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A semiempirical molecular orbital study on the reaction of an aminopyrazolinyl azo dye with singlet molecular oxygen

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Abstract

Semiempirical MO (PM3) calculations were carried out to evaluate the photochemical reaction with singlet molecular oxygen at the azo group for an aminopyrazolinyl azo dye (Yellow-I) and for some hydroxy azo dyes. Structure optimization to give the minimum energy of formation showed that Yellow-I exists more predominantly in the azo form than the hydrazone one in vacuum. The azo and hydrazone forms of Yellow-I were shown to have similar reactivity in the reaction with singlet oxygen via ene reaction or 1,2-cycloaddition mechanism. Singlet oxygen adds to the carbon–nitrogen double bond of the hydrazone tautomer, as well as to the carbon–carbon double bond in the pyrazoline ring of the azo tautomer to give the same end product, i.e. hydroperoxide. The facility with which a dye is photooxidized by singlet oxygen is dependent on the properties of the dye and on the azo-hydrazone tautomerism. The ease of photooxidizability for azo dyes can be estimated by the value of the superdelocalizability at the carbon atoms on which azo groups are substituted for hydroxylated and aminated aromatics.

Keywords: Azo dye; PM3 method; Photo-oxidation; Singlet oxygen; Ene reaction; Azo-hydrazone tautomerism

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1. Introduction

From the similarity between the reaction of singlet molecular oxygen with a carbon–carbon double bond [1–10], and the reaction with azo groups, the latter has been assigned to be an 'ene' reaction [11,12]. Several workers have suggested the reaction of singlet oxygen with the hydrazone tautomer within the azo-hydrazone tautomerism [11–18]. We have previously shown that the photosensitized fading of an aminopyrazolinyl azo dye (Yellow-I) with a copper phthalocyanine dye was due to a singlet oxygen mechanism [19,20]. The ease with which reactive dyes on cellulose are photo-oxidized was examined by exposing the dyed films in aerated Rose Bengal solution, while that in which the dyes were photo-reduced was evident in anaerobic dl-mandelate. Yellow-I was found to be very susceptible to photo-oxidization, and had a low ease with which it was photo-reduced.

In the present study, whether or not semiempirical molecular orbital calculations can estimate the very large ease with which Yellow-I is photo-oxidized is discussed. Since, in the MO calculation, Yellow-I is regarded to exist as an isolated molecule in vacuum, the sodium sulfonate or

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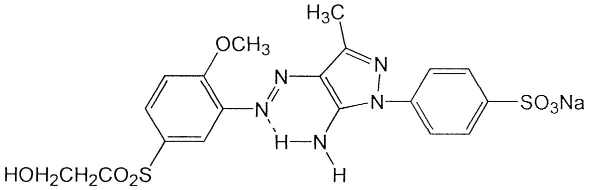
the sulfonic acid group is treated, and the vinylsulfonyl (VS) group is bound with cellulose as the hydroxyethylsulfonyl variety.

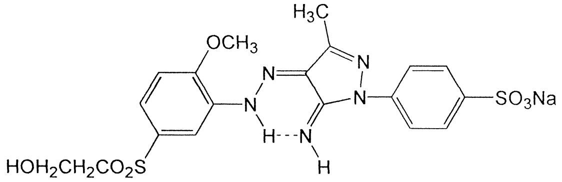
2. Materials

An aminopyrazolinyl azo dye (Yellow-I), a VS reactive dye supplied by Sumitomo Chemical Co. Ltd., and some model hydroxyazo dyes were used. The chemical structures of the azo and hydrazone forms used for the MO calculation are shown below.

1. Azo form of Yellow-I.



2. Hydrazone form of Yellow-I.



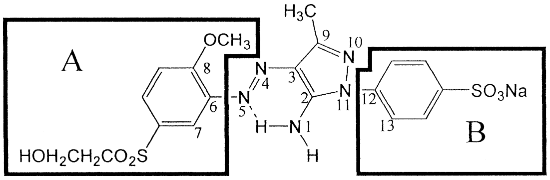
MO calculations were performed by using CAChe MOPAC 94 Ver.3.8 based on MOPAC 6 (CAChe Scientific, Inc.).

