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Dyes and Pigments 59 (2003) 25–41

DYES and PIGMENTS

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Azo-hydrazone tautomerism of phenylazonaphthol sulfonates and their analysis using the semiempirical molecular orbital PM5 method

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Received 20 August 2002; received in revised form 7 September 2002; accepted 26 September 2002

Abstract

The enthalpy of formation for the azo and hydrazone tautomers (A & H Ts) of 1-phenylazo-2-naphthols, 2- and 4-phenylazo-1-naphthols and 4-phenylazo-1-naphthol-2-sulfonic acids was estimated both in the gaseous phase and in water using a semi-empirical molecular orbital PM5 and COSMO method. Substituent effects on the solvation energies for these phenylazonaphthols were analysed in detail. The A & H Ts of azo dyes have small enthalpies of transformation which are the same as heterocyclic tautomers in heterocyclic compounds such as nucleic acid bases and heterocycles of amino acids. The hydroxyazo dyes examined exist mostly as the hydrazone tautomer (HT) in water, since the HTs possess usually larger (minus) values of solvation energy than the azo tautomers (ATs). Dyes whose A & HTs possess comparable energy of solvation result in higher stability of the ATs in water than the HTs since the ATs are more stable in the gas phase. Sulfonic acid groups *ortho* (*o*) to the azo group have unusual solvation energies resulting in dyes whose ATs have higher stability than the HT's in water. Examples of such azo dyes examined are the 4- and 2-(*o*-sulfophenylazo)-1-naphthols and their derivatives. In general, electron-withdrawing substituents have a small effect on the azo-hydrazone tautomerism (AHT) of phenylazonaphthols with the exception for sulfonic acid groups at certain positions in the structures. Examples of commercial reactive azo dyes showing such a tendency are C.I. Reactive Red 1, Red 194 and Red 227. Chloride substituents in the triazine ring imparted strong effects on the AHT of C.I. Reactive Red 1.

Keywords: Azo dye; Reactive dye; Azo-hydrazone tautomerism; Molecular orbital PM5 and COSMO methods; Enthalpy of formation; Solvation energy

1. Introduction

Zincke and Bindewald [1] reported at the end of the 19th century that the product obtained from the coupling reaction of benzene diazonium chloride with naphthol was the same as that obtained from the condensation reaction of

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0143-7208/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0143-7208(03)00093-7

phenylhydrazine with 1,4-naphthoquinone. Since the former coupling reaction gave the azo form and the latter condensation reaction the hydrazone form, the authors suggested that a dynamic equilibrium existed between the two forms. Extensive studies have followed this first observation of azo-hydrazone tautomerism (AHT).

For many organic compounds, there is a mixture of two or more structurally distinct compounds that are in rapid equilibrium. When this phenomenon, called *tautomerism*, exists, there is a rapid shift back and forth among the molecules. In most cases, it is a proton that shifts from one atom of a molecule to another [2–5]. In the field of dyes, it is AHT, while in the field of biological chemistry it is *heterocyclic tautomerism*.

Several workers [6–14] have written reviews on the subject of AHT. Despite the extensive studies on the tautomerism, some essential problems are still open to debate. Thus, the electronic, NMR, IR and Raman spectroscopy of the tautomers in AHT have been investigated in diverse solvents. The existence of more than one tautomer has been spectroscopically confirmed.

Biochemical researches concerning nucleic acid and proteins, on the other hand, have been carried out extensively, resulting in several thousands of papers, in which the importance of the prototropic tautomerism of heterocyclic compounds has been established [15–21]. Solvation effects on the tautomeric equilibrium have been analysed and the validity of various solvation models have been recently established [22–37], although Elguero et al. [17] selected papers only using ab initio calculations to avoid the approximations of semi-empirical methods. The latter methods, however, may be indispensable, since no one has devised an 'ab initio' method of solvation modeling but there exist various simulation methods of solvation using ab initio MO calculation.

In the present paper, based on the principles established in studies of the tautomerism of heterocycles, the similarity between the AHT of azo dyes and the heterocyclic tautomerism is demonstrated by the thermodynamic analyses of AHT reported so far. A semiemprical molecular orbital PM5 method, which has very recently been released as the revised version of PM3 [38], has been applied to some azo dyes to prove the contribution of solvation to AHT.

2. Experimental

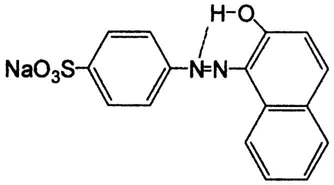
2.1. MO calculation

Semi-empirical MO calculations based on the PM5 Hamiltonian were carried out using the CAChe Work System, MOPAC 2002 [38] on a Mackintosh G4 computer to estimate the enthalpies of formation, H_f (at 25 °C), for the A & HTs of dyes in both the gaseous phase and in water [39]. In the solvation modeling, the COSMO method in MOPAC 2002 was also used.

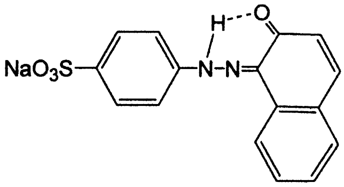
2.2. Dyes used

The monoazo dyes used in the MO calculations were described by the chemical nomenclature. As examples of dyes used, the chemical structures of the A & H T's for C.I. Acid Orange 7 and Orange 20 are shown below:

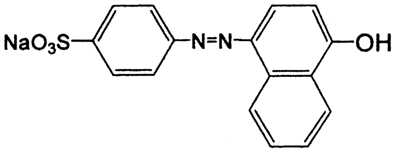
1) AT of C.I. Acid Orange 7, C.I. 15510



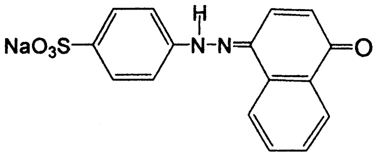
2) HT of C.I. Acid Orange 7, C.I. 15510



3) AT of C.I. Acid Orange 20, C.I. 14600



4) HT of C.I. Acid Orange 20, C.I. 14600



3. Results and discussion

3.1. Tautomerism in organic chemistry

According to Smith and March [2], several organic compounds consist of a mixture of two or more structurally distinct compounds with the same chemical formulae that are in rapid equilibrium. As mentioned, when this phenomenon (*tautomerism*) exists, there is a rapid shift back and forth among the molecules. In most cases, it is a proton that shifts from one atom of a molecule to another. In *o*-hydroxy- or *o*-amino-arylazo compounds, this proton shift comprises a proton stretching vibration in the intramolecular, asymmetrical double-well potential of a hydrogen bonding system, although transfer along the potential surface is not linear [40].

