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An analysis of azo-hydrazone tautomerism of reactive azobenzene and pyrazolinyl-azo dyes using the semiempirical molecular orbital PM5 method

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Abstract

The azo-hydrazone tautomerism (AHT) was analyzed through the enthalpies of formation estimated for ten yellow reactive dyes in their hydrolyzed forms using semiempirical molecular orbital (MO) PM5 and COSMO methods. Introducing a particular substituent at the *o*-position of an azo group caused a separation of the dyes into azo and hydrazone tautomers according to the group additivity analysis of the AHT. These procedures predicted that AHT in both the gas and water phases occurs as follows: Arylazobenzene dyes with *o*-amino, *o*-acetylamino or *o*-ureido groups existed as the azo tautomers (ATs) in both the gas phase and water with some exceptions in the gas phase, while those with *o*-hydroxy groups existed as ATs in the gas phase and as hydrazone tautomers (HTs) in water. Due to the keto-enol tautomerism of a pyrazoline ring, three kinds of azo and hydrazone (azo/enol, azo/keto (A/K) and hydrazone/keto) tautomers existed in phenylazopyrazolinyl dyes. Phenylazopyrazolinyl dyes with *o*-amino groups existed as ATs in both phases, while those with *o*-hydroxy groups occurred as HTs in the gas phase and as A/KTs in water. Results of the AHT analysis showed that the reason hydroxyazo dyes had higher stability in water was the larger hydration energy of the keto structure than that of the enol one. The AHT and acid–base equilibrium (ABE) of C.I. Acid Yellow 23 were analysed using the same MO methods. The dye existed as A/KTs in water. The A/KTs carried out the ABE, and the deprotonated A/KTs showed another tautomerism. The concurrent picture of AHT and ABE for the dye was consistent with the results reported previously.

Keywords: Reactive dye; Azobenzene dye; Pyrazolinylazo dye; Azo-hydrazone tautomerism; Solvation effect; Molecular orbital method; Group additivity

1. Introduction

In previous papers [1,2], the present authors noted that many studies [3–13] of the azo-hydrazone tautomerism (AHT) of hydroxyazo dyes contained ambiguities in the assignment of the

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tautomers. Application of the semiempirical molecular orbital (MO) PM5 method to hydroxyazo dyes suggested that their AHTs could be analysed by calculating the enthalpies of formation ($\Delta_f H^0$) in both the gas phase and water [1,2], as in the case of nucleic acid bases [14–16].

In order to settle this azo and/or hydrazone assignment problem, the strict assignment of azo and hydrazone tautomers (A&HTs) must be made by a precise characterization, such as electronic absorption spectra. Unfortunately, however, many papers on AHT have been published without detailed assignments. There is no method of assignment that is highly reliable, because although the most reliable MO calculation is made in the gas phase, no measurement of absorption spectrum can be obtained for sulfonated azo dyes in a vacuum.

The Pariser–Parr–Pople method based on π-electron approximation, which has often been utilized to analyse the absorption spectra of azo dyes, assumes that sulfonic acid groups have no effect on the electronic spectrum. A sulfonic acid group at the *o*-position of an azo group, however, seems to have a large steric effect on the solvation due to its bulkiness, although the theoretical explanations may be insufficient. The other bulky groups such as methoxy and carboxyl groups seem to have similar effects [1].

In the present paper, the $\Delta_f H^0$ of A&HTs for these dyes were calculated by the semiempirical MO method (PM5 in the gas phase and PM5/COSMO in water) to analyse the AHT. The AHT and acid-base equilibrium (ABE) of C.I. Acid Yellow 23 were analysed using the same procedure as above. In the case of phenylazopyrazolinyl dyes, keto-enol tautomerism of the pyrazoline ring plays an important role in the AHT, where keto tautomers exist in both the A&HTs. As mentioned in the present paper, the predominance of amino groups over hydroxyl ones to promote the ATs should be attributed to the larger solvation energy of the keto tautomers (azo/keto (A/K) and hydrazone/keto (H/K) tautomers) of the pyrazoline ring than that of enol ones in water. Ferodov [5] drew tautomerisms including the A&HTs of the keto and enol forms of pyrazoline ring for both the undeprotonated and deprotonated isomers. Positive experimental indications of the azo structure in aminoazo dyes have already been reported by both ^{1}H [17,18] and ^{13}C NMR spectroscopy data [10,19–21]. In the present paper, in calculating the $\Delta_f H^0$ for these isomers in both the gas and water phases, the tautomerism is quantum-mechanically treated.

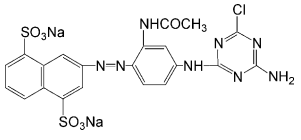
By a preliminary calculation, it was confirmed that some representative yellow azo dyes may exist as ATs in water. The AHT seemed to depend upon *o*-substituents. In order to examine which substituents have such a effect on the AHT of phenylazopyrazolinyl dyes and arylazobenzenes, the bulky substituents such as *o*-sulfonic acid and *o*-methoxy in the azo dyes, as well as the *o*-substituents such as hydroxy, amino, acetylamino and ureido, which separate the dyes into the azo and hydrazone tautomers (A&HTs), were examined using PM5 and PM5/COSMO methods. The reason such an *o*-substituents results in azo tautomers (ATs) or hydrazone tautomers (HTs) in the gas phase and water is analysed in terms of group additivity.

2. Experimental

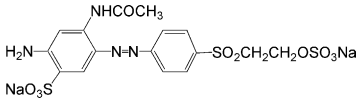
2.1. Dyes used

Five arylazobenzene and three pyrazolinylazo dyes among the yellow azo dyes were examined. To them, an azo dye that can exist only as an AT was added. In order to analyse the dye, two disazo dyes with the same property were also added. An acid pyrazolinylazo dye was used as a model dye. The chemical structures of these eleven dyes are shown below. Colour Index Generic Name, C.I. Constitution Number, if available, the abbreviations (in parenthesis), and the λ_{max} on dyed cellulosic film (except for one acid dye) are given:

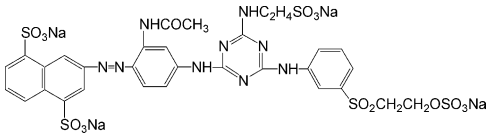
(1) C.I. Reactive Yellow 3, C.I. 13245 (Yellow 3), $\lambda_{max} = 416.0$ nm



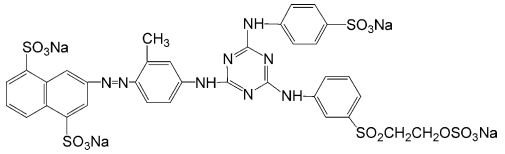
(2) An acetoamidoazo VS dye (AcetylVS1), $\lambda_{max} = 423.5$ nm



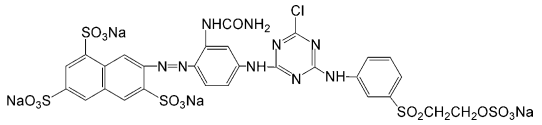
(3) An acetylamidoazo triazinyl VS dye (Acetyl-VS2), $\lambda_{max} = 429.0$ nm



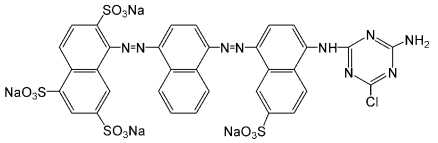
(4) A methylazo triazinyl VS dye (MethylVS), $\lambda_{max} = 405.0$ nm



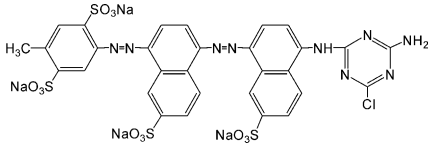
(5) A yellow azo dye with *m*-VS and MCT anchors (UreidoBF), $\lambda_{max} = 432.0$ nm



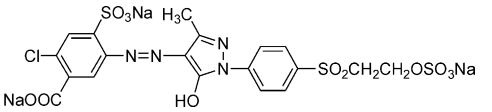
(6) A disazo monochrolotriazinyl dye (MCT-Brown 1), $\lambda_{max} = 488.0$ nm



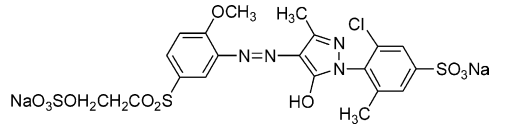
(7) A disazo monochrolotriazinyl brown dye (MCT-Brown 2), $\lambda_{max} = 485.0$ nm



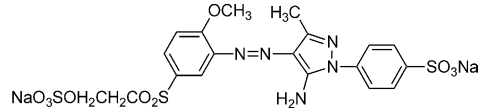
(8) C.I. Reactive Yellow 13, C.I. 18990 (Yellow 13), $\lambda_{max} = 401.0$ nm



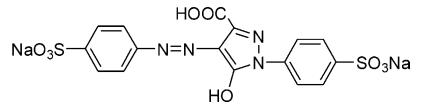
(9) C.I. Reactive Yellow 14, C.I. 19036 (Yellow 14), $\lambda_{max} = 423.5$ nm



(10) An aminopyrazolinylazo dye (Pyr-Yellow), $\lambda_{max} = 397.0$ nm



(11) C.I. Acid Yellow 23, C.I. 19140 (Acid Yellow 23)



2.2. Preparation of dyed samples: dyeing of cellophane sheets

Cellophane films (Futamura Kagaku Kogyo K.K. #300) were scoured in boiling water for more than 2 h and dyed with each reactive dye by the alkali-shock method to obtain the absorbance between 0.8 and 1.0 at the λ_{max} [22,23].

2.3. Semiempirical molecular orbital calculation of dye properties

2.3.1. Enthalpies of formation

MOPAC 2002 (PM5 and COSMO methods), Version 5.02 (Windows edition) was used throughout to obtain the enthalpies of formation, $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) (kcal mol^{-1}), in the gas phase and water at 25 °C after structure optimization.

Unless otherwise stated, the reactive groups of reactive dyes examined were treated as being completely hydrolyzed and the sulfo groups as undissociated forms of sulfonic acid. (The validity

of this assumption was not further argued because no one has found a procedure to examine it.)

3. Results and discussion

3.1. AHT of yellow azo dyes

Reactive dyes with yellow hue have unique chemical structures: phenylazopyrazolinyl dyes and arylazobenzenes with particular *o*-substituents. Since most yellow azo dyes examined exist as ATs, as mentioned below, three dyes that could exist only as ATs, were also added for comparison.

By exchanging the particular *o*-substituents with amino and hydroxy groups, how and why the substituents determine the AHT of the dyes, including the corresponding hypothetical dyes without *o*-substituents, which must perform without AHT, were analysed in terms of group additivity [24–28].

In the treatment of AHT, it has been considered that a linear relationship exists between the logarithm of the tautomeric equilibrium constants, K_T, and enthalpy change [1,2]:

$$\log K_T = -\Delta G_T/2.303RT \cong -\Delta H_T^0/2.303RT = -\Delta H_T^0/1.364 \quad (1)$$

where ΔG_T and ΔH_T^0 (kcal mol^{-1}), respectively, denote the differences in the Gibbs free energy of formation and the $\Delta_f H^0$ (at 25 °C) between two tautomers.

Before advancing the analysis of AHT, the entropy of solvation is discussed [29–34]. Wong et al. [35] showed that the entropy term is quite small. (In other solvation models, solvation effects have been analysed in terms of the free energy of solvation only without separating the entropy term [36–42].) In the case of azo dyes with sulfo groups the absolute values of the enthalpy of solvation, ΔH_{sol}, may become very large. Since there must be a linear free energy relationship between the enthalpy and entropy terms of Gibbs free energy, the entropy of solvation may also decrease considerably [29–34]. This relationship claims that the values of Gibbs energy become a little smaller due to the compensation by the entropy term, resulting in a small approach of the population of A&HTs without reversal, even if the entropy effects were taken into consideration. When the differences in $\Delta_f H^0$(aq) between tautomers increased, those of ΔH_{sol} or the standard entropy (absolute value) of solvation between tautomers may become large. Even if the enthalpy-entropy compensation increased, the compensation effect on the population may be relatively small, since the differences in the population are considerably large. Although the enthalpies of formation for azo dyes with sulfo groups, therefore, may become quite large in water in absolute values, the differences between tautomers in their values may be small compared with the absolute values, indicating the applicability of Eq. (1) to dyes in water.

3.1.1. Substituent effect on the AHT of yellow arylazobenzene dyes

In order to examine the AHT of yellow azo dyes, the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) were calculated for all the dyes using the PM5 and COSMO methods. In the model azo dyes, *o*-substituted bulky substituents had a large effect on the solvation energy resulting in the ATs [1,2]. The substituent effects of the particular substituents such as acetylamino, ureido, amino, and sulfo groups on the values of $\Delta_f H^0$(gas), $\Delta_f H^0$(aq), and ΔH_{sol} for each tautomer of the dyes with such substituents were calculated in addition to the seven reactive dyes examined. Tables 1 and 2 list the results classified into ten groups. Using the relationship of Eq. (1), Table 3 summarizes the analyses of AHT for ten reactive dyes examined.