3. Results and discussion

3.1. PM3 calculation of reactivity for azo and hydrazone tautomers

3.1.1. Structure optimization

The geometries of the azo and hydrazone tautomers for Yellow-I were initially optimized using the PM3 method. In order to illustrate the chemical structure in geometry optimization and reaction schemes, their abbreviated form is used as shown:



(where only the azo form is shown.)

The number in the structure shows the number of the constituent atoms to express the reaction sites. The optimized geometries for four species of Yellow-I are summarized in Table 1, and those for the sodium sulfonate form are shown in Figs. 1 and 2. The intermediate part between A and B (pyrazoline nucleus and hydrogen-bonded azo group) is plainer for the azo and hydrazone tautomers. As for the twist angle, no twisting is described by ±180°, plus angles of rotation and twist mean clockwise, and minus angles anticlockwise. Thus, azo tautomers with sodium sulfonate or sulfonic acid groups are almost linear. Only the A- and B-planes rotate by 43∼45°’ and −45 to −46°, respectively. The two phenyl rings of the azo tautomer rotate in the reverse direction to

Table 1
Dihedral angles between A- or B-plane and azo-pyrazoline-plane (AP plane) in the optimized geometries of Yellow-I in the singlet ground state

Tautomer	Type of solubilizing group	Rotation (°)		Twist (°)	
		A-AP (4-5-6-7)	B-AP (9-10-11-12)	A-AP (4-5-6-7)	B-AP (9-10-11-12)
Azo	SO_3Na	45.02	−44.44	−178.9	178.2
	SO_3H	43.39	−45.81	179.7	−178.9
Hydrazone	SO_3Na	111.9	26.22	−177.1	−149.7
	SO_3H	108.8	26.22	−175.3	−149.5

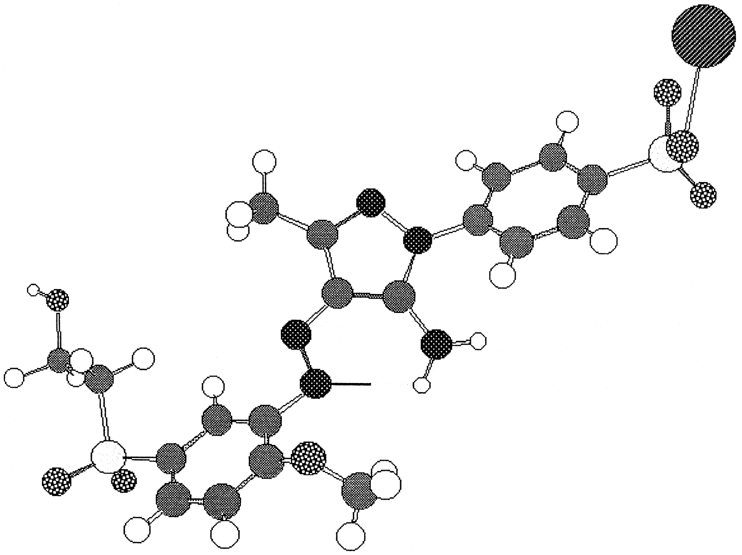


Fig. 1. Optimized structure for the azo tautomer of Yellow-I in the sodium sulfonate form (heat of formation = $-231.2\,\mathrm{kcal\,mol^{-1}}$) (cf. Table 1).

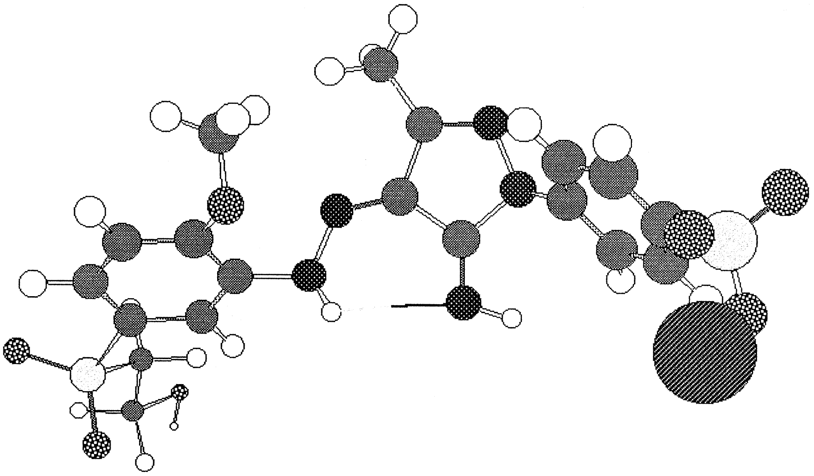


Fig. 2. Optimized structure for the hydrazone tautomer of Yellow-I in the sodium sulfonate form (heat of formation = $-211.2\,\mathrm{kcal\,mol^{-1}}$) (cf. Table 1).