In the field of biochemical researches, a complete survey of the prototropic tautomerism of heteroatomic compounds has been successively published in a review series of Advances in Heterocyclic Chemistry. Several fundamental principles were established in the survey of tautomerism [15–21] such as the Decalogue of tautomerism, the nature of tautomerism, a general overview and methodology, as well as tautomerism in chemical structure classification. General energetic principles of tautomeric equilibrium established in biochemical researches are as follows [15–17]: Tautomerism occurs when two isomers having the same atomic composition exist in mobile equilibrium with each other. In terms of the energy barrier separating two tautomers, when $\Delta G < 25$ kcal mol^{-1}, these two isomers may be regarded as tautomers, whereas when $\Delta G > 40$ kcal mol^{-1} they would not be considered as tautomers.

The general principles of heterocyclic tautomerism may also apply to the case of the AHT of azo dyes, as discussed below.

3.2. Analysis of azo-hydrazone tautomerism

Since the equilibrium between two tautomers is too rapid to be measured on an NMR time-scale [6,41], the NMR spectra of the individual tautomer cannot be measured. Azo-hydrazone content has been calculated as the weighted average of two contributing forms [6]. Saeva [42], Lyčka [43], Reeves and Kaiser [44] measured the equilibrium constant of AHT, as shown in Table 1, and some

Table 1
Thermodynamic parameters of azo-hydrazone tautomeric equilibrium (K_T = [hydrazone]/[azo])

Compound	ΔG (cal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} deg^{-1})	Method/solvent	Temp (K)	Ref.
4-(4′-Methoxyphenylazo)-1-naphthol	807 (293 K)	−4.5	−18.1	NMR/acetone-d_6	252–293	[42]
1-(4′-Methoxyphenylazo)-2-naphthol	−250 (293 K)	−3.1	−9.7	NMR/acetone-d_6	293–322	[42]
1-Phenylazo-2-naphthol	−471 (310 K)	−0.28	−0.90	NMR/CDCl$_3$	230–300	[45][a]
1-Phenylazo-2-naphthol	−435 (310 K)	−0.33	−0.70	NMR/CDCl$_3$	230–330	[46][a]
2-Phenylazo-1-naphthol	−743 (300 K)	−0.24	−1.77	NMR/CDCl$_3$	240–330	[47][a]
2,4-Bisphenylazo-1-naphthol	−631 (300 K)	−0.21	−1.50	NMR/CDCl$_3$	240–330	[47][a]
1-(4′-Fluorophenylazo)-2-naphthol	16.7 (310 K)	0.94	−3.13	NMR/CDCl$_3$	230–330	[43]
1-(2′-Fluorophenylazo)-2-naphthol	−160 (310 K)	0.91	−2.44	NMR/CDCl$_3$	230–330	[43]
2-(4′-Fluorophenylazo)-1-naphthol	−337 (310 K)	1.16	−2.53	NMR/CDCl$_3$	230–330	[43]
4-Phenylazo-1-naphthol-2-sulfonate (K salt)	−308 (298 K)	−11.0	−35.9	Vis/x(EtOH):0.1[b]	288–308	[44]
	724 (298 K)	−0.8	−5.0	Vis/x(t-BuOH):0.1[b]	288–308	[44]
	251 (298 K)	−3.5	−12.4	Vis/x(DMF):0.1[b]	288–308	[44]

[a] Thermodynamic parameters were calculated in the present study from the data of reference.

[b] Mole fraction of organic solvent in aqueous organic solvent.

data were added by the present authors using data provided by Lyčka et al. [45–47]. Reeves and Kaiser [44] used wider ranges of solvent compositions and reported variations in the values of enthalpy and entropy differences between two tautomers. The enthalpy differences decreased with an increase in the composition of organic solvent to a limiting value identical to the difference in the gaseous phase. The tautomerism becomes progressively less exothermic as organic solvent is added to the aqueous binaries [44]. In general, azo dyes exist as the HTs in polar solvents such as water, but this decreases gradually with an increase in the composition of organic solvents such as alcohol, dimethylformamide and dimethylsulfoxide. Several workers found some dyes which existed exclusively as the AT [48], and other dyes predominantly as the HT [9,10,14]; in organic solvents and aqueous organic solvents, they exist as a mixture of two tautomers [6–14,42–65]. The equilibrium constants, K_T, listed in Table 1, were at best order of 2, resulting in small differences in Gibbs free energy and enthalpy of formation between two tautomers. The AHT may exist within a range of heterocyclic tautomerism [15–21], as discussed below (cf. Section 3.3.2).

This fact may suggest small differences between two tautomers in their reaction with different reagents. AHT involves quantum-mechanical proton tunneling across a low barrier in a double well which is accompanied by electron transfer or a shift of a double bond [40]. This results in a small change in chemical structure but a large change in dipole moment.

One may find no large change in the molecular properties of two tautomers, although minor components of tautomerism can give rise to unusual reactivity in the case of nucleic acid bases. [66–73]

In the treatment of heterocyclic tautomerism, entropy changes have not been thoroughly elucidated. Karelson et al. [37,67] and Szafran et al. [74] considered that no large entropy changes should occur in heterocyclic tautomeric equilibria comprising single intramolecular proton transfer. These authors considered that a linear relationship existed between the logarithm of the tautomeric equilibrium constants, K_T, and enthalpy change:

$$\log K_T \cong -\Delta H_T/2.303RT \cong -\Delta H_T/1.364, \quad (1)$$

where ΔH_T (kcal mol^{-1}) denotes the difference in the standard enthalpies of two tautomers. Wong et al. [75] showed that the entropy term is considerably small. In other solvation modeling, many workers treated solvation effects in terms of the free energy of solvation without separating the entropy term [24–36,66,68–73]. In the present study, Eq. (1) is used to discuss AHT, although the entropy term listed in Table 1 may not correspond to these heterocylic tautomeric theories. The reason for the discrepancy remains to be examined.

3.3. Effect of solvation on tautomerism

3.3.1. Solvation effect on heterocyclic tautomerism

As mentioned above, many tautomeric equilibria exist in the unimolecular equilibria of some heterocycles and non-heterocycles, in which the various contributors differ in terms of bond connectivity. Typical hetrocycles are purine, pyridine and pyrimidine bases as the model compounds of nucleic acids. There is a tremendous number of papers on the tautomeric equilibria of nucleic acid pyrimidine and purine bases and their 1-methyl analogues, which have been summarized in reviews [15–21]. Katritzky and Karelson [67] showed that in almost all cases, uracil, thymine, cytosine and guanine exist predominantly in the keto form, whether it be in the crystalline state, in aqueous solution, in solutions of nonpolar solvents or in the gas phase. Contemporary advances in solvation modeling over the last three decades proved that tautomeric equilibria were quite sensitive to solvation or solvent effects and that minor components of tautomers, which might cause, for example, mutation in nucleic acid bases, were produced [68–73]. As an example, the predominance of the keto tautomer of nucleic acid bases in polar solvents over the enol tautomer in the gas phase was recently proved using a quantum-mechanical solvation model. On the other hand, a quantum-mechanical solvation model, an example of the most successful model, was developed using 1786 experimentally measured solvation free energies for 206 solutes in one or more of

90 solvents [27]. Two general parameterizations were carried out, one using the AM1 Hamiltonian (SM5.4/AM1) and another using the PM3 Hamiltonian (SM5.4/PM3). The final mean unassigned error for both the SM5.4/AM1 and SM5.4/PM3 parameterization was less than 0.5 kcal mol^{-1} over the entire data set of 1786 free energies of solvation in 90 organic solvents. Various solvent parameterizations for SM 5.4 have been developed till now.

