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A Study on the Relationship Between Steric Effects and Performance of Some Triazinyl Reactive Dyes

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ABSTRACT

A series of model compounds of triazinyl reactive dyes was synthesized. The dihedral angles between the phenyl and triazinyl ring were calculated using PC Model software (Serena Software Co., USA). and the pseudo first order rate constants of hydrolysis were determined by HPLC. The relationship between steric effects and the reactivity of triazinyl reactive dyes are discussed. © *1998 Elsevier Science Ltd. All rights reserved*

Keywords: Steric effect, dihedral angle, triazinyl reactive dye.

INTRODUCTION

The introduction of bulky substituents causes changes of the molecular configuration of organic compounds, i.e. changes in the bond length, bond angle or rotation of bonds. The energy for changing bond length (E_r,) and that for changing bond angle, (E_θ), increases with the square of the change of the bond lengths ($r-r_0$) and the changes of bond angle Δ_θ [1], as shown in eqn (1):

$$E_r = 0.5K_r(r - r_0)^2$$
$$E_\theta = 0.5K_\theta(\Delta\theta)^2 \quad (1)$$

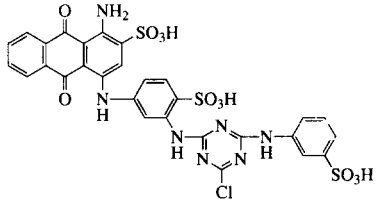
*Corresponding author.

where K_r is the strength constant of stretch;
r is the bond length;
r_0 is the normal bond length;
K_θ is the strength constant of bend;
Δ_θ is the divergent value of bond angle.

Generally, there is a value approximately of 3~7 kcal mol^{-1} for a bond length stretch of 0.01Å. The energy for changing bond angle is lower that for changing the bond length. However, the energy for rotation of a bond is very small, only 0.2 kcal mol^{-1} consumes for a double bond being rotated for an angle of 5°. Therefore, to alleviate the steric hindrance caused by bulky substituents, rotation of the bond is the first requirement. In dye molecules, the rotation of bonds caused by steric hindrance will not only partly interrupt the conjugation system, but also cause sectional deformation of both the linear and planar molecular structures, which would inevitably affect performance of the dyes, mainly the shade, the affinity as well as the reactivity influence of reactive dyes. It is thus very significant to study the relationship between the steric effect and the performance of dyes.

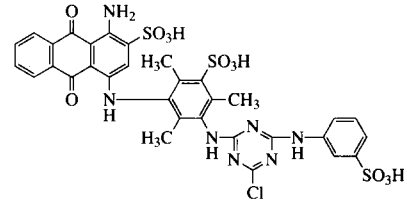
RESULT AND DISCUSSION

The influence of steric effects on the shade and affinity of dyes is well known [2, 3, 4]; for example, whilst C.I. Reactive Blue 5 (1) can be applied for dyeing and printing, C.I. Reactive Blue 49 (2) can only be applied for printing due to the distortion of the molecular configuration of the dye caused by the presence of two methyl groups.



C.I. Reactive Blue 5

(1)



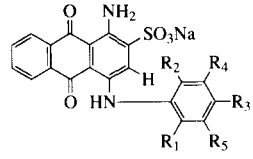
C.I. Reactive Blue 49

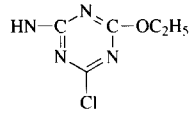
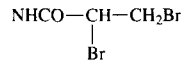
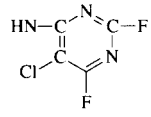
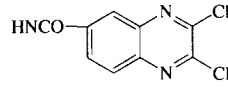
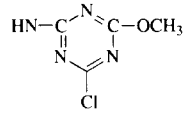
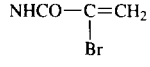
(2)

The steric hindrance arising from the two methyl groups at the 2 and 6 positions on the phenyl residue can be shown by ^{1}H-NMR. The chemical shift of the hydrogen at the 3-position on the anthraquinone moiety moves towards upper field due to the hydrogen being shielded by the phenyl ring. The chemical shifts of the hydrogen atom at the 3-position of the dyes (3–7)

TABLE 1

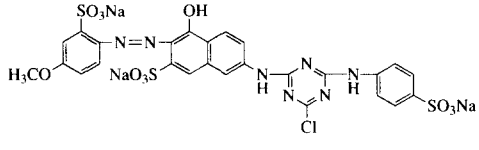
Chemical Shifts of Dyes with Different Substituents [5]