each other (cf. Fig. 1). The hydrazone tautomers with sodium sulfonate and sulfonic acid groups, on the other hand, have almost the same structure to each other with less linear geometry. The A-plane bends a little from the azopyrazoline-plane and B-plane by 30°, and the A-plane rotates 110° and the B-plane by 26° as shown in Fig. 2

3.1.2. Heats of formation for Yellow-I as the sodium sulfonate or sulfonic acid type in optimized geometries

The heats of formation for the azo and hydrazone tautomers of Yellow-I in the sodium sulfonate form with the optimized geometries are shown below the structure. The heat of formation for the azo tautomer was smaller than that for the hydrazone form. The differences were 20 kcal mol^{-1} for the sodium sulfonate type and 17.8 kcal mol^{-1} for the sulfonic acid type, respectively. Since the mean errors of the heats of formation calculated by the PM3 method have been reported to be ± 7.8 kcal mol^{-1} for 660 compounds [21,22] and that polar solvents promote the hydrazone form, the predominance of the azo form in aqueous solution may not completely be concluded. However, Mazurek et al. [23] recently made a study on the azo-hydrazone equilibria of 8-arylazotheophyllines by *ab initio* MO calculation and UV-Vis measurements. Although polar solvents and electron-withdrawing substituents shift the equilibrium slightly towards the hydrazone side, arylazotheophilines exist mainly in azo-form. The heats of formation for the azo tautomers of azotheophylines, calculated by the *ab initio* method in vacuum, were smaller by ca 20 kcal mol^{-1}‘ than those for the hydrazone tautomers, except for the trinitroderivative, as in this present study.

3.2. Mechanistic study by PM3 method

Dewar and Thiel [4] have reported the reaction mechanism of singlet oxygen with a carbon–carbon double bond using the MINDO/3 method, and they concluded a step-wise reaction *via* peroxirane or zwitterionic intermediates. Yamaguchi [5] has reviewed the MO calculations of singlet oxygen reactions. In this present study, the PM3 method was used instead of MINDO/3. In order to obtain a reference for comparing the validity of applying the MO method to azo dyes, the reaction of $(^1\Delta_2)$ O_2 with propene was recalculated by the PM3 method, as shown in Scheme 1. Although the first product of the reaction between propene and $^1O_2$ yields cis- and trans-methylperoxiranes, only the reaction path of cis-isomers is shown in Scheme 1, since cis- and trans-species are similar in energy [4]. A smoother reaction path to the end product, propene-3-hydroxyperoxide, was obtained by the PM3 method than that by the MINDO/3 [4], because the intermediate potential barriers, **3**→**4** and **3**→**5**, disappeared in the case of PM3, although a barrier of **6**→**7** remains in case of the 1,2-cycloaddition pathway by both methods.

3.2.1. Reaction site in Yellow-I in electrophilic reaction with $^1O_2$

Singlet molecular oxygen acts as electrophilic reagent on reaction with carbon–carbon double bonds, to give an ene reaction as well as 1,2-cycloaddition. Whatever sites within a single molecule of Yellow-I have the higher possibility of reacting with $^1O_2$ can be estimated by the frontier electron density ($f_r^{(E)}$) of the HOMO orbital, for electrophilic reactions [24–29]. The superdelocalizability ($S_r^{(E)}$) can compare the reactivity of corresponding atoms in different molecules [24,25,28]. In non-planar molecules, $S_r^{(E)}$ for π-orbitals is defined by [28]:

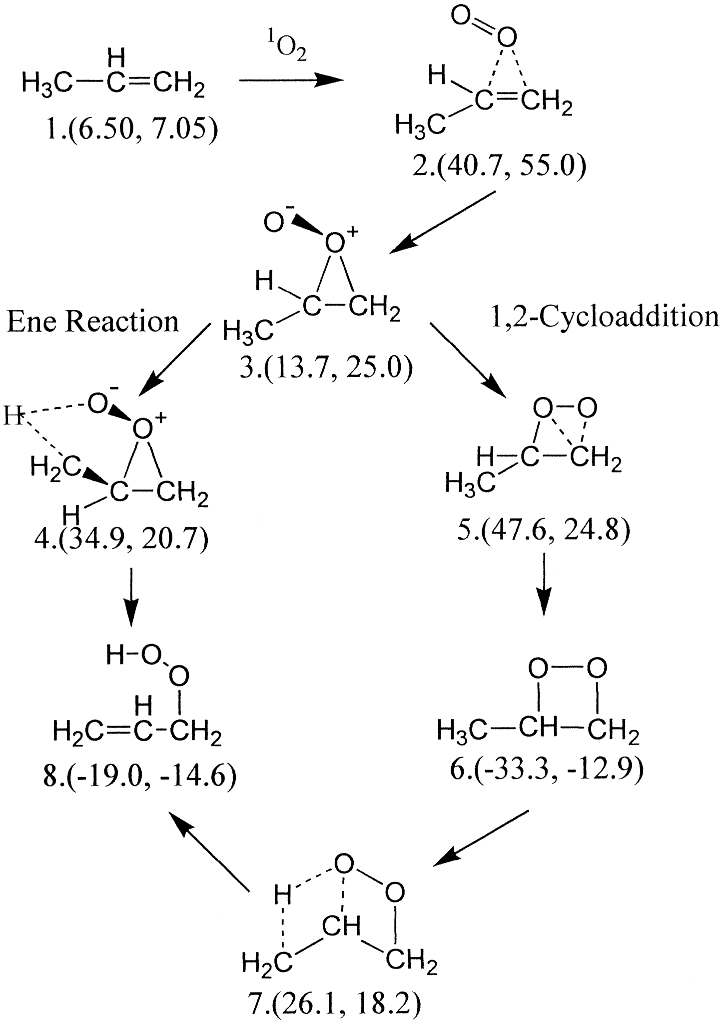
$$S_{r\pi}^{(E)} = \sum_{i}^{occ} \frac{2\beta(C_{r\pi,i})^2}{\epsilon_i - \epsilon_E} \qquad (1)$$

where super- and subscripts E indicate the counter reagents of electrophiles, $^1O_2$, $C_{r\pi,i}$ is the coefficient of p-orbital of the r-atom of the ith MO which is perpendicular to the local plane, β is the resonance integral, and ϵ_E and ϵ_ic, are the orbital energies of the counter reagent and the ith MO of Yellow-I. The value of ϵ_E for the LUMO energy of $^1O_2$ used in the present study was -5.85 eV, while those of ε_i for of the azo and hydrazone tautomers of Yellow-I were -8.765 and -8.713 eV, respectively.

The values of $f_r^{(E)}$ and $S_r^{(E)}$ at several positions for the azo and hydrazone tautomers of Yellow-I are listed in Table 2. The 4-carbon (Site 3) on the pyrazoline ring, substituted by the azo group, was shown to have the highest reactivity to electrophilic reagent in both the hydrazone and azo tautomers of the sodium sulfonate and the sulfonic acid types. Previous studies have reported the same conclusions from the reaction of the hydrazone tautomer with $^1O_2$ [11–18].

3.2.2. Reaction of $^1O_2$with the hydrazone tautomer

As in the case of the reaction of propene with $^1O_2$ (cf. Scheme 1), the reaction of the hydrazone tautomer for Yellow-I was treated by using the PM3 method, as shown in Scheme 2. As a convenience, some simplified presentations are employed. As the first step, $^1O_2$ adds to the $C=N$ double bond of the hydrazone tautomer, as has