These conclusions in the studies of heterocyclic tautomerism may be quite similar and applicable to those of the AHT of azo dyes.

3.3.2. Similarity between AHT and heterocyclic tautomerism

In order to confirm whether solvation effects AHT, MO PM5 calculations for the azo dyes listed in Table 1 were carried out for a series of related phenylazonaphthols. The dyes used were selected from the dyes reported [44,53–65] to elucidate the correlation between AHT and chemical structure. The substituents which were reported to have large effects on AHT were also examined. The enthalpy of formation, H_f, in both the gaseous phase and water, and the energy of solvation, ΔH_{sol} (the difference in the values of H_f in the two phases), for 4-phenylazo-1-naphthols and their 2-sulfonic acids, 2-phenylazo-1-naphthols and 1-phenylazo-2-naphthols are listed in Tables 2–5. Inspecting the values of H_f calculated results in the following conclusions:

1. The values of H_f of the ATs for all the dyes examined were lower than those of the HTs in the gaseous phase, indicating the higher stability of ATs than HTs, while in water, HTs have higher stability with some exceptions. (In many cases, since the differences in H_f between two tautomers are very small, two tautomers coexist even in the gaseous phase.);
2. The values of $-\Delta H_{sol}$ are in the range 15–110 kcal mol^{-1} for ATs and 20–110 kcal mol^{-1} for HTs, respectively;
3. The values of $-\Delta H_{sol}$ of HTs for almost all of the dyes examined are larger than those of ATs with some exceptions, if comparisons are made between tautomers for individual dyes.

Inspecting the values of H_f listed in Tables 2–5, the differences in H_f between two tautomers, in both the gaseous phase and water, were with a few

Table 2
Enthalpy of formation, H_f (kcal mol^{-1}), and energy of solvation, ΔH_{sol} (kcal mol^{-1}), of azo-hydrazone tautomers for 4-phenylazo-1-naphthol, estimated by semiempirical MO (MOPAC 2002, PM5 and COSMO) methods

Azo compound	Molecular weight	Azo tautomer			Hydrazone tautomer		
		H_f		$-\Delta H_{sol}$	H_f		$-\Delta H_{sol}$
		In gas phase	In water		In gas phase	In water	
4-Phenylazo-1-naphthol	248.284	68.74	51.16	17.58	72.56	47.22	25.34
4-(2′-Sulfophenylazo)-1-naphthol	328.324	−51.20	−97.87	46.67	−48.00	−96.91	48.91
4-(4′-Sulfophenylazo)-1-naphthol	328.324	−53.39	−101.83	44.38	−55.17	−107.32	51.24
4-(2′,4′-Disulfophenylazo)-1-naphthol	408.400	−171.80	−242.99	71.19	−169.04	−244.08	75.04
4-(2′,4′,6′-Trisulfophenylazo)-1-naphthol	488.458	−287.94	−381.26	93.32	−287.85	−375.93	88.08
4-(2′-Fluorophenylazo)-1-naphthol	266.274	24.16	4.73	19.43	26.93	4.21	22.72
4-(4′-Fluorophenylazo)-1-naphthol	266.274	22.89	4.22	18.67	27.32	0.979	26.34
4-(4′-Trifluoromethylphenylazo)-1-naphthol	316.282	−93.44	−113.59	20.15	−90.03	−116.61	26.58
4-(2′-Cyanophenylazo)-1-naphthol	273.293	100.07	78.29	21.78	103.44	77.11	26.33
4-(4′-Cyanophenylazo)-1-naphthol	273.293	99.69	78.00	21.69	103.43	74.65	28.78
4-(2′-Carboxyphenylazo)-1-naphthol	292.293	−18.90	−57.31	38.41	−16.11	−51.38	35.27
4-(4′-Carboxyphenylazo)-1-naphthol	292.293	−21.35	−49.95	28.60	−18.28	−53.97	35.69
4-(2′-Methoxyphenylazo)-1-naphthol	278.310	34.09	10.08	24.01	36.05	10.25	25.80
4-(4′-Methoxyphenylazo)-1-naphthol	278.310	31.72	9.67	22.05	36.16	6.43	29.74
4-(4′-Nitrophenylazo)-1-naphthol	293.281	64.91	38.21	26.70	68.01	33.62	34.39
4-(4′-Chlorophenylazo)-1-naphthol	282.729	60.86	43.52	17.34	64.84	40.78	24.06

exceptional cases ca. 20 kcal mol^{-1} and in almost all cases smaller than 4 kcal mol^{-1}. Since the A & HTs possess the same atomic composition and a proton tunneling system per an azo group with a shift of double bonds, the enthalpy differences may, in principle, not become large. However, their values indicate that the solvation energies may change widely for different solvents. Which

Table 3
Heat of formation, H_f (kcal mol^{-1}) and energy of solvation, ΔH_{sol} (kcal mol^{-1}), of azo-hydrazone tautomers for 4-phenylazo-1-naphthol-2-sulfonic acids, estimated by semiempirical MO method (MOPAC 2002, PM5 and COSMO methods)