Four groups of arylazobenzene dyes showed similar tendencies in AHT to each other (Table 1). Three *o*-substituents, amino, acetylamino and ureido groups, promoted the stability of ATs. Four dyes examined and their hypothetical dyes, which possessed one of the three *o*-substituents, exist as ATs in both the media, except for Acetyl VS2 in the gas phase and some hypothetical dyes of Acetyl VS1. In the case of Acetyl VS1, the situations became complex due to the second and third substituents introduced.

Table 1
Additive effect of substituents on the enthalpy of formation, $\Delta_f H^0$(kcal mol^{-1}) and energy of solvation, ΔH_{sol} (kcal mol^{-1}), of azo-hydrazone tautomers for yellow reactive azo dyes, estimated by semiempirical MO PM5/COSMO methods

Substituent	Molecular weight	Azo tautomer			Hydrazone tautomer		
		$\Delta_f H^0$		$-\Delta H_{sol}$	$\Delta_f H^0$		$-\Delta H_{sol}$
		Gas phase	Water		Gas phase	Water	
N-(4′-amino-6′-hydroxytriazin-2′-yl)-4-(1′,5′-disulfonaphthalen-3′-yl)-azoaniline							
No *o*-substituent	517.490	−127.526	−229.716	102.190	–	–	–
3-methyl-	531.517	−133.872	−234.795	100.923	–	–	–
3-amino-	532.505	−129.530	−236.498	106.968	−129.530	−218.238	88.708
3-acetylamino- (Yellow 3)	574.542	−175.597	−292.819	117.222	−172.669	−283.055	110.386
3-ureido-	575.530	−171.181	−299.666	128.485	−162.155	−288.665	126.510
N-(4-(β-sulfoethylamino)-6-(m-VS-anilino)-triazin-2-yl)-4-(1,5-disulfonaphthalen-3′-yl)-azoaniline							
No *o*-substituent	808.827	−294.501	−449.573	155.072	–	–	–
3-methyl-	822.853	−302.062	−455.339	153.277	–	–	–
3-amino-	823.841	−296.481	−454.088	157.607	−288.178	−449.480	161.302
3-acetylamino- (Acetyl VS2)	865.878	−339.887	−517.155	177.268	−344.849	−511.145	166.296
3-ureido-	866.866	−340.119	−514.507	174.388	−337.657	−512.116	174.459
p-VS-phenylazo-(substituted benzene) (VSP)[a]							
2-methyl-	304.363	−32.749	−78.660	45.911	–	–	–
2-methyl-5-sulfo-	384.421	−156.570	−235.074	78.504	–	–	–
2-methyl-5-sulfo-4-amino-	399.436	−161.745	−243.744	81.999	–	–	–
2-acetylamino-	347.388	−73.511	−133.374	59.863	−72.812	−132.188	59.376
2-amino-5-sulfo-	385.409	−154.885	−234.683	79.798	−154.928	−233.931	79.003
2-acetylamino-5-sulfo-	427.466	−194.419	−275.977	81.558	−194.458	−281.024	86.566
2-ureido-5-sulfo-	428.434	−193.429	−293.161	99.732	−193.413	−288.433	95.020
2-acetylamino-4-amino-5-sulfo-[b]	442.461	−200.227	−290.768	90.541	−200.613	−290.093	89.480
2-ureido-4-amino-5-sulfo-	443.449	−197.961	−299.560	101.599	−198.208	−294.904	96.696
N-(4-hydroxy-6-(m-VS-anilino)-triazin-2-yl)-4-(3,6,8-trisulfonaphthalen-2-ylazo)-(substituted)-aniline							
No *o*-substituent	781.758	−338.799	−491.429	152.630	–	–	–
3-methyl-	795.785	−346.276	−504.751	158.475	–	–	–
3-amino-	796.772	−343.316	−506.531	163.215	−343.611	−486.196	142.585
3-acetylamino-	838.810	−386.616	−560.696	174.080	−386.233	−545.934	159.701
3-ureido- (Ureido BF)	839.797	−386.030	−569.749	183.719	−386.060	−555.689	169.629

[a] VSP = *p*-VS-phenylazobenzene, VS = β-hydroxyethylsulfonyl.
[b] Acetyl VS1.

3.1.2. Substituent effect on the AHT of phenylazopyrazolinyl dyes

A pyrazoline ring undergoes a keto-enol tautomerism. The pyrazoline ring in the HTs exists as a keto-form. Whether the keto-form of a pyrazoline ring contributes to the stability of azo tautomers or not needs to be examined, as Fedorov [5], Mustroph [6] and Ball and Nicholls [7] noted in their reviews. Three tautomers: azo, azo/keto (A/K), and hydrazone/keto (H/K), were analysed calculating the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq). The results are listed in Table 2, and the AHT is summarized in Table 3. As can be seen, Pyr-Yellow existed as ATs in both media, while Yellow 13 and Yellow 14 occurred as H/KTs in the gas phase and as A/KTs in water.

The derivatives of C.I. Yellow 14 from which the β-hydroxyethylsulfonyl or *o*-methoxy group was removed existed as H/KTs in both the gas phase and water, implying that substituents other than *o*-substituents had little effect on the AHT.

Table 2
Additive effect of substituents on the enthalpy of formation, $\Delta_f H^0$ (kcal mol^{-1}) and energy of solvation, ΔH_{sol} (kcal mol^{-1}), of AHT for pyrazolinyl azo dyes, estimated by semiempirical MO method (MOPAC 2002, PM5 and COSMO methods)

Substituent	Molecular weight	Azo tautomer			Azo/keto tautomer			Hydrazone tautomer		
		$\Delta_f H^0$		$-\Delta H_{sol}$	$\Delta_f H^0$		$-\Delta H_{sol}$	$\Delta_f H^0$		$-\Delta H_{sol}$
		Gas phase	Water		Gas phase	Water		Gas phase	Water	
*1-N-(*p-*β-hydroxyethylsulfonyl)-phenyl-4-(2′-sulfo-4′-chloro-5′-carboxyphenylazo)-pyrazoline (Yellow 13)*										
No *o*-substituent	514.911	−177.992	−268.964	90.972	–	–	–	–	–	–
3-methyl- (without hydroxy group)	528.938	−186.445	−279.917		–	–	–	–	–	–
5-hydroxy-	530.911	−224.099	−311.479	87.380	−226.437	−333.454	107.017	−229.429	−326.433	97.004
5-amino-	529.926	−186.850	−275.772	88.922	−168.208	−275.061	106.853	−174.568	−271.607	97.039
3-methyl-5-amino-	543.953	−195.636	−294.669	99.033	−179.122	−280.244	101.122	−183.657	−278.689	95.032
3-methyl-5-oxy-[a]	544.938	−233.137	−324.010	90.873	−237.183	−339.623	102.440	−240.724	−336.320	95.596
*1-N-(*p-*β-hydroxyethylsulfonyl)-phenyl-3-methyl-4-(substituted phenylazo)-5-hydroxypyrazoline (Yellow 13)*										
No substituent	386.425	−20.628	−73.483	52.855	−25.950	−87.881	61.931	−29.759	−89.669	59.910
3-methyl-	400.451	−27.715	−82.287							
2′-sulfo-	466.483	−144.656	−225.371	80.715	−146.642	−241.746	95.104	−148.429	−231.008	82.579
5′-carboxy-	430.434	−110.437	−177.778	67.341	−115.226	−194.150	78.924	−118.566	−189.937	71.371
4′-chloro-	420.870	−28.174	−74.169	45.995	−33.600	−93.377	59.777	−36.969	−96.058	59.089
2′-sulfo-4′-chloro-	500.928	−148.429	−229.976	81.547	−152.414	−240.343	87.929	−151.950	−234.251	82.301
4′-chloro-5′-carboxy-	464.880	−115.179	−184.073	68.894	−120.080	−197.124	77.044	−122.945	−193.294	70.349
*1-N-*p-*sulfophenyl-3-methyl-4-(substituted phenylazo)-5-aminopyrazoline (Pyr-Yellow)*										
No substituent	342.372	24.803	−26.997	51.800	–	–		–	–	
2′-methoxy	387.412	−14.663	−75.707	61.044	−2.853	−51.528	48.675	−12.656	−69.432	56.776
5′-(β-hydroxyethyl-sulfonyl)-	465.498	−100.106	−184.521	84.415	−90.484	−166.593	76.109	−98.898	−182.758	83.860
*1-N-*p-*sulfophenyl-4-(2′-methoxy-5′-(β-hydroxyethylsulfonyl)-phenylazo)-pyrazoline (Pyr-Yellow)*										
No substituent (without 3-methyl)	466.483	−126.584	−215.647	89.063	–	–		–	–	
3-methyl-	480.510	−132.359	−223.858	91.499	–	–		–	–	
5-hydroxy-	482.482	−172.745	−256.962	84.217	−172.953	−267.334	94.381	−181.132	−270.172	89.040
5-amino-	481.497	−131.206	−230.174	98.968	−114.806	−211.459	96.653	−127.809	−207.138	79.329
3-methyl-5-amino-[b]	495.524	−139.202	−234.224	95.022	−127.422	−219.708	92.286	−136.662	−213.816	77.154
3-methyl-5-hydroxy-	496.509	−181.276	−271.156	89.880	−183.751	−278.338	94.587	−190.359	−278.048	87.689
1-N-(2-methyl-4-sulfo-6-chlorophenyl)-3-methyl-4-(substituted phenylazo)-5-hydroxypyrazoline (Yellow 14)										
No substituent (+3-methyl)	406.843	−30.764	−79.307	48.543	−33.120	−94.561	61.441	−39.921	−95.453	55.532
2′-methyl-	420.870	−37.405	−85.970		−41.158	−97.756		−46.655	−98.756	
2′-methoxy-	436.869	−66.685	−119.860	53.175	−68.417	−134.984	66.567	−76.250	−132.760	56.510
5′-(β-hydroxyethyl-sulfonyl)-	514.955	−153.919	−235.619	81.700	−156.751	−246.777	90.026	−161.468	−249.203	87.735
2′-methoxy-5′-(β-hydroxyethyl-sulfonyl)-[c]	544.981	−191.002	−277.195	86.193	−193.535	−291.430	97.895	−199.927	−288.310	88.383

[a] Yellow 13.
[b] Pyr-Yellow.
[c] Yellow 14.

Table 3
Analyses of AHT for yellow azo dyes (SO_3H form) by PM5 and COSMO methods

Dye	Characteristics of chemical structure	AHT in both media	λ_{max} (nm) on reactively-dyed cellulosic film	λ_{max} (nm) in water	Notes
2-sulfo-4-{p-(β-hydroxyethylsulfonyl)phenylazo}-5-substituted aniline					
Acetyl VS1	5-acetylamino, VS	ATs dominant in both media.	423.5 (AT)	410.5 (AT)	HT → AT[a]
1-(N-substituted triazinyl)-3-substituted-4-(substituted naphthylazo)-aniline					
Yellow 3	3-acetylamino, MCT	ATs dominant in both media.	416.0 (AT)	391.0 (AT)	HT → AT[a]
Acetyl VS2	3-acetylamino, VS	HTs dominant in gas phase, ATs in H_2O.	429.0 (HT)	402.0 (AT)	
Ureido BF	3-ureido, VS + MCT	ATs dominant in both media.	432.0 (AT)	417.5 (AT)	HT → AT[a]
1-(N-substituted phenyl)-3-methyl-4-(2′-substituted phenylazo)-5-hydroxy (or-5-amino)-pyrazoline					
Yellow 13	5-hydroxy, 2′-sulfo, VS	HTs dominant in gas phase, A/KTs in H_2O.	401.0 (HT)	391.5 (A/KT)	
Pyr-Yellow	5-amino, 2′-MeO, VS	ATs dominant in both media.	397.0 (AT)	391.0 (AT)	
Yellow 14	5-hydroxy, 2′-MeO, VS	HTs dominant in gas phase, A/KTs in H_2O.	423.5 (HT)	421.5 (A/KT)	
1-(N-substituted triazinyl)-3-substituted-4-(substituted naphthylazo)-aniline					
Methyl VS	3-methyl, VS	ATs (No HT exists.)	405.0 (AT)	390.0 (AT)	
Disazo dyes with monochlorotriazinyl group					
MCT-Brown 1	disazo, MCT	ATs (No HT exists.)	488.0 (AT)	467.0 (AT)	
MCT-Brown 2	disazo, MCT	ATs (No HT exists.)	485.0 (AT)	455.0 (AT)	

[a] HTs constructed initially converged into ATs. (After the structure optimization, HTs had practically the same structure as ATs.)

3.2. Values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for substituent radicals

Group additivity is the most widely used method for estimating the values of $\Delta_f H^0$(GA) for molecules either in an ideal gas state or in water [24–28]. To provide the group values for group analysis, a reliable set of key experimental values must be available. Before estimating the $\Delta_f H^0$(GA) values, one must determine the more accurate values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for particular substituent radicals and for the arylazobenzene and phenylazopyrazoline radicals. Table 4 lists values of the radicals estimated by using the difference method [24,26] from typical phenyl derivatives with related substituents.