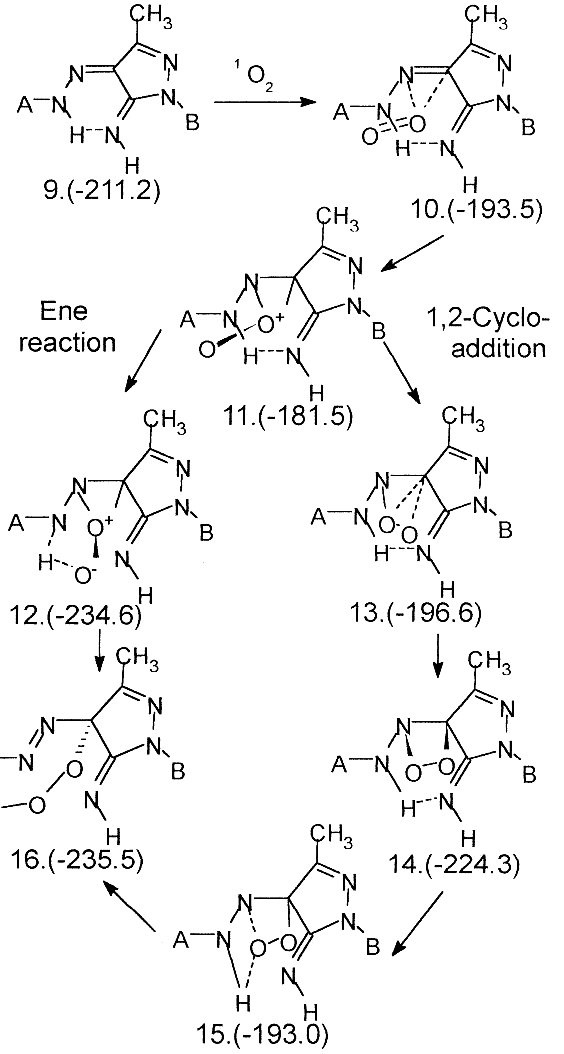
Scheme 1. Reaction scheme of propylene with $^1O_2$. (Numbers in parentheses describe the heats of formation (kcal mol^{-1}): left calculated by MINO/3 method [2] and right by PM3 method, respectively.)

been previously reported [11–18]. Although a common potential barrier **10**→**11** and a barrier in 1,2-cycloaddition path **14**→**15** are observed, both the ene reaction and 1,2-cycloaddition pathways to the common end product, 4-hydroperoxide, are concluded to hold in the reaction of $^1O_2$ with Yellow-I. However, $^1O_2$ adds to the C=N double bond from the front (upper) and back (down) sides of the structure. Thus, as in the case of propene, two kinds of isomers for the corresponding products, except for some exceptions which have no isomer, are formed in the reaction between Yellow-I and $^1O_2$. Since the heats of formation of the products were very similar to those of the corresponding isomers, only one reaction path of their isomers is shown in Scheme 2.

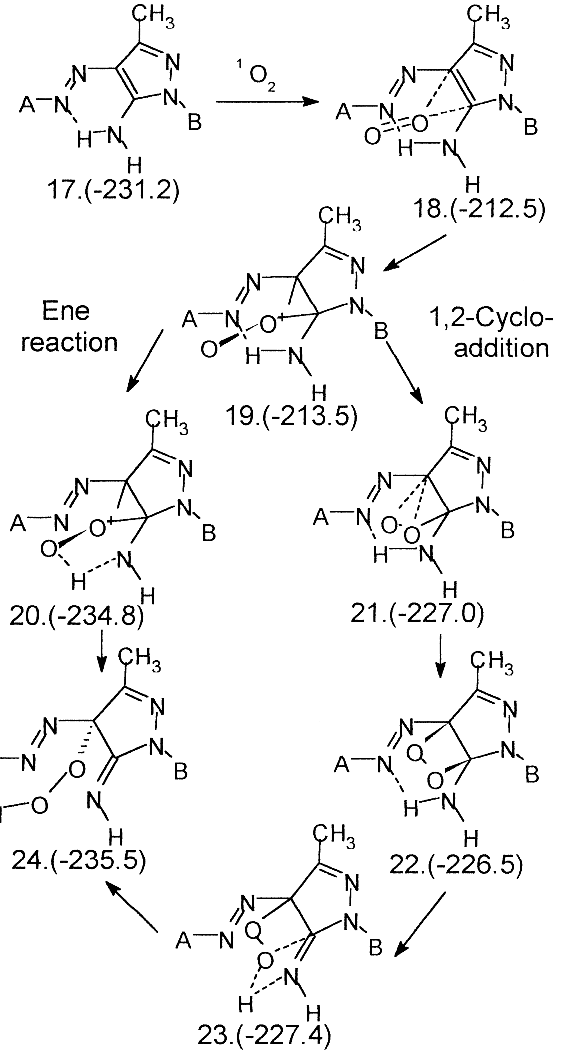
No reaction of $^1O_2$ via 1,4-cycloaddition mechanism was shown to occur by the same procedure.