Azo compound	Molecular weight	Azo tautomer			Hydrazone tautomer		
		H_f		$-\Delta H_{sol}$	H_f		$-\Delta H_{sol}$
		Gas phase	Water		Gas phase	Water	
4-Phenylazo-1-naphthol-2-sulfonic acid	328.342	−49.02	−91.94	42.92	−47.18	−111.84	64.66
4-(2′-Sulfophenylazo)-1-naphthol-2-sulfonic acid	408.400	−170.91	−233.79	62.88	−165.04	−228.48	63.44
4-(4′-Sulfophenylazo)-1-naphthol-2-sulfonic acid	408.400	−174.11	−239.70	65.59	−169.36	−255.48	86.12
4-(2′,4′-Disulfophenylazo)-1-naphthol-2-sulfonic acid	488.458	−292.66	−386.94	94.28	−286.22	−387.84	101.62
4-(2′,4′,6′-Trisulfophenylazo)-1-naphthol-2-sulfonic acid	568.516	−410.63	−521.36	110.73	−405.29	−516.36	110.07
4-(2′-Fluorophenylazo)-1-naphthol-2-sulfonic acid	346.332	−93.17	−134.14	40.97	−87.21	−127.77	40.56
4-(4′-Fluorophenylazo)-1-naphthol-2-sulfonic acid	346.332	−91.27	−134.68	43.41	−88.64	−129.10	40.46
4-(4′-Trifluoromethylphenylazo)-1-naphthol-2-sulfonic acid	396.340	−210.55	−256.44	45.89	−209.40	−274.02	64.62
4-(2′-Cyanophenylazo)-1-naphthol-2-sulfonic acid	353.352	−16.15	−61.54	45.39	−8.96	−50.87	41.91
4-(4′-Cyanophenylazo)-1-naphthol-2-sulfonic acid	353.352	−13.89	−54.67	40.78	−12.42	−53.54	41.12
4-(2′-Carboxyphenylazo)-1-naphthol-2-sulfonic acid	372.352	−135.99	−188.85	52.86	−133.62	−177.11	43.49
4-(4′-Carboxyphenylazo)-1-naphthol-2-sulfonic acid	372.352	−136.58	−188.37	51.79	−133.71	−181.48	47.77
4-(2′-Methoxyphenylazo)-1-naphthol-2-sulfonic acid	358.368	−89.84	−135.39	45.55	−88.49	−149.87	61.38
4-(4′-Methoxyphenylazo)-1-naphthol-2-sulfonic acid	358.368	−85.99	−132.92	46.93	−84.69	−152.74	68.05
4-(4′-Nitrophenylazo)-1-naphthol-2-sulfonic acid	373.339	−56.71	−104.53	47.82	−51.01	−115.93	64.92
4-(4′-Chlorophenylazo)-1-naphthol-2-sulfonic acid	362.787	−53.45	−94.12	40.67	−50.90	−87.94	37.04

Table 4
Enthalpy of formation, H_f (kcal mol^{-1}), and energy of solvation, ΔH_{sol} (kcal mol^{-1}), of azo-hydrazone tautomers for 2-phenylazo-1-naphthols, estimated by semiempirical MO method (MOPAC 2002, PM5 and COSMO methods)

Azo compound	Molecular weight	Azo tautomer			Hydrazone tautomer		
		H_f		$-\Delta H_{sol}$	H_f		$-\Delta H_{sol}$
		In gas phase	In water		In gas phase	In water	
2-Phenylazo-1-naphthol	248.284	66.36	51.09	15.27	68.54	48.52	20.02
2-(2′-Sulfophenylazo)-1-naphthol	328.324	−52.88	−89.87	36.99	−48.13	−88.64	40.51
2-(4′-Sulfophenylazo)-1-naphthol	328.324	−54.91	−97.00	42.09	−52.54	−98.59	46.04
2-(2′,4′-Disulfophenylazo)-1-naphthol	408.400	−173.62	−235.05	61.43	−167.94	−243.86	75.92
2-(2′,4′,6′-Trisulfophenylazo)-1-naphthol	488.458	−287.92	−372.27	84.35	−282.55	−370.79	88.24
2-(2′-Fluorophenylazo)-1-naphthol	266.274	21.17	4.95	16.22	25.46	4.57	20.89
2-(4′-Fluorophenylazo)-1-naphthol	266.274	20.81	4.25	16.56	23.37	2.06	21.31
2-(4′-Trifluoromethylphenylazo)-1-naphthol	316.282	−95.49	−113.39	17.90	−92.30	−115.49	23.19
2-(2′-Cyanophenylazo)-1-naphthol	273.293	97.96	79.14	18.82	102.46	78.89	23.57
2-(4′-Cyanophenylazo)-1-naphthol	273.293	97.60	78.06	19.54	100.82	75.77	25.05
2-(2′-Carboxyphenylazo)-1-naphthol	292.293	−19.42	−51.42	32.00	−16.59	−54.69	38.10
2-(4′-Carboxyphenylazo)-1-naphthol	292.293	−23.48	−48.74	25.26	−20.43	−52.02	31.59
2-(2′-Methoxyphenylazo)-1-naphthol	278.310	31.84	10.81	21.03	33.99	8.39	25.60
2-(4′-Methoxyphenylazo)-1-naphthol	278.310	29.50	10.49	19.01	33.38	7.90	25.48
2-(4′-Nitrophenylazo)-1-naphthol	293.281	62.83	38.38	24.45	65.97	36.27	29.70
2-(4′-Chlorophenylazo)-1-naphthol	282.729	58.65	43.52	15.13	62.18	41.36	20.82

Table 5
Enthalpy of formation, H_f (kcal mol^{-1}), and energy of solvation, ΔH_{sol} (kcal mol^{-1}), of azo-hydrazone tautomers for 1-phenylazo-2-naphthols, estimated by semiempirical MO method (MOPAC 2002, PM5 and COSMO methods)

Azo compound	Molecular weight	Azo tautomer			Hydrazone tautomer		
		H_f		$-\Delta H_{sol}$	H_f		$-\Delta H_{sol}$
		In gas phase	In water		In gas phase	In water	
1-Phenylazo-2-naphthol	248.284	67.59	51.68	15.91	71.68	47.84	23.84
1-(2′-Sulfophenylazo)-2-naphthol	328.324	−51.72	−85.30	33.58	−44.98	−86.81	41.83
1-(4′-Sulfophenylazo)-2-naphthol	328.324	−53.95	−103.68	49.73	−56.36	−104.08	47.72
1-(2′,4′-Disulfophenylazo)-2-naphthol	408.400	−172.70	−240.36	67.66	−166.74	−243.50	76.76
1-(2′,4′,6′-Trisulfophenylazo)-2-naphthol	488.458	−286.15	−368.64	82.49	−284.54	−373.09	88.55
1-(2′-Fluorophenylazo)-2-naphthol	266.274	22.54	6.21	16.33	27.56	4.60	22.96
1-(4′-Fluorophenylazo)-2-naphthol	266.274	22.74	4.06	18.68	22.95	−2.15	25.10
1-(4′-Trifluoromethylphenylazo)-2-naphthol	316.282	−94.33	−111.67	17.34	−90.46	−116.22	25.76
1-(2′-Cyanophenylazo)-2-naphthol	273.293	99.12	79.72	19.40	104.69	77.41	27.28
1-(4′-Cyanophenylazo)-2-naphthol	273.293	98.73	78.66	20.07	102.90	75.15	27.75
1-(2′-Carboxyphenylazo)-2-naphthol	292.293	−18.17	−52.68	34.51	−15.14	−52.14	37.00
1-(4′-Carboxyphenylazo)-2-naphthol	292.293	−22.57	−50.09	27.52	−18.70	−53.77	35.07
1-(2′-Methoxyphenylazo)-2-naphthol	278.310	32.99	12.03	20.96	35.90	8.52	27.38
1-(4′-Methoxyphenylazo)-2-naphthol	278.310	30.67	10.26	20.41	35.30	7.13	28.17
1-(4′-Nitrophenylazo)-2-naphthol	293.281	63.82	39.72	24.10	67.67	35.45	32.22
1-(4′-Chlorophenylazo)-2-naphthol	282.729	59.82	44.12	15.70	64.05	40.63	23.42