The fourth column of Table 4 also lists the observed values of $\Delta_f H^0$(gas) for benzene derivatives cited from the literature [43]. They can be compared with the values calculated by the PM5 method. Within seventeen compounds that have both the observed and calculated data, the simple mean error of the PM5 calculation was estimated to be 1.81, four times as accurate as that of the PM3 one [44,45]. There were a few exceptional compounds with by far larger errors of ca. 5. (Excluding these compounds, the mean error became 1.35.) Taking these errors into consideration, the AHT of azo dyes is discussed afterward. Although few studies on the thermochemistry of azo dyes have been reported [46], the value of $\Delta_f H^0$(gas) for (*E*)-azobenzene (96.13 kcal mol^{-1}) was found [47]. Compared with the values determined by the PM5 method (cf. Table 6), the calculation error is only 0.70 kcal mol^{-1}.

The reference values of typical radicals such as methyl and phenyl are required to calculate the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for the compounds to be examined. They were estimated from the corresponding dimer: $\Delta_f H^0$(gas,CH_3) from ethane and $\Delta_f H^0$(gas,C_6H_5) from biphenyl. On calculating the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for the other radicals, the values obtained from the observed ones were used. If the value of $\Delta_f H^0$(gas,C_6H_5) was used, that of $\Delta_f H^0$(gas,CH_3) could be also estimated from the value of toluene, and vice versa, resulting in good agreement between them (cf. note below Table 4).

In order to confirm the validity of the values of $\Delta_f H^0$(gas) for typical benzene compounds, their values calculated using the PM5 method were compared with the values of the corresponding substituent for different compounds and also with the observed values from reference [43]. Although

Table 4
Enthalpy of formation, $\Delta_f H^0$ (kcal mol^{-1}), of substituent radicals on benzene ring

Compound	Molecular weight	$\Delta_f H^0$(kcal mol^{-1}) In the gas phase: Calculated by PM5 method	Observed	In water: Calculated by PM5/COSMO method	Radical	$\Delta_f H^0$(comp)−$\Delta_f H^0$(C_6H_5) In the gas phase	In water
C_6H_5-SO_3H	158.172	−100.242		−138.428	SO_3H	−121.9	−155.8
C_6H_5-VS	186.225	−99.675		−140.919	VS	−121.4	−158.3
C_6H_5-SES	266.283	−221.229		−288.182	SES	−242.9	−305.6
C_6H_5-NH_2	93.284	22.284	23.71	11.301	NH_2	0.1 [2.0]	−6.1
C_6H_5-$NHCOCH_3$	135.165	−24.777		−49.433	$NHCOCH_3$	−46.5	−66.8
C_6H_5-$NHCONH_2$	136.153	−24.198		−54.007	$NHCONH_2$	−45.9	−71.4
C_6H_5-CH_3	92.140	14.058	12.07	8.277	CH_3	−8.1 [−9.6]	−9.1
C_6H_5-OH	94.113	−22.062	−23.04	−34.450	OH	−44.2 [−44.7]	−51.9
C_6H_5-OCH_3	108.140	−14.531	−16.23	−25.692	OCH_3	−36.6 [−37.9]	−43.1
C_6H_5-Cl	112.559	13.943	12.43	7.787	Cl	−8.2 [−9.3]	−9.6
C_6H_5-COOH	122.123	−68.722	−70.27	−87.741	COOH	−90.8 [−92.0]	−105.1
Benzene with two substituents						$\Delta_f H^0$(comp)−$\Delta_f H^0$(C_6H_4-R)	
o-Cl-C_6H_4-COOH	156.568	−72.175	−77.68	−93.944	*o*-Cl	−10.3	−9.7
					o-COOH	−93.0	−105.2
m-Cl-C_6H_4-SO_3H	192.617	−106.520		−144.569	*m*-Cl	−8.8	−9.5
					m-SO_3H	−121.4	−155.7
m-NH_2-C_6H_4-CH_3	107.155	14.521	13.05	2.955	*m*-NH_2	2.9 [1.4]	−10.1
p-NH_2-C_6H_4-CH_3	107.155	14.231	13.22	3.687	*p*-NH_2	2.6 [1.6]	−10.8
m-NH_2-C_6H_4-COOH	137.138	−68.047	−67.78	−97.979	*m*-NH_2	−2.3 [−2.5]	−10.3
p-NH_2-C_6H_4-COOH	137.138	−71.409	−70.91	−98.507	*p*-NH_2	−1.1 [−0.6]	−10.8
m-NH_2-C_6H_4-SO_3H	173.186	−102.186		−142.070	*m*-NH_2	−4.6	−7.0
p-NH_2-C_6H_4-SO_3H	173.186	−106.338		−152.805	*p*-NH_2	−8.8	−17.7
Model compounds							
Ethane	30.069	−15.222	−20.08	−15.651	CH_3[a]	−7.6 (−10.0$_4$)	−7.8 [−10.3]
Biphenyl	154.211	44.203	43.36	34.789	C_6H_5[a]	22.1 (21.6$_8$)	17.4 [17.4]
p-Xylene	106.167	5.979	4.30	0.137	*p*-C_6H_4	22.0 [24.4]	18.3 [20.7]
m-Xylene	106.167	5.997	4.13	0.106	*m*-C_6H_4	20.1 [24.2]	18.3 [20.7]
o-Xylene	106.167	6.303	4.56	0.344	*o*-C_6H_4	20.6 [24.6]	18.5 [20.9]
Mesitylene	120.194	−2.011	−3.80	−8.121	*Sym*-C_6H_3	20.0 [25.0]	19.2 [20.4]

( ) and [ ] denote the values calculated with only the observed values and with both the observed and calculated values, respectively.
[a] From toluene, $\Delta_f H^0$(gas,C_6H_5) = [22.1], $\Delta_f H^0$(gas,CH_3) = [−9.6].

the number of examples was small, the agreement between the calculated and observed values was confirmed to be quite good with an exception of an amino radical, as shown in Table 4. However, although the absolute errors for the value of $\Delta_f H^0$(gas,NH_2) determined from aniline derivatives were not especially large if sulfanilic acid was excluded, their relative errors were very large, and moreover the gas phase values depended on the amino compounds from which the value of $\Delta_f H^0$(gas,NH_2) was estimated (cf. Section 3.3.1).

In order to examine these circumstances, the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for hydroxy, amino and methyl derivatives of 1-*N*-phenylpyrazolines were estimated using the *difference method* [24,26]. Table 5 demonstrates that the keto–enol tautomerism has little effect on the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for 3-methyl radicals in 1*N*-phenylpyrazolines: although some calculation errors were recognized, there was no definite tendency. This fact may imply that one can utilize a methyl radical as a probe to examine the *o*-substituent effects on the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq), a procedure used in the present study.

The values of $\Delta_f H^0$(OH) in the gas phase and water had a profound effect on the tautomerism.

Table 5
Contribution of 5-hydroxy, 5-amino and 3-methyl radicals on the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) (kcal mol^{-1}) for the keto and enol tautomers for phenylpyrazolines in the gas phase and water calculated by PM5 and PM5/COSMO methods

Compound	M.W.	Enol form				Keto form			
		$\Delta_f H^0$		$\Delta_f H^0$(substituent radical)		$\Delta_f H^0$		$\Delta_f H^0$(substituent radical)	
		Gas phase	Water	Gas phase	Water	Gas phase	Water	Gas phase	Water
1-N-(p-(β-hydroxyethylsulfonyl)-pyrazoline (P)									
P	252.287	−38.613	−88.351	$\Delta_f H^0$(comp)-$\Delta_f H^0$(P)		−38.613	−88.351	$\Delta_f H^0$(comp)-$\Delta_f H^0$(P)	
5-OH-P	268.287	−83.495	−138.946	−42.2	−49.9	−89.852	−150.639	−51.2	−62.1
5-amino-P	267.302	−40.569	−96.807	−2.0	−8.5	−29.698	−86.589	8.9	1.8
3-Me-P	266.314	−46.940	−96.573	−8.3	−8.2	−46.940	−96.316	−8.3	−8.0
				$\Delta_f H^0$(comp)-$\Delta_f H^0$(3-Me-P)				$\Delta_f H^0$(comp)-$\Delta_f H^0$(3-Me-P)	
3-Me-5-OH-P	282.314	−91.965	−144.803	−42.5	−45.6	−99.703	−156.741	−52.8	−63.0
3-Me-5-amino-P	281.329	−50.903	−106.865	−4.0	−10.3	−42.005	−98.688	4.9	−2.4
1-N-(p-sulfophenyl)-pyrazoline (R)									
R	224.234	−39.321	−87.028	$\Delta_f H^0$(comp)-$\Delta_f H^0$(R)		−39.321	−87.028	$\Delta_f H^0$(comp)-$\Delta_f H^0$(R)	
5-OH-R	240.233	−81.396	−131.466	−42.1	−44.4	−87.590	−137.179	−48.3	−50.2
5-amino-R	239.248	−40.019	−94.830	−0.7	−7.8	−30.738	−82.929	8.6	4.1
3-Me-R	238.261	−47.528	−92.974	−8.2	−5.9	−47.528	−92.974	−8.2	−5.9
				$\Delta_f H^0$(comp)-$\Delta_f H^0$(3-Me-R)				$\Delta_f H^0$(comp)-$\Delta_f H^0$(3-Me-R)	
3-Me-5-OH-R	254.260	−90.006	−140.245	−42.5	−47.3	−97.824	−151.763	−50.3	−58.8
3-Me-5-amino-R	253.275	−48.647	−100.377	−1.1	−7.4	−40.250	−88.294	−7.3	4.7
1-N-phenyl-pyrazoline (S)									
S	144.176	83.400	67.121	$\Delta_f H^0$(comp)-$\Delta_f H^0$(S)		83.400	68.465	$\Delta_f H^0$(comp)-$\Delta_f H^0$(S)	
5-OH-S	160.175	40.364	19.214	−43.0	−47.9	34.540	7.154	−48.9	−61.3
5-NH_2-S	159.190	80.440	57.585	−3.0	−9.5	92.497	68.387	9.1	−0.1
1-N-phenyl-3-methyl-pyrazoline (MP)									
MP	158.202	74.829	59.573	$\Delta_f H^0$(comp)-$\Delta_f H^0$(MP)		74.829	59.573	$\Delta_f H^0$(comp)-$\Delta_f H^0$(MP)	
3-Me-5-OH-MP	174.202	34.022	10.736	−40.8	−48.8	24.921	−2.931	−49.9	−62.5
3-Me-5-NH_2-MP	173.217	72.832	49.230	−2.0	−10.3	83.190	59.701	8.4	0.1

The values of $\Delta_f H^0$(OH) for the keto tautomers in the gas phase and water were always considerably lower (larger minus) than those for the enol ones, although their values in water were certainly lower than those in the gas phase. This fact may indicate that the keto tautomers, or the K/HTs, and in some cases the A/KTs of azo dyes, have higher stability than the ATs or enol tautomers. The higher stability of keto tautomers in water may be attributed to the property of hydroxy groups.

Besides the fact that $\Delta_f H^0$(aq,NH_2) is smaller than $\Delta_f H^0$(gas,NH_2), on the other hand, the values of $\Delta_f H^0$(NH_2) in Table 5, estimated from *N*-phenylpyrazoline derivatives, depended on the compounds as in the case of phenyl derivatives in Table 4. As mentioned above, since the absolute values of $\Delta_f H^0$(gas,NH_2) and $\Delta_f H^0$(aq,NH_2) were small, the relative errors of the estimations were also very large. Since the values of $\Delta_f H^0$(gas,NH_2) obtained from the observed values, listed in Table 4, also varied with the compounds, all the scatter of the values may not be responsible for the calculation errors in the MO methods. The reason the values of $\Delta_f H^0$(gas,NH_2) and $\Delta_f H^0$(aq,NH_2) depend on the compounds remains open to debate. These facts, however, made the AHT analysis of azo dyes with amino groups using group additivity difficult. The values of $\Delta_f H^0$(gas,NH_2) and $\Delta_f H^0$(aq,NH_2) should be used carefully in the AHT analysis (see below and Section 3.3.1).