3.2.3. Reaction of $^1O_2$ with the azo tautomer

The application of the PM3 method to the reaction of $^1O_2$ with the azo tautomer of Yellow-I is shown in Scheme 3. In this scheme, $^1O_2$ adds to the C=C double bond of the pyrazoline ring of the azo tautomer as the first step. As in case of the hydrazone tautomer, only one reaction path from



Scheme 2. Reaction scheme for Yellow-I of hydrazone tautomer and sodium sulfonate form with $^1O_2$ (Numbers in parentheses describe the heats of formation (kcal mol^{-1}), calculated by PM3 method.)



Scheme 3. Reaction scheme for Yellow-I of azo tautomer and sodium sulfonate form with $^1O_2$. (Numbers in parentheses describe the heats of formation (kcal mol^{-1}), calculated by PM3 method.)

the two pathways is shown in the scheme, although two kinds of isomers for the corresponding products are formed. Compared with Schemes 1 and 2, more facile reaction pathways of the ene reaction, as well as 1,2-cycloaddition, were obtained, except for a very small potential barrier **21**→**22**. Thus, the azo tautomer reacts with $^1O_2$ at the common reaction site to give the same end product, i.e. the 4-hydroperoxide of Yellow-I, as that of hydrazone tautomer via a different reaction path. The ease with which azo dyes are photo-oxidized is thus determined by the dye property itself, and not by whether or not the dyes exist in the hydrazone form. The large ease with which Yellow-I is photo-oxidized [19] can be explained by the high reactivity of the 4-carbonation on the pyrazoline ring, and not by the azo-hydrazone tautomerism (cf 3.3).

3.2.4. Decomposition of hydroperoxide of Yellow-I

The end product of photo-oxidation in Schemes 2 and 3, the 4-hydroperoxide of Yellow-I, is decomposed to give quinones and diazonium compounds [11]. Frimer [1,5] summarized Hock-cleavage of hydroperoxide to carbonyl fragments via acid-catalyzed heterolysis, occurring even in absence of any added acid.

Table 2
Reactivities ($f_r^{(E)}$ and $S_r^{(E)}$) at several sites in the azo and hydrazone tautomers of Yellow-I in its sodium sulfonate and sulfonic acid forms

	Azo tautomer				Hydrazone tautomer			
Type	SO_3Na		SO_3H		SO_3Na		SO_3H	
Site (r)	$f_r^{(E)}$	$S_r^{(E)}$	$f_r^{(E)}$	$S_r^{(E)}$	$f_r^{(E)}$	$S_r^{(E)}$	$f_r^{(E)}$	$S_r^{(E)}$
1	0.129	0.543	0.119	0.487	0.153	0.491	0.141	0.479
2	0.142	0.428	0.141	0.400	0.026	0.384	0.116	0.363
3	0.339	0.559	0.365	0.608	0.325	0.513	0.375	0.543
4	0.060	0.522	0.083	0.488	0.064	0.454	0.086	0.489
5	0.072	0.474	0.099	0.426	0.051	0.471	0.124	0.479
6	0.044	0.449	0.072	0.432	0.005	0.424	0.047	0.427
7	0.029	0.434	0.046	0.416	0.003	0.401	0.024	0.400
8	0.029	0.397	0.046	0.382	0.004	0.370	0.034	0.352
9	0.089	0.444	0.085	0.411	0.159	0.441	0.116	0.396
10	0.111	0.543	0.165	0.584	0.066	0.496	0.141	0.509
11	0.157	0.547	0.167	0.505	0.173	0.490	0.097	0.494
12	0.034	0.429	0.019	0.367	0.120	0.466	0.041	0.383
13	0.032	0.478	0.028	0.426	0.122	0.420	0.062	0.454