Table 6
Effects of sulfonic acid (S) groups and substituents of 4-phenylazo-1-naphthols on H_f and solvation or AHT (kcal mol^{-1})

Original dye	4-phenylazo-1-naphthol						4-phenylazo-1-naphthol-2-sulfonic acid					
Tautomer	Azo			Hydrazone			Azo			Hydrazone		
Addition of substituents	Changes[a] in H_f		$\Delta\Delta H_{sol}$[a]	Changes[a] in H_f		$\Delta\Delta H_{sol}$[a]	Changes[a] in H_f		$\Delta\Delta H_{sol}$[a]	Changes[a] in H_f		$\Delta\Delta H_{sol}$[a]
	In gas	In water		In gas	In water		In gas	In water		In gas	In water	
2-S	−117.8	−143.1	25.3	−121.0	−158.1	37.0						
2′-S	−119.9	−149.0	29.1	−120.6	−144.1	23.6	−121.9	−141.9	20.0	−117.9	−116.6	−1.22
4′-S	−122.1	−153.0	30.9	−127.7	−154.5	26.8	−125.1	−147.8	22.7	−122.2	−143.6	21.5
2S (2′,4′-)	−240.5	−294.2	53.6	−241.6	−291.3	49.7	−243.6	−295.0	51.4	−239.0	−276.0	37.0
3S[b]	−356.7	−432.4	75.7	−360.4	−423.2	62.7	−361.6	−429.4	66.6	−358.1	−404.5	45.4
4S[b]	−479.4	−572.5	93.2	−477.9	−563.6	85.7						
2′-F	−44.6	−46.4	1.85	−45.6	−43.0	−2.62	−44.2	−42.2	−1.95	−40.0	−15.9	−24.1
4′-F	−45.9	−43.0	−1.09	−45.2	−46.2	1.00	−42.3	−42.7	0.49	−41.5	−17.3	−24.2
4′-CF_3	−162.2	−164.8	−2.57	−162.59	−163.83	1.24	−161.5	−164.5	2.97	−162.2	−162.2	−0.04
2′-CN	31.3	27.1	−4.20	30.9	29.9	−0.99	−32.9	−30.4	−2.47	−38.2	−61.0	22.8
4′-CN	31.0	26.8	4.11	30.9	27.4	3.44	−35.1	−37.3	2.14	−34.8	−58.3	23.5
2′-COOH	−87.6	−108.5	20.8	−88.7	−98.6	9.93	−87.0	−96.9	9.94	−86.4	−65.3	−21.2
4′-COOH	−90.1	−101.1	11.0	−90.8	−101.2	10.4	−87.6	−96.4	8.87	−86.5	−69.6	−16.9
2′-OMe	−34.7	−41.0	−14.2	−36.5	−37.0	−0.46	−40.8	−43.5	2.63	−41.3	−38.0	−3.28
4′-OMe	−37.0	41.5	−4.47	−36.4	−40.8	−4.40	−37.0	−41.0	4.01	−37.5	−40.9	3.39
4′-NO_2	−3.83	−12.95	9.12	−4.55	−13.60	9.05	−7.69	−12.6	4.90	−3.83	−4.09	0.260
4′-Cl	−7.88	−7.64	−0.24	−7.72	−6.44	−1.28	−4.43	−2.18	−2.25	−3.72	23.9	−27.6

[a] Calculated from data listed in Tables 2 and 3. $\Delta\Delta H_{sol} = (\Delta H_{sol}$ of original dye) $-$ ΔH_{sol} of dye with corresponding substituent(s).

[b] 3S = 2′,4′,6′-; 4S = 2,2′,4′,6′-

Table 7
Effects of sulfonic acid (S) groups and substituents of 2-phenylazo-1-naphthols and 1-phenylazo-2-naphthols on H_f and solvation or AHT (kcal mol^{-1})

Original dye	2-phenylazo-1-naphthol						1-phenylazo-2-naphthol					
Tautomer	Azo			Hydrazone			Azo			Hydrazone		
Addition of substituents	Changes[a] in H_f		$\Delta\Delta H_{sol}$[a]	Changes[a] in H_f		$\Delta\Delta H_{sol}$[a]	Changes[a] in H_f		$\Delta\Delta H_{sol}$[a]	Changes[a] in H_f		$\Delta\Delta H_{sol}$[a]
	In gas	In water		In gas	In water		In gas	In water		In gas	In water	
2′-S	−119.2	−141.0	21.7	−116.7	−137.2	20.5	−119.3	−137.0	17.7	−116.7	−134.7	18.0
4′-S	−121.3	−148.1	26.8	−121.1	−147.1	26.0	−121.5	−155.4	33.9	−128.0	−151.9	23.9
2S (2′-, 4′-)	−240.0	−286.1	46.2	−236.5	−292.4	55.9	−240.3	−292.0	51.8	−238.4	−291.3	52.9
3S[b]	−354.3	−423.4	69.1	−351.1	−419.3	68.2	−353.7	−420.3	66.6	−356.2	−148.9	64.7
2′-F	−45.2	−46.1	0.950	−43.1	−44.0	0.870	45.1	45.5	0.42	44.1	43.2	0.88
4′-F	−45.6	−46.8	1.29	−45.2	−46.5	1.29	44.9	47.6	2.77	48.7	50.0	1.26
4′-CF_3	−161.9	−164.5	2.63	−160.8	−164.0	3.17	−161.9	−163.4	1.43	−162.1	−164.1	1.92
2′-CN	31.6	28.1	3.55	33.9	30.4	3.55	31.5	28.0	3.49	33.0	29.6	3.44
4′-CN	31.2	27.0	4.27	32.3	27.3	5.03	31.1	27.0	4.16	31.2	27.3	3.91
2′-COOH	85.8	102.5	16.7	82.8	105.8	18.1	85.8	104.4	18.6	86.8	100.0	13.2
4′-COOH	89.8	99.8	9.99	89.0	100.5	11.6	90.2	101.8	11.6	90.4	101.6	11.2
2′-OMe	34.5	61.9	5.76	34.6	40.1	5.58	34.6	39.7	5.05	35.8	39.3	3.54
4′-OMe	36.9	40.6	3.74	35.2	40.6	5.46	36.9	41.4	4.50	36.4	40.7	4.33
4′-NO_2	3.53	12.7	9.18	2.57	12.3	9.68	3.77	12.0	8.19	4.01	12.4	8.38
4′-Cl	7.71	7.57	0.14	6.36	7.16	0.80	7.77	7.56	0.21	7.63	7.21	0.42

[a] Calculated from data listed in Tables 4 and 5. $\Delta\Delta H_{sol} = (\Delta H_{sol}$ of original dye) − ΔH_{sol} of dye with corresponding substituent(s).
[b] 3S = 2′-, 4′-,6′-; 4S = 2-, 2′-, 4′-, 6′

tautomer has higher stability in a solvent may depend upon various factors such as the solvent used and the substituents in the azo dyes.