3.3. Analysis of $\Delta_f H^0$ for azo dyes in terms of group additivity

The values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for 2-hydroxy-, 2-amino-, 2-acetylamino- and 2-ureido-

Table 6
Additive effect of substituents on the enthalpy of formation, $\Delta_f H^0$(kcal mol^{-1}) and energy of solvation, ΔH_{sol} (kcal mol^{-1}), of azo-hydrazone tautomers for azobenzene dyes, estimated by semiempirical MO PM5/COSMO methods

Substituent	M. W.	Azo tautomer			Hydrazone tautomer		
		$\Delta_f H^0$		$-\Delta H_{sol}$	$\Delta_f H^0$		$-\Delta H_{sol}$
		Gas phase	Water		Gas phase	Water	
Prototypes							
No *o*-substituent	182.224	95.432	83.435	11.997	–	–	–
2-sulfo-	262.283	−23.663	−65.943	42.280	–	–	–
4-sulfo-	262.283	−25.581	−68.353	42.772	–	–	–
2-Hydroxy-azobenzenes							
2-hydroxy-	198.224	50.442	35.786	14.656	55.781	32.238	23.543
2-hydroxy-2′-sulfo-	278.282	−66.137	−109.096	42.959	−62.537	−110.269	47.732
2-hydroxy-4′-sulfo-	278.282	−70.625	−115.801	45.176	−66.840	−119.399	52.559
2-hydroxy-4-sulfo-	278.282	−67.986	−113.706	45.720	−60.657	−115.882	55.225
2-Aminoazobenzenes							
2-amino-	197.239	94.449	78.306	16.143	110.426	89.332	21.094
2-amino-2′-sulfo-	277.297	−24.487	−73.649	49.162	−13.368	−54.991	41.623
2-amino-4′-sulfo-	277.297	−28.782	−76.632	47.850	−12.856	−64.278	51.422
2-amino-4-sulfo-	277.297	−25.893	−70.884	44.991	−10.737	−56.224	45.487
2-Acetylaminoazobenzene							
2-acetylamino-	239.276	49.167	15.063	34.104	49.167	26.196	22.971
2-acetylamino-2′-sulfo	319.334	−67.542	−124.486	56.944	−54.888	−107.683	52.795
2-acetylamino-4′-sulfo	319.334	−71.923	−130.464	58.541	−58.642	−116.022	57.380
2-acetylamino-4-sulfo	319.334	−71.549	−131.580	60.031	−70.331	−113.268	42.937
2-Ureidoazobenzene							
3-ureido-	240.264	50.593	14.278	36.315	62.165	25.965	36.200
2-ureido-2′-sulfo	320.322	−68.929	−129.228	60.299	−58.364	−115.312	56.948
2-ureido-4′-sulfo	320.322	−70.722	−133.969	63.247	−62.515	−123.703	61.188
2-ureido-4-sulfo	320.322	−70.473	−137.727	67.254	−56.113	−122.502	66.389
o-Methyl prototypes					$\Delta_f H^0$(comp)−$\Delta_f H^0$(CH_3) = $\Delta_f H^0$(radical)		
o-methyl-azobenzene (A)	196.251	89.257	75.707	–	99.30	86.01	–
2-sulfo-A	276.309	−30.477	−71.152	–	−20.44	−60.85	–
4-sulfo-A	276.309	−32.479	−75.918	–	−22.44	−65.62	–

azobenzenes with 2′-, 4′-, and 4-sulfo groups, estimated by the same methods, are listed in Table 6. The effects of *o*-substituents on the AHT for these model compounds were very distinctive. Amino, acetylamino and ureido groups resulted in the ATs in both the gas phase and water irrespective of whether they contained sulfo groups or not, while hydroxy ones resulted in ATs in the gas phase and HTs in water.

The reason the *o*-substituents have such distinctive effects on the AHT is discussed in terms of group additivity, whose results are listed in Table 7 with notes on the results. The calculations for the radicals attached to the benzene ring of arylazobenzene and phenylazopyrazoline dyes were made as follows: (1) Introducing a methyl group at the *o*-position of azo group. (2) MO calculation of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for the hypothetical *o*-methyl derivatives. (3) Calculation of $\Delta_f H^0$(GA) in both the media for the hypothetical *o*-methyl radicals by use of $\Delta_f H^0$(gas,CH_3) or $\Delta_f H^0$(aq,CH_3). (4) Analysis of AHT for the corresponding dyes in terms of group additivity, as mentioned below. The values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for radicals of model compounds obtained are listed in the lowest three rows in Table 6, and those for substituents used for the group analysis of model compounds in Table 4.

Table 7
AHT analysis of model azobenzenes in the gas phase and water in terms of group additivity (cf. Tables 4 and 6)

Compound	Phase	Estimation of $\Delta_f H^0$(GA) in terms of group additivity[a]	$\Delta_f H^0$ calcd	Notes
2-Hydroxyazobenzene				
2-hydroxy derivative	Gas	$\Delta_f H^0$(No Me-rad) + $\Delta_f H^0$(2-OH) = 99.3 + (−44.7) = 54.6	50.4 (AT)	AT is dominant and GA[a] holds.
	H_2O	A ditto = 86.0 + (−51.9) = 34.1	32.2 (HT)	HT is dominant and GA holds.
2-hydroxy-2′-sulfo derivative	Gas	$\Delta_f H^0$(2′-sulfo) + $\Delta_f H^0$(2-OH) = −20.4 + (−44.7) = −65.1	−66.1 (AT)	AT is dominant and GA holds.
	H_2O	A ditto = −60.9 + (−51.9) = −112.8	−110.3 (HT)	HT is dominant and GA holds.
2-hydroxy-4′-sulfo derivative	Gas	$\Delta_f H^0$(4′-sulfo) + $\Delta_f H^0$(2-OH) = −22.4 + (−44.7) = −67.1	−70.6 (AT)	AT is dominant and GA holds.
	H_2O	A ditto = −65.6 + (−51.9) = −117.5	−119.4 (HT)	HT is dominant and GA holds.
2-hydroxy-4-sulfo derivative	Gas	$\Delta_f H^0$(4-sulfo) + $\Delta_f H^0$(2-OH) = −22.4 + (−44.7) = −67.1	−68.0 (AT)	AT is dominant and GA holds.
	H_2O	A ditto = −65.6 + (−51.9) = −117.5	−115.9 (HT)	HT is dominant and GA holds.
2-Aminoazobenzene[b]				
2-amino derivatives	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(2-NH_2) = 99.3 + (−4.6) = 94.7	94.4 (AT)	
	H_2O	A ditto = 86.0 + (−7.0) = 79.0	78.3 (AT)	AT is dominant and GA holds.
2-amino-2′-sulfo derivative	Gas	$\Delta_f H^0$(2′-sulfo) + $\Delta_f H^0$(2-NH_2) = −20.4 + (−4.6) = −25.0	−24.5 (AT)	
	H_2O	A ditto = −60.9 + (−7.0) = −67.9	−73.6 (AT)	$\Delta_f H^0$(GA) < $\Delta_f H^0$(AT) < $\Delta_f H^0$(HT)
2-amino-4′-sulfo derivative	Gas	$\Delta_f H^0$(4′-sulfo) + $\Delta_f H^0$(2-NH_2) = −22.4 + (−4.6) = −27.0	−28.8 (AT)	
	H_2O	A ditto = −65.6 + (−7.0) = −72.6	−76.6 (AT)	AT is dominant and GA holds.
2-amino-4-sulfo derivative	Gas	$\Delta_f H^0$(4-sulfo) + $\Delta_f H^0$(2-NH_2) = −22.4 + (−4.6) = −27.0	−25.8 (AT)	
	H_2O	A ditto = −65.6 + (−7.0) = −72.6	−70.9 (AT)	
2-Acetylaminoazobenzene				
2-acetylaminoazobenzene (AB)	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(2-acetylamino) = 99.3 + (−46.5) = 52.8	49.2 (AT)	
	H_2O	A ditto = 86.0 + (−66.8) = 19.2	15.1 (AT)	
2′-sulfo-AB	Gas	$\Delta_f H^0$(2′-sulfo) + $\Delta_f H^0$(2-acetylamino) = −20.4 + (−46.5) = −66.9	−67.5 (AT)	
	H_2O	A ditto = −60.9 + (−66.8) = −127.7	−124.5 (AT)	AT is dominant and GA holds.
4′-sulfo-AB	Gas	$\Delta_f H^0$(4′-sulfo) + $\Delta_f H^0$(2-acetylamino) = −22.4 + (−46.5) = −68.9	−71.9 (AT)	
	H_2O	A ditto = −65.6 + (−66.8) = −132.4	−130.5 (AT)	
4-sulfo-AB	Gas	$\Delta_f H^0$(4-sulfo) + $\Delta_f H^0$(2-acetylamino) = −22.4 + (−46.5) = −68.9	−71.5 (AT)	
	H_2O	A ditto = −65.6 + (−66.8) = −132.4	−131.6 (AT)	
2-Ureidoazobenzene				
2-ureidoazobenzene (UAB)	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(2-ureido) = 99.3 + (−45.9) = 53.4	50.6 (AT)	
	H_2O	A ditto = 86.0 + (−71.4) = 14.6	14.3 (AT)	
2′-sulfo-UAB	Gas	$\Delta_f H^0$(2′-sulfo) + $\Delta_f H^0$(2-ureido) = −20.4 + (−45.9) = −66.3	−68.9 (AT)	
	H_2O	A ditto = −60.9 + (−71.4) = −132.3	−129.2 (AT)	AT is dominant and GA holds.
4′-sulfo-UAB	Gas	$\Delta_f H^0$(4′-sulfo) + $\Delta_f H^0$(2-ureido) = −22.4 + (−45.9) = −68.3	−70.7 (AT)	
	H_2O	A ditto = −65.6 + (−71.4) = −137.0	−134.0 (AT)	
4-sulfo-UAB	Gas	$\Delta_f H^0$(4-sulfo) + $\Delta_f H^0$(2-ureido) = −22.4 + (−45.9) = −68.3	−70.5 (AT)	
	H_2O	A ditto = −65.6 + (−71.4) = −137.0	−137.7 (AT)	

[a] GA = group additivity.
[b] The values of amino radical estimated from methanil acid were used.

3.3.1. *Effect of* o-*substituents on the AHT of model azobenzene dyes without sulfo groups*

Addition of *o*-substituents, a hydroxy, amino, acetylamino or ureido group, to azobenzenes validated group additivity in the change of $\Delta_f H^0$ for predominant tautomers in the gas phase and water, as shown in Table 7. An example of the calculation is as follows: For 2-hydroxy derivative, $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) of azobenzene-*o*-radical are 99.3 and 86.0 kcal mol^{-1}, respectively, from Table 6. Using the values of the hydroxy radical in Table 4, the results of the $\Delta_f H^0$(GA) calculation are shown in the third and forth rows in Table 7.

In the cases of *o*-hydroxy compounds, the dominance of ATs in the gas phase was reversed by the transfer into water due to the certainly larger energies of solvation of HTs than those of the corresponding ATs. This fact has been widely recognized in the field of heterocyclic chemistry because of the higher stability of the tautomers of keto form than those of enol form [14–16].

Amino groups resulted in the predominance of ATs in both the phases. Since no AHT exists without introducing these substituents, the substituents cause the AHT and decide which tautomers predominate. In the GA analyses, the values of $\Delta_f H^0$(2-NH_2) used were, respectively, −4.6 in the gas phase and −7.0 kcal mol^{-1} in water from Table 4. [As shown in Table 4, $\Delta_f H^0$(gas,NH_2) and $\Delta_f H^0$(aq,NH_2) were in the range, respectively, between 2.9 and −8.8 in the gas phase and between −6.1 and −17.7 in water. In order to minimize the calculation errors, the values of methanil acid, which lay in the intermediate position, were used.] By use of these values, the $\Delta_f H^0$(GA) value of 2-aminoazobenzene was calculated as described in Table 7. (Thus, $\Delta_f H^0$(GA) (kcal mol^{-1}) in the gas phase: $\Delta_f H^0$(azobenzne *o*-radical) + $\Delta_f H^0$(2-NH_2) = 99.3 + (−4.6) = 94.7 and that in water: A ditto = 86.0 + (−7.0) = 79.0. Both the $\Delta_f H^0$(GA) values coincided in the two media, respectively, with the $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) values of ATs.

Since the ATs of *o*-amino-, *o*-acetylamino- and *o*-ureido-azobenzenes had larger (large minus) values of $\Delta_f H^0$ than the HTs had, the ATs were overwhelmingly dominant in both the gas phase and water, except for that of the *o*-acetylamino derivative in the gas phase. The $\Delta_f H^0$(GA) values of *o*-acetylamino- and *o*-ureido-azobenzenes described in Table 7 coincide with those of ATs, indicating the predominance of ATs in two media.

Thus, the AHT of azobenzene dyes without sulfo groups could be very surely explained.

3.3.2. *Effect of* o-*substituents on the AHT of model azobenzene dyes with sulfo groups*

The introduction of sulfo groups into a particular position of azo dyes often resulted in ATs [1,2]. In order to confirm whether sulfo groups promote ATs or not, the effects of 2′-, 4′-, and 4-sulfo groups on the AHT were examined calculating the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for model azobenzene compounds as shown in Table 6. Table 7 summarizes their analysis in terms of group additivity.

An example of the calculation in Table 7 is explained as follows: for the 2-amino-2′-sulfo derivative of 2-aminoazobenzene, the predominant tautomers were the ATs in both the gas phase and water from the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) listed in Table 6, which were −24.5(AT) and −73.6(AT) kcal mol^{-1}, respectively. The values of $\Delta_f H^0$(2-sulfo-A *o*-radical) are, respectively, −20.4 in the gas phase and −60.9 kcal mol^{-1} in water from the *o*-methyl prototypes in Table 6. The calculations of $\Delta_f H^0$(GA) are listed in the corresponding rows in Table 7, indicating a good agreement between $\Delta_f H^0$(aq) and $\Delta_f H^0$(GA), but the $\Delta_f H^0$(gas) value showed a considerable shift, the only exception in Table 7. Shifts larger than 5 kcal mol^{-1} are described by the expressions of inequality in the fifth column in Table 7.