Table 3
Heats of formation (kcal mol^{-1}) for various species with the optimal geometry for aminopyrazolinyl azo dye reacted with singlet oxygen by means of the semiempirical PM3 method

	Type of solubilizing group		
Species	D-SO_3Na	D-SO_3H	Difference
9	−211.2	−112.2	99.00
10	−193.5	−93.90	99.60
11	−181.5	−81.61	99.89
12	−234.6	−135.5	99.10
13	−196.6	−96.83	99.77
14	−224.3	−125.2	99.10
15	−193.0	−93.90	99.10
16	−235.5	−130.0	105.5
17	−231.2	−127.0	104.2
18	−212.5	−107.6	104.9
19	−213.5	−108.5	105.0
20	−234.8	−128.8	106.0
21	−227.0	−121.7	105.3
22	−226.5	−121.0	105.5
23	−227.4	−121.9	105.5
24 (=16)	−235.5	−130.0	105.5

In the oxidative photo-decomposition of azo dyes, an ene reaction or 1,2-cycloaddition of both the azo and hydrazone tautomers with $^1O_2$ is the rate-determining step to give hydroperoxides, which may be easily and thermally decomposed to carbonyl fragments.

3.2.5. Comparison between the sodium sulfonate and sulfonic acid of the dye

Although the heats of formation for Yellow-I of both the sulfonate and sulfonic acid types in the optimized geometries were calculated in Sections 3.1.2, 3.2.2, and 3.2.3, those for all the species of both the types in Schemes 2 and 3 are listed in Table 3. The differences between both the types in the heats of formation were 99.4 kcal mol^{-1} for the hydrazone tautomer and 105.2 kcal mol^{-1} for the azo tautomer, respectively, except for species **16** (=**24**).

In spite of whether the solubilizing groups of 'Yellow-1' are sodium sulfonate or sulfonic acid, it was confirmed that the same conclusions were obtained from the optimized geometries, the smaller heats of formation of the azo tautomer, the sites of highest reactivity, and the reaction mechanism with $^1O_2$.

3.3. Ease with which dyes are photo-oxidized

The photo-reactivities of typical azo dyes, 2- and 4-hydroxyphenylazobenzenes, 1-phenylazo-2-naphthol, 4-phenylazo-1-naphthol, and related dyes, in the reaction with $^1O_2$ were also examined by the PM3 method. Heats of formation and optimized geometries for both the azo and hydrazone tautomers of these four dyes with optimized geometries were calculated as shown in Table 4, in which results for Yellow-I of sodium sulfonate type are also listed. All the azo tautomers for these dyes have smaller heats of formation than the hydrazone tautomers. Except for Yellow-I and the hydrazone form of CI Solvent Yellow 12, all the azo and hydrazone tautomers of the six dyes have a fully planar structure.

Table 4
Heat of formation (kcal mol^{-1}) and reactivity with singlet oxygen for azo and hydrazone tautomers of some azo dyes in optimized geometries by the PM3 method

Dye	Tautomer	Heat of formation	Dihedral angle		Position of highest reactivity	$f_r^{(E)}$	$S_r^{(E)}$
			Rotation[a]	Twist[b]			
Yellow-I	Azo	−231.2	45.02	−178.9	C-atom in pyrazoline nucleus substituted by azo group	0.339	0.559
	Hydrazone	−211.2	111.9	−177.1		0.325	0.513
2-Hydroxyphenyl-azo-benzene	Azo	45.80	0.000	−180.0	C-atom in hydroxy-phenyl group substituted by azo group	0.279	0.489
	Hydrazone	59.90	0.001	−180.0		0.303	0.472
CI Solvent Yellow 12	Azo	28.51	−0.015	−179.9		0.246	0.494
	Hydrazone	44.31	−6.683	166.8		0.334	0.517
4-Hydroxyphenylazobenzene	Azo	45.24	−0.001	180.0		0.264	0.473
	Hydrazone	64.92	−0.001	180.0		0.223	0.468
CI Solvent Yellow 10	Azo	36.05	0.002	−179.9		0.306	0.481
	Hydrazone	56.06	−0.001	−180.0		0.321	0.485
1-Phenylazo-2-naphthol	Azo	64.06	0.000	−180.0	C-atom in naphthyl group substituted by azo group	0.373	0.518
	Hydrazone	71.72	0.001	−179.9		0.391	0.539
4-Phenylazo-l-naphthol	Azo	67.08	−0.001	−180.0		0.349	0.500
	Hydrozone	76.15	−0.001	−180.0		0.331	0.494