These results imply that the nature of AHT is essentially similar to that of the tautomerism of heterocycles and that the nature of the AHT observed so far can also be described through MO calculation, although the solvation energy of sulfonated azo dyes is extraordinarily large. Besides the general features summarized above, several exceptional substituent effects exist which result in the higher stability of ATs in water and the higher stability of HTs in the gaseous phase, examples of which are mentioned below.

Irrespective of the tautomers, introducing a sulfonic acid group into a molecule resulted in a very large reduction in the values of H_f or a very large increase in the values of$-\Delta H_{sol}$. When one analyses the solvation effects on the tautomerism using the MO calculations, one must first take the influence of sulfonic acid groups into consideration.

3.4. *Effect of substituents on H_f and ΔH_{sol}*

3.4.1. *Analysis of the substituent effects for phenylazonaphthols whose coupling component contains no sulfonate group*

Since the effects of sulfonic acid groups on the values of H_f were very large, the substituent effect other than sulfonate groups was analysed initially. The values of H_f for A & H Ts of phenylazonaphthols calculated using a PM5 method are shown in Tables 2–5. How the addition of substituents resulted in the changes of H_f as well as in those of ΔH_{sol} is summarized in Tables 6 and 7, although the existence of 2-sulfonic acid groups in 1-naphthols has a specific effect an the changes. Differences in solvation energy with substituents are shown in Fig. 1, although no plots were made for 2′-fluoro and 2′-cyano groups because of the small change in the substituent effect with the position of substitution.

Common features in the changes of H_f and ΔH_{sol} of the two tautomers for four series of dyes by the addition of each substituent, which are clearly illustrated in Fig. 1, are as follows:

1. The size of the changes in H_f and ΔH_{sol} of the two tautomers imparted by substituents was similar among the four series of dyes with some exceptions, although the absolute values of the changes varied with the substituents;
2. Large deviations from the common values of the changes were found in the addition of sulfonic acid groups, especially in those of the 2′-sulfonate groups against the azo group;
3. The deviations were especially large for virtually all of the substituents in the series of 4-(substituted phenylazo)-1-naphthol-2-sulfonic acids, an introduction of the sulfonate group into the naphthalene ring next to the hydroxy group (cf. Section 3.5);
4. The addition of 2′- and 4′-fluoro, 4′-chloro, and trifluoromethyl groups resulted in very small changes of ΔH_{sol}, which were common for the four series of dyes;
5. 2′-Cyano, 4′-cyano, 2′-methoxy, 4′-methoxy, and 4′-carboxy groups resulted in

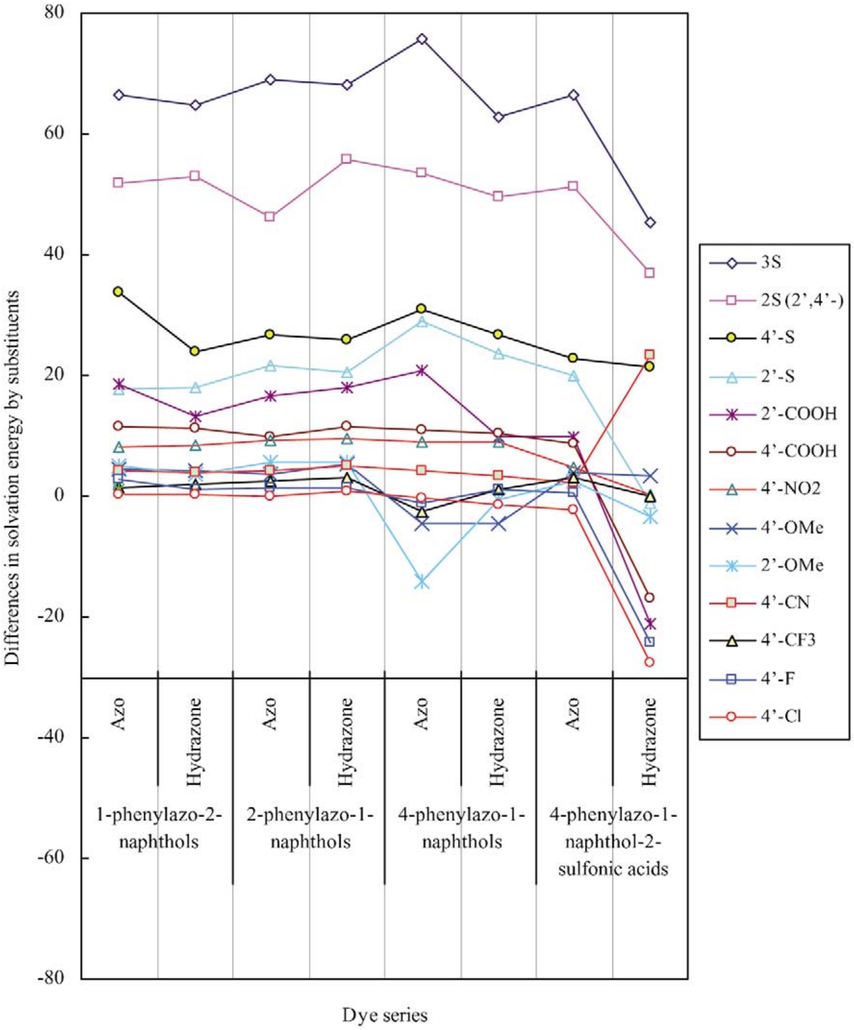


Fig. 1. Effects of substituents on $\Delta\Delta H_{sol}$, differences in ΔH_{sol} by substituents, estimated by MOPAC 2002, PM5 and COSMO methods (cf. Tables 6 and 7).

small changes of ΔH_{sol} irrespective of the original dyes and tautomers, although 2′- and 4′-cyano groups in 4-phenylazo-1-naphthol-2-sulfonic acids exhibited large deviations in the reverse direction composed by other substituents;

6. The addition of 4′-carboxy and 4′-nitro groups resulted in moderate changes of ΔH_{sol} irrespective of the dyes and tautomers;
7. The effects of the 2′-carboxy group were small in terms of changes in ΔH_{sol} but changed drastically with the dyes as well as with the tautomers;
8. The effects of the 4′-nitro groups were common for the dyes without sulfonate groups, but in 4-(substituted phenylazo)-1-naphthol-2-sulfonic acids these effects were small and varied between tautomers;

Since the enthalpies of formation and solvation for two tautomers and the changes in the solvation energies between two tautomers varied with substituents and moreover they were dependent upon solvent, the AHT of azo dyes became complicated. The present analysis suggests that dyes with substituents which promote ATs may have higher stability than HTs, although other conditions have effects on AHT also.