In spite of systematic study, no definite effect of sulfo groups or of its position was characterized, although the *o*-sulfo groups of azobenzene dyes seemed to have some effects on the AHT in water in cases of the coexistence of acetylamino groups.

3.3.3. *AHT analysis for azobenzene reactive dyes*

The analysis of AHT for arylazobenzene dyes, including hypothetical dyes whose substituents were exchanged or removed, was carried out in terms of group additivity. Table 8 summarizes the results obtained using data listed in Tables 1 and 4. As the results of analysis describe, the values of

Table 8
AHT analysis of phenylazobenzene and azobenzene dyes in the gas phase and water in terms of group additivity, exchanging *o*-substituents of the azo group (cf. Tables 1 and 4)

Compound	phase	Estimation of $\Delta_f H^0$(GA) in terms of group additivity	$\Delta_f H^0$ by MO method	Notes
Yellow 3 group				
3-amino derivative	Gas	$\Delta_f H^0$(3-Me)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(3-NH_2) = −133.9−(−10.0) + (−4.6) = −128.5	−129.5(AT)	AT is dominant and GA holds for AT.
	H_2O	A ditto = −234.8−(−10.3) + (−7.0) = −231.5	−236.5(AT)	$\Delta_f H^0$(AT) < $\Delta_f H^0$(GA) < $\Delta_f H^0$(HT)
3-acetylamino derivative (Yellow 3)	Gas	$\Delta_f H^0$(3-Me)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(3-AA) = −123.9 + (−46.5) = −170.4	−172.7(AT)	AT is dominant and GA holds for AT.
	H_2O	A ditto = −234.8−(−10.3) + (−66.8) = −291.3	−292.8(AT)	
3-ureido derivative	Gas	$\Delta_f H^0$(3-Me)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(3-ureido) = −123.9 + (−45.9) = −169.8	−171.7(AT)	
	H_2O	A ditto = −224.5 + (−71.4) = −295.9	−299.7(AT)	
Acetyl VS2 group				
3-amino derivative	Gas	$\Delta_f H^0$(3-Me)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(3-NH_2) = −302.1−(−10.0) + (−4.6) = −296.7	−296.5(AT)	AT is dominant and GA holds for AT.
	H_2O	A ditto = −455.3−(−10.3) + (−7.0) = −452.0	−454.1(AT)	
3-acetylamino derivative (Acetyl VS2)	Gas	$\Delta_f H^0$(3-Me)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(3-AA) = −292.1 + (−46.5) = −338.6	−344.8(HT)	$\Delta_f H^0$(HT) < $\Delta_f H^0$(AT) < $\Delta_f H^0$(GA)
	H_2O	A ditto = −445.0 + (−66.8) = −511.8	−517.2(AT)	$\Delta_f H^0$(AT) < $\Delta_f H^0$(GA) < $\Delta_f H^0$(HT)
3-ureido derivative	Gas	$\Delta_f H^0$(3-Me)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(3-ureido) = −292.1 + (−45.9) = −338.0	−340.1(AT)	AT is dominant and GA holds for AT.
	H_2O	A ditto = −445.0 + (−71.4) = −516.4	−514.5(AT)	
Acetyl VS1 group				
2-acetylamino	Gas	$\Delta_f H^0$(2-Me-VSP[a])-$\Delta_f H^0$(Me) + $\Delta_f H^0$(2-AA[b]) = −32.7−(−10.0) + (−46.5) = −69.2	−73.5(AT)	$\Delta_f H^0$(AT) < $\Delta_f H^0$(HT) < $\Delta_f H^0$(GA)
	H_2O	A ditto = −78.7−(−10.3) + (−66.8) = −135.2	−133.4(AT)	AT is dominant and GA holds for AT.
2-amino-5-sulfo	Gas	$\Delta_f H^0$(2-Me-5S-VSP)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(2-NH_2) = (−156.6)−(−10.0) + (−4.6) = −151.2	−154.9(AT)	
	H_2O	A ditto = (−235.1)−(−10.3) + (−7.0) = −231.8	−234.7(AT)	
2-acetylamino-4-amino-5-sulfo (Acetyl VS1)	Gas	$\Delta_f H^0$(2-Me-4-NH_2-5S-VSP)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(2-AA) = (−161.7)−(−10.0) + (−46.5) = −198.2	−200.3(AT)	
	H_2O	A ditto = (−243.7)−(−10.3) + (−66.8) = −300.2	−290.8(AT)	$\Delta_f H^0$(GA) < $\Delta_f H^0$(AT) < $\Delta_f H^0$(HT)
2-ureido-4-amino-5-sulfo	Gas	$\Delta_f H^0$(2-Me-4-NH_2-5S-VSP)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(2-ureido) = (−151.7) + (−45.9) = −197.6	−198.2(AT)	AT is dominant and GA holds for AT.
	H_2O	A ditto = (−233.4) + (−71.4) = −304.8	−299.6(AT)	$\Delta_f H^0$(GA) < $\Delta_f H^0$(AT) < $\Delta_f H^0$(HT)
Ureido BF group				
o-amino derivative	Gas	$\Delta_f H^0$(*o*-Me)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(*o*-NH_2) = −346.3−(−10.0) + (−4.6) = −340.9	−343.6 (AT)	AT is dominant.
	H_2O	A ditto = −504.8−(−10.3) + (−7.0) = −501.5	−506.5 (AT)	$\Delta_f H^0$(AT) < $\Delta_f H^0$(GA) < $\Delta_f H^0$(HT)

(*continued on next page*)

Table 8 (*continued*)

Compound	phase	Estimation of $\Delta_f H^0$(GA) in terms of group additivity	$\Delta_f H^0$ by MO method	Notes
o-acetylamino derivative	Gas	$\Delta_f H^0$(*o*-Me)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(*o*-AA) = −336.3 + (−46.5) = −382.8	−386.6(AT)	AT is dominant and GA holds for AT.
	H_2O	A ditto = −494.5 + (−66.8) = −561.3	−560.7(AT)	
o-ureido derivative (Ureido BF)	Gas	$\Delta_f H^0$(*o*-Me)-$\Delta_f H^0$(Me) + $\Delta_f H^0$(*o*-ureido) = −336.3 + (−45.9) = −382.2	−386.1(AT)	
	H_2O	A ditto = −494.5 + (−71.4) = −565.9	−569.7(AT)	

A = agreement within experimental errors.
[a] AB = azobenzene.
[b] AA = acetylamino.

$\Delta_f H^0$(GA) calculated in terms of group additivity coincide well with the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for the tautomers with the highest stability in the corresponding phases, although the cases of deviation greater than 5 kcal mol^{-1} are described by the expressions of inequality.

Within six groups of four arylazobenzene dyes whose analysis results are listed in Table 8, the ATs of C.I. Reactive Yellow 3, Acetyl VS1 and Ureido BF (except for Acetyl VS2) had very high stability in both the gas phase and water, compared with the HTs. It was observed that the A&HTs of several dyes including hypothetical dyes with different *o*-substituents had the same stability in the gas phase. Both the tautomers seemed to possess nearly identical structures to each other in the gas phase after structure optimization using the PM5 method. The A&HTs may co-exist in the gas phase and in aprotic solvents, although why only these particular dyes have such properties remains to debatable.

An example of the calculation in terms of GA is explained as follows: for Acetyl VS1 (cf. Acetyl VS1 group in the third group in Table 8), from the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) listed in Table 1, which were between −200.2(AT) and −200.6(HT) and between −290.8(AT) and −290.1(HT) kcal mol^{-1}, respectively, both the tautomers co-existed in both the gas phase and water. The values of $\Delta_f H^0$(2-Me-4-NH_2-5-sulfo-VSP) were, respectively, −161.7 in the gas phase and −243.7 kcal mol^{-1} in water from Table 1. Eliminating $\Delta_f H^0$(CH_3 radical) from them to estimate $\Delta_f H^0$(gas,dye 2-radical) [−161.7−(−10.0) = −151.7 kcal mol^{-1} in the gas phase] and $\Delta_f H^0$(aq,dye 2-radical) [−243.7−(−10.3) = −233.4 kcal mol^{-1} in water], and adding $\Delta_f H^0$(acetylamino radical), the values of $\Delta_f H^0$(gas,GA) and $\Delta_f H^0$(aq,GA) for Acetyl VS1 were obtained: [−151.7 + (−46.5) = −198.2 kcal mol^{-1} in the gas phase, and −233.4 + (−66.8) = −300.2 kcal mol^{-1} in water.]

The same explanation of the calculation of $\Delta_f H^0$(GA) for Yellow 3, Acetyl VS2 and Ureido BF in Table 8 may be made as in the case of Acetyl VS1. The other calculations of $\Delta_f H^0$(GA) are described in the third column of Table 8. Although some deviations of $\Delta_f H^0$(GA) from the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) estimated by

the PM5 method were observed, their coincidence was as a whole good.

The results of the analysis described in Table 8 were completely consistent with the model analysis in the previous section: Azobenzene dyes with *o*-amino substituents including acetylamino and ureido groups existed as ATs in the gas phase as well as in water. Substituents introduced into amino groups further promoted the tendency towards ATs in the following order: $-NH_2 \cong -NHCOCH_3 < -NHCONH_2$.

According to Fedorov [5], the conditions for formation of an iminoquinone hydrazone structure are less favourable in aromatic aminoazo dyes such as 4-phenylazo-1-naphthylamine than the corresponding hydroxyazo dyes such as 4-phenylazo-1-naphthol due to the lower acidity of the NH proton compared to the OH proton. As mentioned above and also in the next sections (3.4 and 3.5), the predominance of amino groups over hydroxyl ones to promote the ATs of phenylazopyrazolinyl dyes in water was confirmed by the quantum-mechanical calculation of $\Delta_f H^0$, although the relative predominance of ATs and A/Ks in both the gas and water phases was complex.

3.4. Analysis of $\Delta_f H^0$ for pyrazolinyl azo dyes and the effect of keto–enol tautomerism of pyrazoline ring on their AHT

Parent [48] reviewed the past studies on the chemical structures of pyrazolinylazo dyes and characterized some 30 synthesized pyrazolinyl dyes as HTs by IR spectroscopy [49]. Since then, the tautomeric structures of phenylazopyrazolinyl dyes have been investigated mainly by NMR spectroscopy to give a similar conclusion [4–8,50–58], although most spectral measurements were made in organic solvents and only a few in water [59–61].

Besides the AHT of hydroxyazo structure, however, pyrazolinylazo dyes perform multiple tautomerism, since pyrazoline ring itself conducts a prototropic keto-enol tautomerism [14], as mentioned above (cf. Section 3.1.2). As far as this point is concerned, some confusion seems to remain, as mentioned below.

3.4.1. Substituent effect in benzene ring on the AHT of pyrazolinyl azo dyes in terms of group additivity

The effects of substituents in the benzene ring of the diazo component of pyrazolinylazo dyes on the AHT were also analysed in terms of group additivity. The mean difference of $\Delta_f H^0$(gas) between the non-substituted and methyl-substituted compounds, whose substituent was introduced in the diazo (phenyl) component were 7.5 kcal mol^{-1} from their values listed in Tables 1 and 2. This value almost equals the corresponding one calculated from the model compounds listed in the lowest group of Table 4 [24.4 (the mean value of *o*-, *m*-, and *p*-C_6H_4 radicals) −21.7 (phenyl radical) −10.0 (methyl radical) = −7.3 kcal mol^{-1}]. The corresponding value in water was estimated as −6.9 kcal mol^{-1}. From these differences, $\Delta_f H^0$(gas,H) and $\Delta_f H^0$(aq,H) were estimated to be −2.7 and −3.4 kcal mol^{-1}, respectively. [Although the mean difference of $\Delta_f H^0$(aq) in water showed considerable scatter, the value of −6.9 kcal mol^{-1} was used for the calculation of AHT analysis.]

The results of the AHT analysis are listed for Yellow 13 in Table 9 and for Pyr-Yellow and Yellow 14 in Table 10, respectively, using the values of $\Delta_f H^0$ listed in Tables 2 and 4. The AHT was determined by the *o*-substituents in the benzene ring, indicating the same tendency as that of azobenzene dyes mentioned above.

Some hypothetical dyes of Yellow 13 and Yellow 14 having a 5-hydroxy group and substituents: 5′-carboxy, 2′-sulfo, and 4′-chloro-5′-carboxy, on the benzene ring exist as H/KT in the gas phase, but as A/KT in water, with some exceptions. No general rule of the substituent effects on the benzene ring of phenylazopyrazolinyl dyes with a 5-hydroxy group was extracted. Substituents on the benzene ring of Pyr-Yellow with a 5-amino group, however, had no effect on the AHT.

