities of MD-4 are shown in Fig.4. From this relationship, it is clear that HBSs having low dielectric constants (probably provide the low hydrogen bond activity) needed in order to employ intra-molecular hydrogen bonding for the stabilization of dyes.

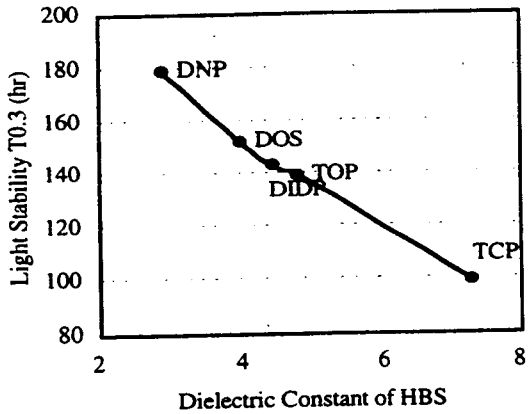


Fig.4 Relation between light stability of MD-4 and dielectric constant of HBS as a dye solvent

Finally, we examined the influence of the substituents of MD-4 for intra-molecular hydrogen bond formation using analogues of MD-4 as shown in Fig. 5. We found that all of them were able to form hydrogen bonds similar to MD-4. Therefore, both the bulkiness of substituents which attached to the PT nucleus and the type of joining group is unrelated to the formation of hydrogen bonds, and it can be seen that only the length of linking group plays a significant role.

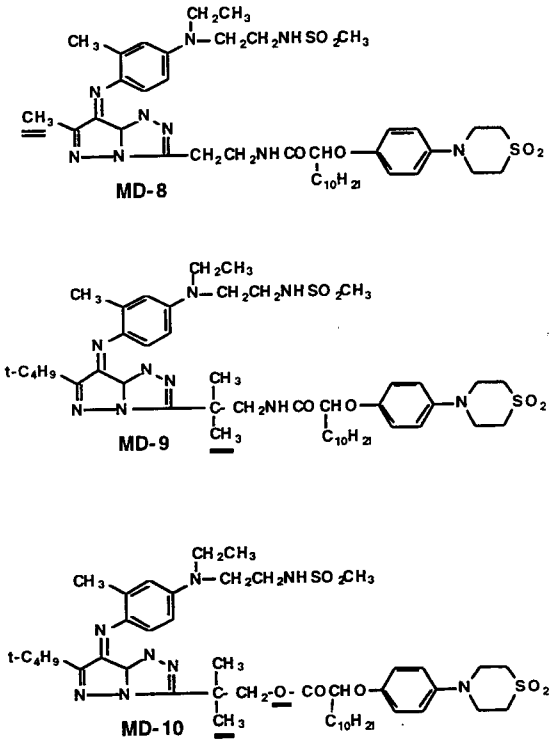


Fig.5 Structures analogues to MD-4

Conclusion

We investigated PT-CD-3 dyes linked to light stabilizers possessing sulfonyl units. It was found that the light stability of these dyes appeared to depend on an optimum length of the group linking the coupler nucleus and the stabilizer moiety, with a 5-atom-long linking group being most effective in achieving light stability. The reason for this high light stability was the formation of macro-cyclic intra-molecular hydrogen bonds in the dye, as indicated by molecular dynamic calculation and ^{1}HNMR studies.

References

1) N.Furutachi, U.S.Patent 4588679,T.Nishijima, JP 64-90445

2) H.Kita and Y.Kaneko, J. Soc. Photgr. Sci. Tec. Jpn., 57(5), 344-348 (1994)