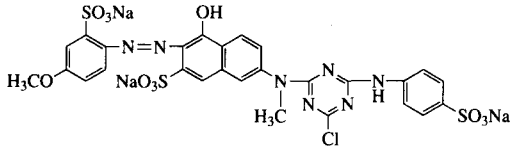
Entry	*Substituents*					*Chemical shift*	*Remark*
	R_1 R_2	R_3	R_4	R_5		δ *(ppm)*	
3	CH_3CH_3	CH_3	SO_3H	NH_2		7.07	Chromophore of C.I. Reactive Blue 74
4	CH_3CH_3	CH_3	SO_3H			7.17	Reactive Blue K- 3R
5	CH_3CH_3	CH_3	SO_3H			7.25	C.I. Reactive Blue 50
6	CH_3CH_3	CH_3	SO_3H			7.03	C.I. Reactive Blue 166
7	CH_3CH_3	SO_3H	—			7.10	—
8	H H	SO_3H	—			~8.0	—
9	H H	SO_3H		—		~8.0	—

in Table 1 are all in the region of 7.00~7.25 ppm (solvent: CF_3COOH), while, dyes (8,9), without steric hindrance, are near 8.00 ppm. The chemical shift to upper field of about 1 ppm results from the shielding effect caused by steric hindrance. A similar effect also exists if the solvent is DMSO-d_6.

When a methyl residue was introduced to the bridge (the imido residue) the affinity of dye (11) is much less than that of dye (10).

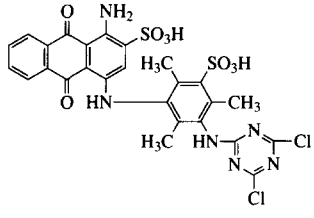


(10)



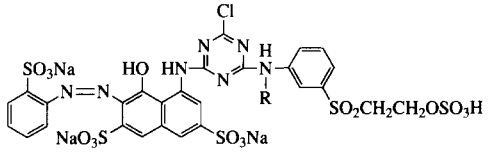
(11)

Little is known about the influence of the steric effect on the reactivity of reactive dyes, but there does exist a steric effect in reactive dyes which could affect their reactivity. For example, dye (12) could be condensed with the amine at 0–5°C and pH 7 and hydrolysis would surely take place in the process.



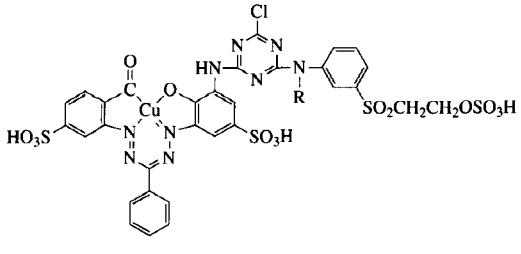
(12)

If an N-ethyl residue is introduced into a bifunctional reactive dye of the MCT-VS type, the affinity of the dye becomes low, but the reactivity of the dye is enhanced due to the steric hindrance caused by the introduction of such a bulky substituent [6, 7]. For example, the reactivity of this type of reactive dye, in which the same chromphore is either bridged by an imido residue or a N-ethyl imido residue, are compared. It has been shown that dye (13) is more reactive than dye (14); the same is also true for dye (15) and dye (16).



R = C_2H_5 (13)

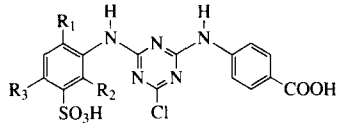
R = H (14)



R = CH_3 (15)

R = H (16)

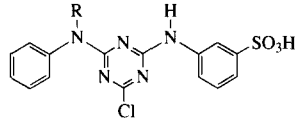
These facts demonstrate the existence of steric effects in reactive dyes, and which would reflect different degrees of influences on the reactivity of the dyes. In order to study the relationship of steric hindrance and reactivity of reactive dyes, a series of model compounds (Mod-1 to Mod-5) were synthesized.



Mod-1: $R_1 = R_2 = R_3 = H$

Mod-2: $R_1 = CH_3$ $R_2 = R_3 =$

Mod-3: $R_1 = R_2 = R_3 = CH_3$



Mod-4: R = H

Mod-5: $R = CH_3$

The configurations of the above model compounds were distorted to different extents depending on the bulkiness of the substituents. Such distortion will cause a change in the dihedral angle between the triazinyl residue and the phenyl residue of the different substituents. The dihedral angles of these model compounds were calculated using the PC Model software produced by Serena Software Corporation, USA; the distortion angles of these model compounds were found.