Group additivity of $\Delta_f H^0$ for the tautomers with the highest stability held in the analysis exchanging the substituents in both the pyrazoline and benzene rings, but with a few exceptions. The deviations of $\Delta_f H^0$ calculated by the two methods (calculations in terms of group additivity and direct calculation by MO methods) were in a range of 5–10 kcal mol^{-1}. Bulky *o*-substituents of the

Table 9
AHT analysis of Yellow 13 in the gas phase and water in terms of group additivity (cf. Tables 2, 4 and 5)

Compound	Phase	Estimation of $\Delta_f H^0$(GA) in terms of group additivity	$\Delta_f H^0$ by MO method	Notes
Yellow 13 group: Effect of substituents on pyrazoline ring				
5-hydroxy derivative	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(5-OH) = −178.0 + (−51.2) = −229.2	−229.4 (H/KT)	H/KT is dominant and GA holds.
	H_2O	A ditto = −269.0 + (−62.1) = −331.1	−333.5 (A/KT)	A/KT is dominant and GA holds.
3-methyl-5-hydroxy derivative (Yellow 13)	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(3-Me) + $\Delta_f H^0$(5-OH) = −178.0 + (−8.3) + (−52.8) = −239.1	−240.7 (H/KT)	H/KT is dominant and GA holds.
	H_2O	A ditto = −269.0 + (−8.0) + (−63.0) = −340.0	−339.6 (A/KT)	A/KT is dominant and GA holds.
5-amino derivative	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(5-NH_2) = −178.0 + (−2.0) = −180.0	−186.9 (AT)	$\Delta_f H^0$(AT) < $\Delta_f H^0$(GA) < $\Delta_f H^0$(H/KT)
	H_2O	A ditto = −269.0 + (−8.5) = −277.5	−275.8 (AT)	AT is dominant and GA holds.
3-methyl-5-amino derivative	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(3-Me) + $\Delta_f H^0$(5-NH_2) = −178.0 + (−8.3) + (−4.0) = −190.3	−195.6 (AT)	$\Delta_f H^0$(AT) < $\Delta_f H^0$(GA) < $\Delta_f H^0$(H/KT)
	H_2O	A ditto = −269.0 + (−8.2) + (−10.3) = −287.5	−294.7 (AT)	
Yellow 13 group: Effect of substituents on benzene ring				
4′-chloro derivative	Gas	$\Delta_f H^0$(No sub) − $\Delta_f H^0$(H) + $\Delta_f H^0$(4′-Cl) = −29.8 − (−2.7) + (−9.3) = −36.4	−37.0 (H/KT)	H/KT is dominant and GA holds.
	H_2O	A ditto = −89.7 − (−3.4) + (−9.6) = −95.6	−96.1 (H/KT)	
5′-carboxy derivative	Gas	$\Delta_f H^0$(No sub) − $\Delta_f H^0$(H) + $\Delta_f H^0$(5′-carboxy) = −29.8 + (−92.0) = −119.1	−118.6 (H/KT)	
	H_2O	A ditto = −87.9 − (−3.4) + (−105.1) = −189.6	−194.2 (A/KT)	A/KT is dominant and GA holds.
2′-sulfo derivative	Gas	$\Delta_f H^0$(No sub) − $\Delta_f H^0$(H) + $\Delta_f H^0$(2′-sulfo) = −29.8 − (−2.7) + (−121.9) = −149.0	−148.4 (H/KT)	H/KT is dominant and GA holds.
	H_2O	A ditto = −89.7 − (−3.4) + (−155.8) = −242.1	−241.7 (A/KT)	A/KT is dominant and GA holds.
2′-sulfo-4′-chloro derivative	Gas	$\Delta_f H^0$(No sub) − $\Delta_f H^0$(H) + $\Delta_f H^0$(2′-sulfo) + $\Delta_f H^0$(4′-Cl) = −29.8 − (−2.7) + (−121.9) + (−9.3) = −158.3[a]	−152.4 (A/KT)	$\Delta_f H^0$(GA) < $\Delta_f H^0$(A/KT) < $\Delta_f H^0$(H/KT)
	H_2O	A ditto = -89.7 − (−3.4) + (−155.8) + (−9.6) = −251.7[a]	−240.3 (A/KT)	
4′-chloro-5′-carboxy derivative	Gas	$\Delta_f H^0$(No sub) − $\Delta_f H^0$(H) + $\Delta_f H^0$(4′-Cl-5′-carboxy) = −29.8 − (−2.7) + (−9.3) + (−92.0) = −128.4[a]	−122.9 (H/KT)	(GA) < (H/KT) < (A/KT)
	H_2O	A ditto = −89.7 − (−3.4) + (−9.6) + (−105.1) = −201.0[a]	−197.1 (A/KT)	A/KT is dominant and GA holds.
2′-sulfo-4′-chloro-5′-carboxy deriv.[a]	Gas	$\Delta_f H^0$(No sub) − $\Delta_f H^0$(H) + $\Delta_f H^0$(2′-sulfo-4′-Cl-5′-carboxy) = −29.8 − (−2.7) + (−9.3) + (−92.0) + (−121.9) = −250.3[a]	−240.7 (H/KT)	$\Delta_f H^0$(GA) < $\Delta_f H^0$(H/KT) < $\Delta_f H^0$(A/KT)
	H_2O	A ditto = −89.7 − (−3.4) + (−9.6) + (−105.1) + (−155.8) = −356.8[a]	−339.6 (A/KT)	$\Delta_f H^0$(GA) < $\Delta_f H^0$(A/KT) < $\Delta_f H^0$(H/KT)

[a] The same revision as the second hydrogen radical for the removal of third one was made.

Table 10
AHT analysis of pyrazolinyl azo dyes in the gas phase and water in terms of group additivity [cf. Tables 2, 4 and 5) (Enthalpy of formation is described in $\Delta_f H^0$ (kcal mol^{-1})]

Compound	Phase	Estimation of $\Delta_f H^0$(GA)in terms of group additivity	$\Delta_f H^0$ by MO method	Notes
Pyr-Yellow group: Effect of substituents in pyrazoline ring				
3-methyl derivative	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(3-Me) = −126.6 + (−8.3) = −134.9	−132.4 (–)	GA holds.
	H_2O	A ditto = −215.6 + (−8.2) = −223.8	−223.9 (–)	
5-hydroxy derivative	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(5-OH) = −126.6 + (−51.2) = −177.8	−181.1(H/KT)	H/KT is dominant and GA holds.
	H_2O	A ditto = −215.6 + (−62.1) = −277.7	−270.2 (A/KT)	A/KT is dominant and GA holds.
5-amino derivative	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(5-NH_2) = −126.6 + (−2.0) = −128.6	−131.2 (AT)	AT is dominant and GA holds.
	H_2O	A ditto = −215.6 + (−8.5) = −224.1	−230.2 (AT)	$\Delta_f H^0$(AT) < $\Delta_f H^0$(GA) < $\Delta_f H^0$ (A/KT)
3-methyl-5-hydroxy derivative	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(3-Me) + $\Delta_f H^0$(5-OH) = −126.6 + (−8.3) + (−52.3) = −187.2 $\Delta_f H^0$(3-Me-P) + $\Delta_f H^0$(5-OH) = −132.4 + (−52.3) = −184.7	−190.4 (H/KT)	H/KT is dominant and GA holds.
	H_2O	A ditto = −215.6 + (−8.2) + (−62.1) = −285.9; A ditto = −215.6 + (−62.1) = −277.7	−278.3 (A/KT)	A/K is dominant and GA holds.
3-methyl-5-amino derivative	Gas	$\Delta_f H^0$(No sub) + $\Delta_f H^0$(3-Me) + $\Delta_f H^0$(5-NH_2) = −126.6 + (−8.3) + (−4.0) = −138.9 $\Delta_f H^0$(3-Me-P) + $\Delta_f H^0$(5-NH_2) = −132.4 + (−4.0) = −136.4	−139.2 (AT)	AT is dominant and GA holds.
	H_2O	A ditto = −215.6 + (−8.2) + (−8.5) = −232.3; A ditto = −223.9 + (−8.5) = −232.4	−234.2 (AT)	AT is dominant and GA holds.
Pyr-Yellow group: Effect of substituents in benzene ring				
2′-methoxy derivative	Gas	$\Delta_f H^0$(No sub)−$\Delta_f H^0$(H) + $\Delta_f H^0$(2′-OMe) = 24.8−(−2.7) + (−37.9) = −10.4	−14.7 (AT)	AT is dominant and GA holds.
	H_2O	A ditto = −27.0−(−3.4) + (−43.1) = −66.7	−75.7 (AT)	$\Delta_f H^0$(AT) < $\Delta_f H^0$(GA) < $\Delta_f H^0$ (HT)
5′-VS derivative	Gas	$\Delta_f H^0$(No sub)−$\Delta_f H^0$(H) + $\Delta_f H^0$(5′VS) = 24.8−(−2.7) + (−121.4) = −93.9	−100.1 (AT)	AT is dominant and GA holds.
	H_2O	A ditto = −27.0−(−3.4) + (−158.3) = −181.9	−184.5 (AT)	
2′-methoxy-5′-VS derivative	Gas	$\Delta_f H^0$(5′-VS-P)- $\Delta_f H^0$(H) + $\Delta_f H^0$(2′-OMe) = (−100.1)−(−2.7) + (−37.9) = −135.3	−139.2 (AT)	
	H_2O	A ditto = −184.5−(−3.4) + (−43.1) = −224.1	−234.2 (AT)	$\Delta_f H^0$(AT) < $\Delta_f H^0$(GA) < $\Delta_f H^0$ (HT)
Yellow 14 group: Effect of substituents in benzene ring				
2′-methoxy derivative	Gas	$\Delta_f H^0$(No sub)−$\Delta_f H^0$(H) + $\Delta_f H^0$(2′-OMe) = (−39.9)−(−2.7) + (−37.9) = −75.1	−76.2 (AT)	AT is dominant and GA holds.
	H_2O	A ditto = (−94.6)−(−3.4) + (−43.1) = −134.3	−135.0 (A/KT)	A/KT is dominant and GA holds.
5′-VS derivative	Gas	$\Delta_f H^0$(No sub)−$\Delta_f H^0$(H) + $\Delta_f H^0$(5′-VS) = (−39.9)−(−2.7) + (−121.4) = −158.6	−161.5 (H/KT)	H/KT is dominant and GA holds.
	H_2O	A ditto = (−95.5)−(−3.4) + (−158.3) = −250.4	−249.2 (H/KT)	
2′-methoxy-5′-VS derivative	Gas	$\Delta_f H^0$(No sub)−$\Delta_f H^0$(H) + $\Delta_f H^0$(2′-OMe) + $\Delta_f H^0$(5′-VS) = (−39.9)−(−2.7) + (−37.9) + (−121.4) = −196.5	−199.9 (H/KT)	
	H_2O	A ditto = (−94.6)−(−3.4) + (−43.1) + (−158.3) = −292.6	−291.4 (A/KT)	A/KT is dominant and GA holds.

azo group and neighbouring bulky substituents resulted in considerable deviations from group additivity due to so-called nearest neighbour interactions [24]. It may mean that the tautomers with the highest stability cause the relaxation of the nearest neighbour interaction and ring strain corrections by the *o*-amino group including the *o*-ureido one, compared with the tautomers with lower stability.

3.4.2. Substituent effect in pyrazoline ring on the AHT of phenylazopyrazolinyl dyes in terms of group additivity

The values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) were calculated using the same MO methods for three tautomers, azo, A/K and H/K, as shown in Table 2. The analysis of AHT in terms of group additivity of $\Delta_f H^0$(GA) was also carried out. As in the cases of azobenzene dyes, the group additivity of $\Delta_f H^0$ held for the tautomers with the highest stability in the corresponding phase. The results of AHT analysis, which were performed using the data listed in Tables 4 and 5, are listed for Yellow 13 in Table 9 and for Pyr-Yellow and Yellow 14 in Table 10, respectively. Group additivity was discussed by introducing or removing the substituents in pyrazoline and benzene rings.

The substituents in the pyrazoline ring of Pyr-Yellow had the same effects on the values of $\Delta_f H^0$ as the substituents in the model azobenzene dyes (cf. Section 3.3.2). Amino groups resulted in the highest stability of the ATs in both the gas phase and water, while the hypothetical dyes of Pyr-Yellow with a 5-hydroxy group (cf. Table 10) showed the highest stability in the keto tautomers: the H/KTs in the gas phase and the A/KTs in water. As in the case of Pyr-Yellow, Yellow 13 with a 5-hydroxy group irrespective of 3-methyl group existed as H/KTs in the gas phase and as A/KTs in water. The hypothetical dyes of Yellow 13 with a 5-amino group existed as ATs in both the gas phase and water. The substituents in the pyrazoline ring of Yellow 14 had similar effects as that of Pyr-Yellow, although no results of the MO calculation were listed. The substituent effects on the AHT of phenylazopyrazolinyl dyes including the hypothetical dyes with amino or hydroxy groups were identical to each other without exception.

Especially in the case of 5-amino derivatives, several considerable deviations in the calculated values of $\Delta_f H^0$(GA) in terms of group additivity from those of $\Delta_f H^0$ obtained by the same MO method were also found.