[a] Rotation = Rotation (4-5-6-7) (°).
[b] Twist = Twist (4-5-6-7 (°)

The position or atoms of highest reactivity can be determined by searching the largest values of $f_r^{(E)}$ for the optimized geometries of each dye. They were carbon atoms on which azo groups were substituted by phenols, naphthols, and the pyrazoline ring of Yellow-I (cf. Table 4). The position of reaction may be a general rule for azo dyes. It should be noted that proton transfer in the azo-hydrazone tautomerism and the proton abstraction in the ene reaction and 1,2-cycloaddition (cf. Scheme 3) for *p*-hydroxyl isomers may occur via a solvent proton, although this mechanism has not yet been reported.

The ease with which these dyes are photo-oxidized can be compared among different dyes by the values of $S_r^{(E)}$ at the carbon atoms of highest reactivity, as shown in Table 4. Except for 1-phenylazo-2-naphthol, the values of $S_r^{(E)}$ for the azo tautomers were larger than the hydrazone ones. The differences in the values of $S_r^{(E)}$ between both the tautomers were 0.46–0.005. The precise value of $S_r^{(E)}$ for a dye cannot be determined, since no real composition of azo/hydrazone tautomers can be estimated on cellulose, but the real value may be regarded to exist in the range between those for both the tautomers. Then, if the differences of $S_r^{(E)}$ between dyes are larger than 0.5, the photo-oxidizability of azo dyes may be estimated by the values of $S_r^{(E)}$. If the photo-oxidation with $^1O_2$ occurs only between the hydrazone tautomer this rule does not hold. It also shows that the treatment of Scheme 3 is viable, since there is no evident exclusion principle of the azo tautomer in the application of MO theory to the reactivity of azo dyes.

Yellow-I has the largest value of $S_r^{(E)}$ among these dyes, which shows that Yellow-I has very large ease with which it is photo-oxidized.

The photo-reactivities of these dyes can be found in Colour Index [30] as the light fastness of solvent dyes, although some dyes contain methyl substituents (cf. Table 5). Although the effect of methyl groups cannot be estimated, there was found good correlation between the values of $S_r^{(E)}$ and the light fastness. The photo-oxidizability of

Table 5
Lightfastness for dyes used and of related dyes [30]

Dyes	2-Hydroxy-5-methylphenyl-azo-2′-methylbenzene	3-Methyl-4-hydroxy-phenylazobenzene	1-Phenylazo-2-naphthol	4-Phenylazo-2-naphthol
CI generic name	CI Solvent Yellow 12	CI Solvent Yellow 10	CI Solvent Yellow 14	CI Solvent Brown 4
Lightfastness (in solvent)	Very good (in mineral oil)	Fair (in mineral oil)	Poor–fair	Fair (in oil)

azo dyes, or light fastness to photo-oxidation may be estimated by the superdelocalizability of the carbon atom substituted by an azo group in hydroxylated or aminated aromatics, irrespective of azo and hydrazone tautomers.

4. Summary

High reactivity of an aminopyrazolinyl azo dye in an electrophilic reaction, i.e. reaction with singlet molecular oxygen, was proved by use of the semiempirical molecular orbital PM3 method. Although former reports have stated that only the hydrazone tautomer had high reactivity with $^1O_2$, it was confirmed that both the azo and hydrazone tautomers have similarly high reactivity with $^1O_2$ to give a common end product (hydroxyperoxide) by way of an ene reaction or 1,2-cycloaddition. Thus, $^1O_2$ reacts with the 4-carbon atoms of the pyrazoline nucleus of the azo tautomer, as well as that of the hydrazone form, to give the same end product, by way of different reaction intermediates from both tautomers.

The reactivity of azo dyes with $^1O_2$ does not depend on whether or not they exist as the hydrazone tautomer but upon their basic chemical structure.

The ease with which azo dyes are photo-oxidized can be estimated by the values of superdelocalizability at the carbon atom, substituted by an azo group, in hydroxylated and aminated aromatics by using the semiempirical MO method.

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