A kinetic study for these model compounds under the conditions of pH 11, 90°C and pH 9, 90°C, respectively, were conducted. By high pressure liquid chromatography, a linear relationship between the natural logarithm of the concentration of the product of hydrolysis and time and the pseudo first-order rate constants of hydrolysis of various model compounds was obtained. By correlating the calculated distortion angles and the pseudo first order rate constants of hydrolysis for various model compounds, the relationship between the distortion angle caused by steric hindrance and the reactivity of the corresponding model compounds is shown in Table 2.

The rate of hydrolysis of Mod-3 is distinctly faster than that of Mod-1 at pH 11.0, $T = 90°C$, and the rate of hydrolysis of Mod-3 is about two times that of Mod-1. This result is most likely caused by the distortion of the molecular configuration by the presence of two methyl groups at the ortho positions to the imido residue. The planar configuration of the molecule is destroyed thus lessening the flow of electrons from the imido residue to the triazinyl residue, and the low electronic density of the triazinyl residue would greatly enhance the reactivity of the carbon atom attached to the active chlorine atom. Although the methyl residue is an electron donating group, its passivation effect on the reactivity of the dye caused by its electronic effect is

negligible compared to its positive contribution to the reactivity of the dye caused by its steric effect. If bulkier substituents are introduced at the ortho positions of the imido residue, it would be expected that the reactivity of the active dyes will be further enhanced. From Fig. 1, it is apparent that if the distortion angle is widened, reactivity of the corresponding model compounds increases. Although the distortion angle may not be a real value (only obtained by computer calculation, which varies with the selected calculation method and parameters) the general pattern is applicable. This could explain why the reactivity of dye (10) is higher. The regular pattern also exists when the hydrolysis condition is pH 9, $T=90°C$ as shown in Fig. 1; the rate of hydrolysis of Mod-3 is 2.7 times that of Mod-1, a very appreciable difference. An explanation would be that the dehydrogenation of the imido bridge of the model compounds Mod-1~Mod-3 under the strong alkaline conditions of pH 11.0, the relatively small volume of the inborn nitrogen anion would alleviate the steric congestion to some extent, but at pH 9.0 the equilibrium constant of dehydrogenation is very small, and the volume of hydrogen predominates and the steric hindrance prevails. These results could provide an explanation of the difference as to why the rates of hydrolysis between Mod-1 and Mod-3 become greater at pH 9.0 than pH 11.0.

Introduction of the N-methyl residue would distinctly widen the distortion angle (compare the distortion angle of Mod-5 and Mod-4) to alleviate the steric hindrance, and this widening of the distortion angle would have an influence on the reactivity of Mod-5. The pseudo first-order rate constants of hydrolysis of Mod-4 and Mod-5 under the condition of pH 11, $T=90°C$ by HPLC are shown in Table 3. The rate of hydrolysis of Mod-5 is evidently faster than that of Mod-4, $k_{11(Mod\text{-}5)}$ is 5.9×10^{-2} min^{-1}, and $k_{11(Mod\text{-}4)}$ is 8.0×10^{-3} min^{-1}, and the rate of hydrolysis of Mod-5 is 7.4 times that of Mod-4.

TABLE 2
Relationship Between the Distortion Angle and the Reactivity of the Dyes

Entry	*Distortion angle (degree)*	*Pseudo first-order rate constants of hydrolysis (min^{-1})*		*Ratio of hydrolysis (%)*	
		k_{11}[a] *(pH 11)*	k_9[a] *(pH 9)*	y_{11}[a]	y_9[b]
Mod-1	12.3	0.035	0.0036	32.0	4.68
Mod-2	44.2	0.048	0.0052	45.6	7.21
Mod-3	68	0.071	0.0098	88.1	15.1

[a] k_{11} and y_{11} stand for the pseudo first-order rate constants of hydrolysis and the ratio of hydrolysis of various model compounds at pH 11, $t=40$ min, $T=90°C$.
[b] k_9 and y_9 stand for the pseudo first-order rate constants of hydrolysis and the ratio of hydrolysis of various model compounds at pH 9, $t=40$ min, $T=90°C$.