In general, the values of $\Delta_f H^0$(GA) coincided with those of $\Delta_f H^0$ for the tautomers with the largest stability in the phase, listed in the fourth column of Tables 7–10, which were calculated by PM5 methods, with a few exceptions. They are noted in the last column of the tables. The deviations are described by expressions of inequality when they are larger than 5 kcal mol^{-1}. Since the deviations in $\Delta_f H^0$ were in a range of 5–10 kcal mol^{-1}, which might be within the calculation errors in water, no further analysis of the deviation could be made.

3.4.3. Analysis of AHT for hypothetical dyes derived from azo dyes existing only as ATs

In order to prove the validity of the present procedure, exchanging the methyl group with the hydroxy group of Methyl VS and adding newly the *o*-hydroxy group to MCT-Brown 1 and MCT-Brown 2, the AHT of the resultant dyes was analysed by the same methods or the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) were calculated for the hypothetical dyes. Table 11 shows the results.

The exchange of the *o*-methyl group with an *o*-hydroxy one for Methyl VS resulted in ATs with high stability in the gas phase and HTs with high stability in water, while the exchange with an amino group resulted in the ATs in both the gas phase and water, demonstrating a typical tendency of the *o*-substituents.

In the cases of disazo dyes, there are three and four *o*-positions for MCT-Brown 1 and MCT-Brown 2, respectively. Adding a hydroxy group to another *o*-position next to the imino bridge group of the triazine ring, the effects of a hydroxy group at every four and five *o*-positions, respectively, in the two dyes on the AHT were examined by calculating the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for the hypothetical dyes. Although dyes with an *o*-hydroxy group next to an imino bridge group had no possibility of existing as HTs, the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) were within the range of the other seven hypothetical dyes examined. All the hypothetical

Table 11
Effect of introduction of *o*-substituents, hydroxyl and amino groups, on the enthalpy of formation, $\Delta_f H^0$(kcal mol^{-1}), and energy of solvation, ΔH_{sol} (kcal mol^{-1}), of azo-hydrazone tautomers for yellow monoazo and brown disazo reactive dyes, estimated by semi-empirical MO PM5/COSMO methods

Substituent	M.W.	Azo tautomer			Hydrazone tautomer		
		$\Delta_f H^0$		$-\Delta H_{sol}$	$\Delta_f H^0$		$-\Delta H_{sol}$
		Gas phase	Water		Gas phase	Water	
Methyl VS							
Methyl VS	870.897	−274.649	−425.879	151.230	–	–	–
Me → OH	872.870	−311.427	−464.766	153.339	−306.277	−468.662	162.385
Me → NH_2	871.885	−269.715	−426.693	156.978	−251.184	−407.582	156.398
MCT-Brown 1							
MCT-Brown 1	881.837	−258.796	−427.392	168.596	–	–	–
1-azo-4-imino-7-sulfonaphthalene(1st)[a] (ASN) →3-OH-ASN	897.837	−304.218	−463.280	159.062	–	–	–
1-azo-4-imino-7-sulfonaphthalene (1st)[a] →2-OH-ASN	897.837	−302.313	−464.459	162.146	−307.911	−478.452	170.541
1,4-diazonaphthalene (2nd)[b] (AN) →2-OH-AN[d]	897.837	−301.989	−466.059	164.070	−301.469	−478.240	176.771
1,4-diazonaphthalene (2nd)[b] →3-OH-AN[e]	897.837	−304.729	−459.979	155.250	−302.804	−463.267	160.463
MCT-Brown 2							
MCT-Brown 2	845.804	−284.307	−436.181	151.874	–	–	–
1-azo-4-imino-7-sulfonaphthalene (1st)[a] (ASN) →3-OH-ASN	861.804	−329.602	−483.737	154.231	–	–	–
1-azo-4-imino-7-sulfonaphthalene (1st)[a] →2-OH-ASN	861.804	−327.577	−488.808	161.231	−327.426	−498.726	171.300
1,4-diazo-7-sulfo-naphthalene (2nd)[b] (DSN) →2-OH-DSN[d]	861.804	−328.128	−481.105	152.977	−329.329	−490.211	160.882
1,4-diazo-7-sulfo-naphthalene (2nd)[b] →3-OH-DSN[e]	861.804	−328.242	−486.901	158.659	−326.894	−484.900	158.006
1-azo-2,5-disulfo-4-methylbenzene (SMA)[c](3rd)→6-OH-SMA	861.804	−333.523	−495.875	162.352	−324.706	−495.149	170.443

[a] 1st naphthalene from triazine ring.
[b] 2nd naphthalene from triazine ring.
[c] 3rd phenyl ring from triazine ring.
[d] *o*-Position of the 1st azo group from triazine ring.
[e] *o*-Position of the 2nd azo group from triazine ring.

dyes from MCT-Brown 1 with an *o*-hydroxy group existed as HTs in water, while in the gas phase the stability of ATs was increased with an increase in the distance of the hydroxy group from the reactive groups.

In the case of MCT-Brown 2, a different tendency from that of MCT-Brown 1 was observed in both the gas phase and water with further exceptions. The two dyes with an *o*-hydroxy group of the azo group nearest to the reactive group existed as HTs in water and as ATs in the gas phase, while two dyes with a hydroxy group at the *o*-position of the second azo group showed a rather reverse tautomerism.

These facts may indicate that the general rule of AHT holds also for azo dyes with any kind of chemical structure, although MCT-Brown 2 exhibited a different tendency. Sulfo groups at the *o*-positions of azo and hydroxy groups in the phenyl ring of MCT-Brown 2 may have some influence on the tendency. The reason for the deviation from the general rule for the dyes with an *o*-hydroxy group was not further examined.

3.5. Analysis of AHT and ABE for C.I. Acid Yellow 23

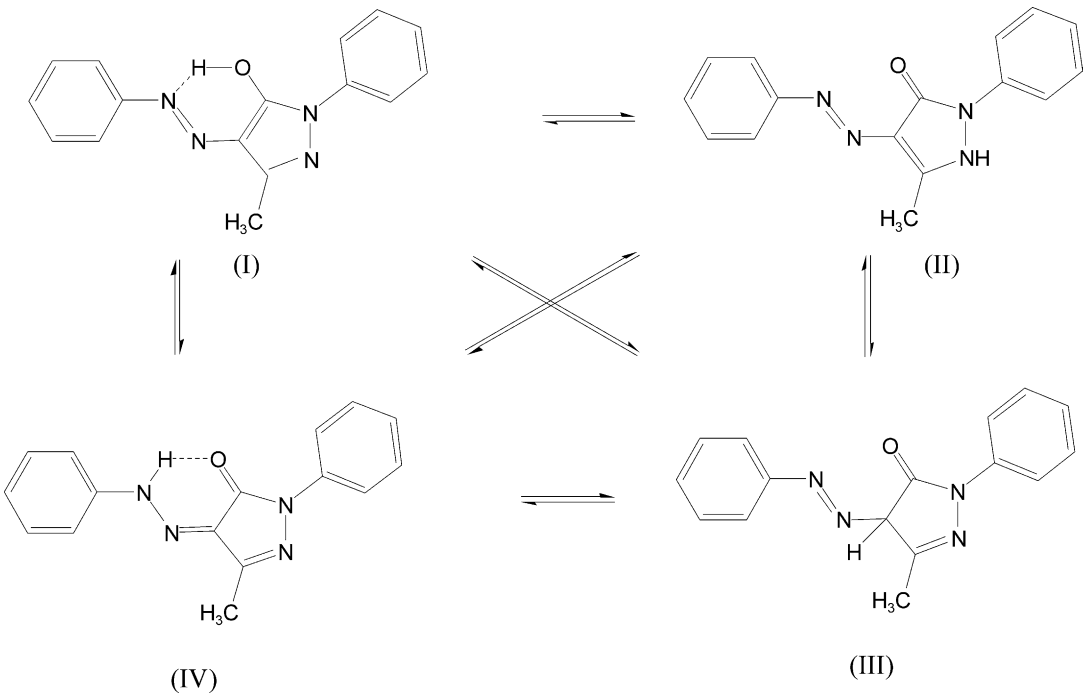
Bell et al. [59] and Mazzola et al. [61] analysed in detail the AHT of a sulfonated pyrazolinylazo dye in aqueous solution, while all the other pyrazolinylazo dyes, which had no sulfo groups, were examined in organic solvents. The pK_a of Acid Yellow 23 was estimated to be 10.3, which was attributed to NH/N$^-$ or OH/O$^-$ by ^{15}N-NMR [58]. The maximum ^{13}C-NMR spectral line-broadening effect was observed at pH 10.3, which was the second equivalence point. The line-broadening disappeared at pH 12. From these observations, they

concluded that Acid Yellow 23 exists almost exclusively as HTs at pH 7 and as the azo-anion above pH 11. In succeeding reports, they confirmed these conclusions by adding ^{13}C- and ^{1}H-NMR data [61]. In the discussion, however, they seemed to take no effect of A/KTs (cf. Scheme 1) into consideration. In the present paper, however, the AHT of Acid Yellow 23 is analysed by the same procedure as before [1,2], taking the keto-enol tautomerism of the pyrazoline ring into consideration. In the case of Acid Yellow 23 and related compounds, the effects of dissociation of carboxyl groups on the AHT are also to be examined by the same assumption.

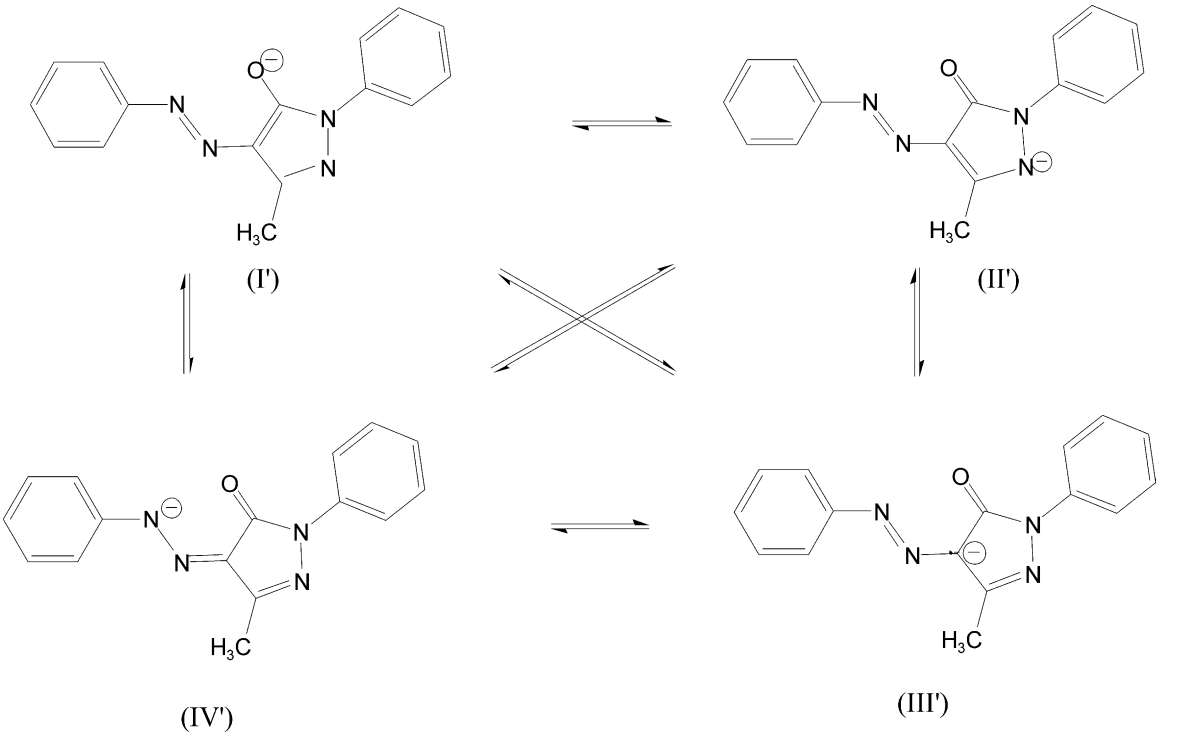
3.5.1. Concurrent occurrence of AHT and ABE

In the present discussion, the AHT of Acid Yellow 23 is analysed in three steps: (1) a dye with no sulfo groups, (2) a dye with carboxyl groups but no sulfo groups, and (3) a dye with carboxyl and two sulfo groups. When the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for Acid Yellow 23 were calculated using MO methods, problems of dissociation of substituent groups arise. In a series of MO calculations, all the sulfo groups were treated as the sulfonic acid (undissociated) form in the previous papers [1,2] as well as in the present paper. This assumption seems to give reasonable results in spite of the number of sulfo groups. In the case of Acid Yellow 23 and its related compounds, the effects of dissociation of carboxyl groups on the AHT are examined on the basis of the same assumption.