3.4.2. Analysis of phenylazonaphthols with a sulfonic acid group

Reeves and Kaiser [44] reported the order of the stability of the HT's of 4-(substituted phenylazo)-1-naphthol-2-sulfonic acids in an organic solvent as the substituent effects on AHT without showing the name of the solvent as follows:

$$\begin{aligned}&p\text{-nitro} > p\text{-sulfo} \approx p\text{-trifluoromethyl} >\\&\text{no substituent} > p\text{-methoxy}\end{aligned} \qquad (2)$$

When the differences (kcal mol^{-1}) in H_{f} between two tautomers in the gaseous phase and those in water are chosen from Table 3, they do not correspond to this order (1). The differences in H_{f} correspond to the relative stability of HTs, a larger difference indicating higher stability. Since the authors gave no solvent name for the order (1), no detailed discussion is possible. Antonov et al. [53–59] reported that the tautomeric equilibrium position of AHT was specific to the combination of dye and solvent and that there was no correlation between K_{T} and the dielectric constant of the solvents [44]. A large change in the value of K_{T} with mole fraction of organic solvent was also observed in mixture solutions of water and organic solvents [44]. If one wants a good correlation between using MO methods, one must calculate the enthalpy of formation with a precision smaller than one kcal in the solvent, which is probably beyond the precision of the PM5 method. In the solvation modeling of heterocyclic chemistry, solvent-specific parameterizations were made to treat the correlation quantitatively [27].

Besides the three terms mentioned above (cf. Section 3.3.2), when dyes containing one sulfonic acid group in a naphthalene nucleus are considered (cf. Table 3), several exceptional features were found:

1. The values of $-\Delta H_{\mathrm{sol}}$ of the HTs are smaller than those of the ATs for dyes with the following substituents: 2′,4′,6′-trisulfonate (the smallest difference), 2′-cyano, 2′- and 4′-carboxy, and 4′-chloro;
2. Since the differences in $-\Delta H_{\mathrm{sol}}$ between two tautomers are relatively small, although the values of $-\Delta H_{\mathrm{sol}}$ for the HTs are larger than those for ATs for many dyes, the ATs for some dyes have higher stability than the HTs in water, depending upon the differences in H_{f} in the gaseous phase. The dyes which exhibit such properties have the following substituents: 2′-sulfonate, 2′- and 4′-fluoro and 4′-cyano;
3. 4-(Substituted phenylazo)-1-naphthol-2-sulfonic acids have a large possibility that the ATs have a higher stability than the HTs in water than the other series of dyes, whose results are listed in Tables 2, 4 and 5 (for the other cases, see Section 3.5).

Reeves and Kaiser [44] did not explain why they selected this series of dyes. According to them, introducing electron-withdrawing substituents into 4-phenyl nucleus of 4-(substituted phenylazo)-1-naphthol-2-sulfonic acids resulted in HTs even in the gaseous phase. But the analyses of the results of MO calculations illustrated that solvation has a large effect on the formation of HTs in polar solvents such as water. Substituents which promote solvation such as sulfonate groups showed a more marked tendency to bring about HTs than electron-withdrawing substituents such as nitro groups.

Since the energy of solvation for HTs in a polar solvent is usually larger than that for ATs and the energy barrier of AHT is small, azo dyes which carry out AHT may have a tendency to become HTs in polar solvents by solvation and in some cases may exist as a mixture of both tautomers.

Solvation mechanisms in hetrocyclic chemistry have been thoroughly studied using various models employing diverse methods [22–37]. For example, Luque et al. [30] determined the free energy of solvation by summing up three terms: cavitation, van der Waals and electrostatic, while Hawkins et al. [32] the determined standard-state free energy of solvation using two terms; namely the change in the electronic internal energy by solvation including electric polarization of solvent and the solvation free energy effects such as cavitation, dispersion, and solvent-structure rearrangement. Compared with heterocycles, the azo dyes examined possess sulfonate groups which have very large solvation energy. Moreover, the sulfonate groups substituted at certain positions have a profound effect on AHT, as mentioned above.

3.4.3. *Effect of sulfonate groups in phenylazonaphthols*

The addition of sulfonate groups to azo dyes which possess very small substituent effects on the chemical reactivity resulted in the largest decrease in H_f among substituents in the four series of dyes examined. The position of substituent also had a profound effect on solvation energies, ΔH_{sol}, although the reason for the position effect has not been clarified.

The counter ions of the sulfonate groups caused a considerable change in the values of H_f. Sodium sulfonate reduced the values of H_f lower than those of sulfonic acids by 30–50 kcal mol^{-1}. Since the sodium sulfonate groups made many molecules uncalculable especially using the PM5/COSMO method, the sulfonate groups of all the dyes were calculated using the sulfonic acid form, although sodium sulfonate might simulate better the real energetically.

Common features of the addition of sulfonate groups are summarized as follows:

1. Addition of sulfonate groups results in the largest reduction in H_f and ΔH_{sol} of the substituents examined. The position of the groups in the original dye structure influences this reduction.
2. Other sulfonate groups have common effects in the change of H_f and ΔH_{sol}.
3. 2′-Sulfonate groups in the phenyl ring of phenylazonaphthols exhibit exceptional behaviour in that AT's have higher stability in water than HTs, depending on the difference in H_f between the two tautomers in the gaseous phase;
   (a) $\Delta\Delta H_{sol}$ of the ATs is larger than that of HTs by 5 kcal mol^{-1} for 4-phenylazo-1-naphthol, 1 kcal mol^{-1} for 2-phenylazo-1-naphthol, and nearly equal each other for 1-phenylazo-2-naphthol, but for 4-phenylazo-1-naphthol-2-sulfonic acid.
   (b) Further introduction of the 4′-sulfonate group into a phenyl ring makes $\Delta\Delta H_{sol}$ of the ATs larger by 5 kcal mol^{-1} than HTs for 4-phenylazo-1-naphthol, by more than 10 kcal mol^{-1} for 2-phenylazo-1-naphthol and 4-phenylazo-1-naphthol-2-sulfonic acid but for 1-phenylazo-2-naphthol.

Since there are other features in the results shown in Tables 2–7, the present analyses are not sufficient to derive a complete description of the substituent effects of sulfonate groups on AHT, although the selection of samples examined to obtain the answers may also be incomplete. In the results reported so far, essential problems with the assignment of the two tautomers may exist, since dipole moment, calculated in the present study (not listed) was often changed between in the gaseous phase and in water. Of course, since MOPAC 2002 (PM5 and COSMO methods) may not always give the right result, the AHT should be reviewed carefully.