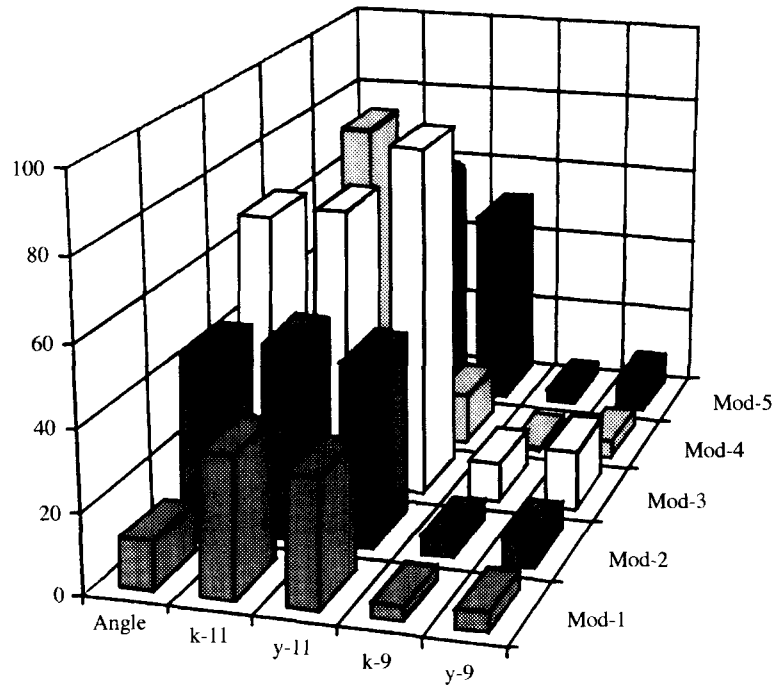


Fig. 1. Relationship between the distortion angle and the reactivity of model compounds. k11 and y11 stand for the pseudo first-order rate constants of hydrolysis and the ratio of hydrolysis of various model compounds at pH 11, $t=40$ min, $T=90$°C; K-9 and y9 stand for the pseudo first-order rate constants of hydrolysis and the ratio of hydrolysis of various model compounds at pH 9, $t=40$ min, $T=90$°C.

By plotting the data from Tables 2 and 3, the influence of the steric effect on the reactivity of reactive dyes is shown in Fig. 1.

In previous papers [8–10] the only explanation offered was that under strong alkaline condition of pH 11, the imido bridge of Mod-4 will partly dehydrogenate and the reactivity of the inborn nitrogen anion is very low, the N-methyl imido bridge of Mod-5 could therefore not dehydrogenate, so the rate of hydrolysis of Mod-5 is faster than that of Mod-4. The large difference of the kinetic constants at pH 11 of Mod-4 and Mod-5 also shows that steric hindrance factors are not negligible. A study to determine the pseudo first-order rate constant of the hydrolysis of Mod-4 and Mod-5 under the conditions of pH 9, $T=90$°C by HPLC shown in Table 2 is a supplement to this explanation. From the results, the rate of hydrolysis of Mod-5 is also faster than that of Mod-4 at pH 9.0, $T=90$°C, $k_{9(\text{Mod-5})}$ is $3.6\times10^{-3}\,\text{min}^{-1}$, and $k_{9(\text{Mod-4})}$ is $8.0\times10^{-4}\text{min}^{-1}$; the rate of hydrolysis of Mod-5 is 4.5 times that of Mod-4. Under such conditions, the equilibrium constant of the dehydrogenation is very small, and the influence of dehydrogenation on the reactivity of model compounds can be neglected. The above phenomenon can

TABLE 3
Relationship Between the Distortion Angle and the Reactivity of Dyes

Entry	*Distortion angle (degree)*	*Pseudo first-order rate constants of hydrolysis (min^{-1})*		*The ratio of hydrolysis (%)*	
		$k_{11}{}^a$*(pH 11)*	$k_9{}^a$*(pH 9)*	$y_{11}{}^a$	$y_9{}^b$
Mod-4	10.6*	0.008	0.0008	12.8	4.47
Mod-5	72.6*	0.059	0.0036	50.9	8.20

[a] k_{11} and y_{11} stand for the pseudo first-order rate constants of hydrolysis and the ratio of hydrolysis of various model compounds at pH 11, $t = 40$ min, $T = 90$°C.
[b] k_9 and y_9 stand for the pseudo first-order rate constants of hydrolysis and the ratio of hydrolysis of various model compounds at pH 9, $t = 40$ min, $T = 90$°C.

only be interpreted by a steric effect, i.e. the steric congestion caused by the introduction of the N-methyl residue leading to distortion of the molecular configuration, thus impeding $p = \pi$ conjugation between electron pairs on the nitrogen and the triazinyl ring.

To indicate the influence of the steric effect on the reactivity of reactive dyes, the ratios of hydrolysis for various model compounds at the same conditions are shown in Fig. 2. As is apparent from Fig. 2, as the distortion angles of the model compounds were widened, their ratios of hydrolysis increased accordingly.

The influence of the steric effect on the performance of dyes, especially the reactivity of reactive dyes is thus apparent and the development of these conclusions may be helpful in the design of the dyes and the prediction of the reactivity of reactive dyes.