According to the MO calculation [2], the undissociated and dissociated tautomers of 1*N*-phenyl-3-methyl-4-phenylazo-5-hydroxypyrazolines may be described as shown in Schemes 1 and 2, respectively. The tautomerism among the undissociated tautomers may occur via intramolecular proton tunneling accompanied with intramolecular electron transfer or shifts of double bonds, while that among the dissociated tautomers via intramolecular electron transfer. Dynamically the rate of the latter tautomerism may be much faster than that of the former one. The population ratios of corresponding tautomers may be given by Eq. (1) or proportional to the differences in the $\Delta_f H^0$



Scheme 1. Azo-hydrazone tautomerism of 1*N*-phenyl-3-methyl-4-phenylazo-5-oxypyrazoline. I: Azo-enol tautomers, II: Azo-keto tautomers (N(2)-H), III: Azo-keto tautomers (C(4)-H), IV: Hydrazone-keto tautomer.



Scheme 2. Azo-hydrazone tautomerism of deprotonated 1*N*-phenyl-3-methyl-4-phenylazo-5-oxypyrazoline. I′: Azo-O$^-$ anion tautomer, II′: Azo-keto-N$^-$ anion tautomer (N(2)$^-$), III′: Azo-keto-C$^-$ anion tautomer (C(4)$^-$), IV′: Hydrazone-keto-N_{β}^- anion tautomer (N(β)$^-$).

between the tautomers. The ABE should occur only between the corresponding undissociated and dissociated tautomers, i.e., I ⇌ I′, II ⇌ II′, III ⇌ III′, IV ⇌ IV′, depending upon the hydrogen ion concentration in the solution as well as the pK_a of the undissociated tautomers.

3.5.2. AHT for C.I. Acid Yellow 23 with no sulfo groups

The results for dyes with no sulfo or carboxyl groups were, as listed in Table 12, relatively simple. The H/KTs in the gas phase and the H/KTs followed by the A/KTs have the highest stability, indicating a typical behaviour of pyrazolinylazo dyes with 5-hydroxy groups. When the deprotonation occurred, the tautomers of A/K, Azo/C4H (cf. Scheme 1), and H/K all had the same highest stability in the gas phase, while in the ATs in water, a completely reverse tendency was seen (cf. Schemes 1 and 2).

3.5.3. AHT for C.I. Acid Yellow 23 with a carboxyl but no sulfo groups

The values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for Acid Yellow 23 with no sulfo groups, estimated by the present MO calculation, are listed in Table 12. Acid Yellow 23 with a carboxyl group existed as HTs in the gas phase, and as A/KTs in water, which corresponded to the dyes solved in the acidic aqueous solution. When carboxyl groups of Acid Yellow 23 (with no sulfo group) dissociated, the HTs had the highest stability in both the gas phase and water.

When the deprotonation of Acid Yellow 23 (with no sulfo group) with undissociated carboxyl groups occurred, the tautomers of A/K and Azo/C4H had the highest and the same stability in both the gas phase and water. In the case of the dyes with dissociated carboxyl groups, the HTs existed in both the gas phase and water. Thus, since 3-carboxyl groups may have a pK_a value of smaller than

Table 12
AHT and ABE analyses of undeprotonated and deprotonated tautomers for C.I. Acid Yellow 23 and related compounds in terms of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) (kcal mol^{-1}) and ΔH_{sol} (kcal mol^{-1}), estimated by semiempirical MO method (MOPAC 2002, PM5 and COSMO methods)

Substituent	M.W.	Azo tautomer			Azo/keto tautomer			Azo/C4H tautomer			Hydrazone tautomer		
		$\Delta_f H^0$		$-\Delta H_{sol}$	$\Delta_f H^0$		$-\Delta H_{sol}$	$\Delta_f H^0$		$-\Delta H_{sol}$	$\Delta_f H^0$		$-\Delta H_{sol}$
		Gas phase	Water		Gas phase	Water		Gas phase	Water		Gas phase	Water	
1-N-phenyl-3-methyl-4-phenylazo-5-hydroxy-pyrazoline													
Undissociated	278.313	100.264	77.596	22.668	98.270	64.700	33.570	98.871	70.439	28.432	92.258	64.392	27.866
Deprotonated form of tautomer	Position	O of 5-hydroxy group			2-N of pyrazoline ring			4-C of pyrazoline ring			β-N of azo group		
	277.305	39.356	−48.714	88.070	36.538	−47.534	84.072	36.538	−47.017	83.555	36.538	−46.488	83.026
1-N-phenyl-3-carboxy-4-phenylazo-5-hydroxy-pyrazoline													
Undissociated	308.296	24.969	−8.532	33.501	23.120	−22.129	45.249	24.927	−18.705	43.632	19.716	−19.319	39.035
Deprotonated tautomer of COOH form	Position	O of 5-hydroxy group			2-N of pyrazoline ring			4-C of pyrazoline ring			β-N of azo group		
	307.288	−44.252	−134.309	90.057	−51.975	−146.077	94.102	−51.975	−146.077	94.102	−46.201	−137.725	91.524
COO^- form	307.288	−42.635	−141.209	98.574	−39.075	−147.362	108.287	−38.775	−144.077	105.302	−51.975	−150.514	98.539
Deprotonated tautomer of COO^- form	Position	O of 5-hydroxy group			2-N of pyrazoline ring			4-C of pyrazoline ring			β-N of azo group		
	306.280	−36.259	−258.950	222.691	−26.263	−271.361	245.098	−33.160	−269.709	236.549	−33.160	−262.765	229.605
*1-N-(p-sulfophenyl)-3-carboxy-4-(*p-*sulfophenylazo)-5-hydroxy-pyrazoline*													
Undissociated	468.412	−214.595	−266.663	52.068	−213.737	−317.927	104.190	−213.407	−306.388	92.981	−222.745	−314.527	91.782
Deprotonated tautomer of COOH form	Position	O of 5-hydroxy group			2-N of pyrazoline ring			4-C of pyrazoline ring			β-N of azo group		
	467.404	−311.558	−444.216	132.658	−311.559	−444.672	133.113	−311.559	−444.703	133.144	−310.203	−431.286	121.083
COO^- form	467.404	−299.754	−430.821	131.067	−297.105	−436.746	139.641	−295.648	−439.446	143.798	−311.559	−446.542	134.983
Deprotonated tautomer of COO^- form	Position	O of 5-hydroxy group			2-N of pyrazoline ring			4-C of pyrazoline ring			β-N of azo group		
	466.396	−322.372	−566.409	244.037	−316.475	−578.558	262.083	−316.475	−566.479	250.004	−316.472	−566.031	249.559

6, the dye with dissociated carboxyl groups in an aqueous solution at neutral pH may exist almost predominantly as HTs. With an increase in pH, only the hydrogen of the –NH–N= groups of HTs can dissociate. Since no the other tautomers existed, the deprotonation of the –NH–N= proton must occur. The pK_a value determined for Acid Yellow 23 [59,61] may be attributed to the acid dissociation of the –NH–N= groups. Since the deprotonated HTs, however, had much lower stability than the deprotonated A/KTs (cf. Table 12), the former tautomers might perform very rapid tautomerism resulting in the deprotonated A/KTs after the acid dissociation from the undissociated HTs.

3.5.4. AHT of Acid Yellow 23

When two sulfo groups were introduced, the tautomers of this dye with an undissociated carboxyl group, which had the highest stability, were HTs in the gas phase and A/KTs in water, indicating that sulfo groups had no effect on the AHT. When only the deprotonation occurred without dissociation of carboxyl groups, the tautomers of AT, A/KT and Azo/C4H had the highest and the same stability in both the gas phase and water. Sulfo groups had a small effect on the AHT, a small increase in the stability of ATs. Moreover, acid dissociation of carboxyl groups without deprotonation had no effect on the AHT at all.

When acid dissociation of carboxyl groups occurred, only H/KTs existed in both the gas phase and water, indicating that sulfo groups had no effect on the AHT. The same explanation should apply to those dyes with no sulfo groups as mentioned above.

This explanation based on the present MO calculation may be completely consistent with the NMR observation by Mazzola et al. [59,61]. The deprotonated A/KTs may correspond to their azo-anion. The line-broadening of the NMR-spectra may be attributed to the coexistence of undissociated HTs and deprotonated A/KTs in the dye, or the slow deprotonation of –NH–N= groups.

Sulfo groups in Acid Yellow 23 had little effect on the AHT. The concurrent ABE and AHT may be described by Schemes 1 and 2. Acid Yellow 23 with dissociated carboxyl groups exists as HTs. Deprotonation of the –NH–N= proton occurs and the deprotonated tautomers exist as A/KTs in water, which corresponds to a 'common anion' or 'azo-anion.' The results of the MO calculation were completely consistent with the experimental results so far reported, although it required some modifications of the interpretations [59,61]. In other words, spectral measurements are required to prove the results of the MO calculation, but detailed MO calculations of various kinds of species (with dissociated and undissociated carboxyl groups) including hypothetical deprotonated and undeprotonated tautomers may be able to elucidate the total pictures of the AHT and ABE.

3.6. Relationship between the absorption spectra and AHT of azo dyes

It is recognized that the positions, intensities and shapes of the absorption band are usually modified by solvents with different polarities [62,63]. Electronic absorption spectra of dyes examined on reactively-dyed cellulosic films and of active reactive dyes in aqueous solution had different λ_{max}'s from each other, as shown in Table 3, although no dye spectra are described. The single peaks of the visible band were confirmed for all the dyes. This fact may be consistent with the results of the MO calculation showing the existence of either one of the tautomers. Small differences in the shape of the UV and visible absorption spectra of each dye, however, were recognized between different media. Some blue shifts of the λ_{max} for the visible main absorption from cellophane to water were also observed for all the dyes. The λ_{max} on cellulosic film may be regarded as close enough to the λ_{max} in the gas phase, because the dielectric constant of cellophane film is 6.7–7.6 [64], a much closer value in a vacuum than that in water. There is no method to simulate the absorption spectrum of a molecule in the polymer medium with such a low dielectric constant. The λ_{max} of each dye was always on the longer wave length side on cellulosic films than in water, and the shifts of the visible bands between them varied with dyes.

When either one of the tautomers predominated in a given medium, however, there is no method to

determine which tautomer exists. More than one tautomer of hydroxyazo or aminoazo dyes coexisted in the gas phase or probably in a solvent with a small dielectric constant [1,2]. For example, in the case of phenylazo naphthalene dyes derived from H-acid, both tautomers existed even in water. Since the population ratio of tautomers depends on the solvent mixture or solvents with different polarities [9–13], one could determine spectroscopically a predominant tautomer in a given solvent, although it sometimes depended on speculation.

For the reasons mentioned above, experimental verification of the AHT of azo dyes analysed by MO theory in the present paper remains to be further examined.

4. Summary

The AHT of arylazobenzenes and phenylazopyrazolinyl dyes, including hypothetical ones with *o*-hydroxy and *o*-amino substituents toward azo groups, was examined by calculating the values of $\Delta_f H^0$(gas) and $\Delta_f H^0$(aq) for the various types of tautomers using semiempirical MO (PM5 and COSMO) methods in the gas phase and water. The quantum-mechanical procedure implied following conclusions:

1. *o*-Amino-, o-acetylamino- or o-ureido-azobenzenes suggested to exist as ATs in both the gas phase and water, while *o*-hydroxyazobenzenes occur as ATs in the gas phase and as HTs in water. Although a few exceptions were found among dyes examined in the gas phase, the AHT of arylazobenzenes could be explained very clearly.
2. The exchange of an *o*-methyl group with an *o*-hydroxy one in monoazo dyes, which can exist only as ATs, resulted in ATs with high stability in the gas phase and HTs with high stability in water, while the exchange with an amino group resulted in ATs in both the phases, indicating a typical tendency of the *o*-substituents.
3. The hypothetical dyes of naphthalene disazo brown dyes to which an hydroxy group was added to the *o*-position of azo group nearest to the reactive group existed as HTs in water and as ATs in the gas phase.
4. Due to the keto-enol tautomerism of a pyrazoline ring, phenylazopyrazolinyl dyes resulted in various tautomers: azo, A/K, keto/C4H, and K/H tautomers. Pyrazolinylazo dyes with a 5-hydroxy group existed as HTs in the gas phase, and as A/KTs in water. The dyes with a 5-amino group existed as ATs in both the gas phase and water. The AHT of pyrazolinylazo dyes is simple as is the case of arylazobenzenes.
5. The high stability of dyes with *o*-hydroxy groups and keto-tautomers especially in water is attributed to the large solvation energy of keto groups.
6. C.I. Acid Yellow 23 with an undissociated carboxyl group exists as HTs in the gas phase and as A/KTs in water, while the same dye with the dissociated group exists as HTs in both the gas phase and water. Since this dye exists only as HTs above pH 7, the deprotonation of the $-NH-N=$ proton occurs with an increase in pH. Although the HTs of dyes with a dissociated carboxyl group without deprotonation have the highest stability in water, the deprotonated tautomers exists predominantly as A/KTs due to the AHT of deprotonated species.
7. The concurrent picture of the AHT and ABE of C.I. Acid Yellow 23 obtained by MO calculation is consistent with the results reported previously.
8. The single peaks of a visible band for all the dyes on reactively-dyed cellulosic films and in water are consistent with the results of MO calculations, implying the existence of either one of the tautomers.

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