EXPERIMENTAL

Synthesis of the model compounds

The model compounds were synthesized by condensation of cyanuric chloride with the appropriate aromatic amines by conventional methods. After purification, the dye structures were characterized by ^{1}H-NMR. The corresponding hydrolysis products were obtained by hydrolysis of the model compounds.

Hydrolysis of model compounds

Hydrolysis of the model compounds was carried out in 0.2 M buffer solutions of pH 11 and pH 9 at 90°C, sampling at 3, 6, 10, 15, 25, 40, 60, 80, 120, 140 and 160 min, diluting the sample with cold distilled water and neutralizing the solutions with 0.3% HCl.

Determination of pseudo first-order rate constants

The above solutions were analyzed by HPLC; the positions of the model compounds and their hydrolysis products were identified by the samples prepared in advance. The chromatographic conditions for HPLC analysis are shown in Table 4. The results show a linear relationship between the logarithm of the concentration of the hydrolysis product and time, indicating that the reaction was a pseudo first-order reaction.

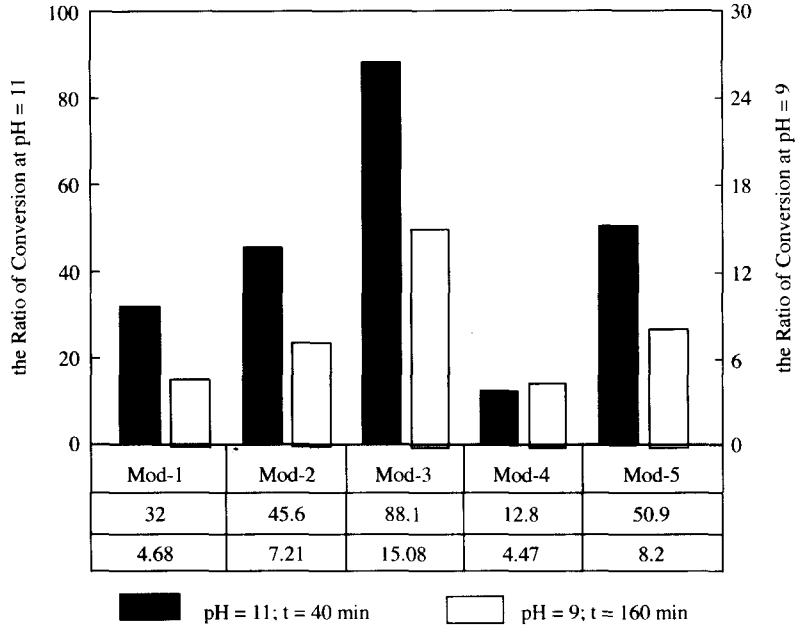


Fig. 2. The ratio of hydrolysis of various model compounds. pH 11, $t = 40$ min, $T = 90°C$ refers to the data in the first line of the table pH 9, $t = 160$ min, $T = 90°C$ refers to the data in the second line of the table.

TABLE 4
The Chromatographic Conditions for HPLC Analysis

Apparatus	LDC/Milton Roy
Column	C-18 reverse ion pair, 5μ, ID: 4.6 mm
Pressure	2500–3000PSI
Rate of elution	1 ml min^{-1}
Column temperature	25°C
Detector UV/vis detector	Wavelength = 285(Mod-1~Mod-3), 268 nm(Mod-4, Mod-5)
Mobile phase:	Mod-1 $CH_3OH:H_2O = 60:40 + 0.005$ M TBAI
	Mod-2 $CH_3OH:H_2O = 60:40 + 0.005$ M TBAI
	Mod-3 $CH_3OH:H_2O = 65:35 + 0.005$ M TBAI
	Mod-4 $CH_3OH:H_2O = 70:30 + 0.005$ M TBAI
	Mod-5 $CH_3OH:H_2O = 55:45 + 0.005$ M TBAI

CONCLUSION

The relationship between the distortion angle caused by steric hindrance and the reactivity of reactive triazinyl dyes was demonstrated by a kinetic study on the hydrolysis of the models of these dyes. Bulky substituents present on the ortho position to the imino group or N-alkyl group on the imino bridge of chlorotriazinyl aniline derivatives cause sectional distortion coplanarity between the phenyl and triazine rings, and partial impediment of p–π conjugation of the imino group with the triazinyl ring, thus leading to a reactivity increase. The results outlined are helpful in the interpretation of some abnormal reactivity of reactive dyes, and also to the design of the molecular structures of such dyes and the prediction of the reactivity of reactive dyes.

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