Moreover, the present MO calculation was carried out for molecules in both the gaseous phase and in water. NMR measurements to determine the AHT were made in almost all cases in organic solvents. Since there should be some shift in AHT caused by a change of solvent, one must discuss carefully the solvent effects on AHT. The AHT in an organic solvent such as DMSO and chloroform and in aqueous organic solvents should be different from that in water, since in general the differences between two tautomers in H_f and the solvation energy are small compared with the differences between the media.

3.5. *Specific effect of sulfonate groups, which result in ATs with higher stability in water*

In order to analyse further the effect of sulfonate groups on the AHT of phenylazonaphtholes and to find the specific position of sulfonate groups which have the promotion effect on AT's, four kinds of naphthalene sulfonic acids with *o*-, *p*-sulfonate-, *o*-,*p*-disulfonate- and *p*-chloro-phenylazo groups were examined using PM5 and COSMO methods. The results are listed in Table 8; analysis by the same method as that of Tables 6 and 7, are illustrated in Fig. 2.

No specific effect of 3-, 6-sulfonate and 3,6-disulfonate groups on the solvation energies of phenylazonaphthols to promote the existence of ATs in water was found, unlike the 2-sulfonate group of 4-phenylazo-1-naphthols. Absence of substituent effect by 4-chloro groups on the phenylazo groups confirmed also this fact as shown in Fig. 2.

Specific effects of 2′-sulfonate groups, on the other hand, which resulted in ATs with higher stability in water than HTs, are clearly shown in Fig. 2 as the differences in the solvation energy between two tautomers. They are the same as those shown in Fig. 1. 2′-sulfonate groups displayed

Table 8
Enthalpy of formation, H_f (kcal mol^{-1}) and energy of solvation, ΔH_{sol} (kcal mol^{-1}), of azo-hydrazone tautomers for 1-phenylazo-2-naphthol sulfonic acids and 2-phenylazo-1-naphthol sulfonic acids, estimated by semiempirical MO method (MOPAC 2002, PM5 and COSMO methods)

Azo compound	Molecular weight	Azo tautomer			Hydrazone tautomer		
		H_f		$-\Delta H_{sol}$	H_f		$-\Delta H_{sol}$
		Gas phase	Water		Gas phase	Water	
1-Phenylazo-2-naphthol-3-sulfonic acids							
1-Phenylazo-2-naphthol-3-sulfonic acid	328.342	−55.66	−105.97	47.16	−50.77	−108.57	57.80
1-(4′-Chlorophenylazo)-2-naphthol-3-sulfonic acid	362.787	−59.17	−109.25	50.08	−57.80	−115.60	57.80
1-(2′-Sulfophenylazo)-2-naphthol-3-sulfonic acid	408.400	−176.86	−243.20	66.34	−166.18	−238.47	72.29
1-(4′-Sulfophenylazo)-2-naphthol-3-sulfonic acid	408.400	−176.04	−254.24	78.20	−171.90	−253.44	81.54
1-Phenylazo-2-naphthol-6-sulfonic acids							
1-Phenylazo-2-naphthol-6-sulfonic acid	328.342	−55.78	−100.60	44.82	−50.70	−103.27	52.57
1-(4′-Chlorophenylazo)-2-naphthol-6-sulfonic acid	362.787	−62.34	−106.81	44.47	−57.72	−108.67	50.95
1-(2′-Sulfophenylazo)-2-naphthol-6-sulfonic acid	408.400	−169.84	−243.85	74.01	−167.63	−237.27	69.64
1-(4′-Sulfophenylazo)-2-naphthol-6-sulfonic acid	408.400	−175.36	−244.01	68.65	−165.61	−247.44	79.83
1-Phenylazo-2-naphthol-3,6-disulfonic acids							
1-Phenylazo-2-naphthol-3,6-disulfonic acid	408.400	−176.06	−251.37	75.31	−171.75	−256.29	84.54
1-(4′-Chlorophenylazo)-2-naphthol-3,6-disulfonic acid	442.845	−183.20	−258.69	75.49	−178.50	−262.67	84.17
1-(2′-Sulfophenylazo)-2-naphthol-3,6-disulfonic acid	488.458	−295.42	−381.47	86.05	−287.86	−390.51	102.65
1-(4′-Sulfophenylazo)-2-naphthol-3,6-disulfonic acid	488.458	−295.45	−397.69	102.24	−291.16	−403.35	112.19
2-Phenylazo-1-naphthol-3-sulfonic acids							
2-Phenylazo-1-naphthol-3-sulfonic acid	328.342	−51.20	−93.68	42.48	−47.75	−94.34	46.59
2-(4′-Chlorophenylazo)-1-naphthol-3-sulfonic acid	362.787	−58.67	−101.03	42.36	−54.90	−101.62	46.72
2-(2′-Sulfophenylazo)-1-naphthol-3-sulfonic acid	408.400	−172.77	−239.88	67.11	−167.47	−233.07	65.60
2-(4′-Sulfophenylazo)-1-naphthol-3-sulfonic acid	408.400	−171.18	−242.02	70.84	−170.73	−245.11	74.38

promotion effects on AT's in water as well as in the case of 4-phenylazo-1-naphthols (cf. Fig. 1) except for 1-phenylazo-2-naphthol-3,6-disulfonic acid; 4′-sulfonate groups reduced the promotion effects in all the cases. However, in the case of 1-phenylazo-2-naphthol-3-sulfonic acids, 4′-sulfonate groups reversed the effect of 2′-sulfonate groups when used together with 2′-sulfonate groups, even though 4′-sulfonate groups had a small promotion effect when being added singly. In the present study, since no essential reason to different solvation energies to the two tautomers was found, the effects of the addition of sulfonate groups and those of their position were analysed qualitatively.

3.5.1. Some examples of reactive azo dyes with o-sulfonate groups

Some commercial reactive dyes are hydroxyazo dyes with *o*-sulfophenylazo groups. As a result of the above discussion, in such dyes, their ATs may have higher stability in water than their HTs, although many of them are believed to exist as HTs.

As typical examples of such dyes the enthalpy of formation of two tautomers for various, originally active, partially active and completely hydroxidized species for C.I. Reactive Red 1, Red 194 and Red 227 were examined. The results are listed in Table 9. ATs for almost all the species had a higher stability than the HTs in water and as in the gaseous phase except for the active and partially active species of C.I. Reactive Red 227 in water. The dyes examined had larger (minus) values of solvation energy with some exceptions.

The present MO PM5 calculation indicated that many reactive azo dyes having *o*-sulfophenylazo groups may exist as ATs in water, although this speculation may not be in agreement with the result reported so far. Bredereck

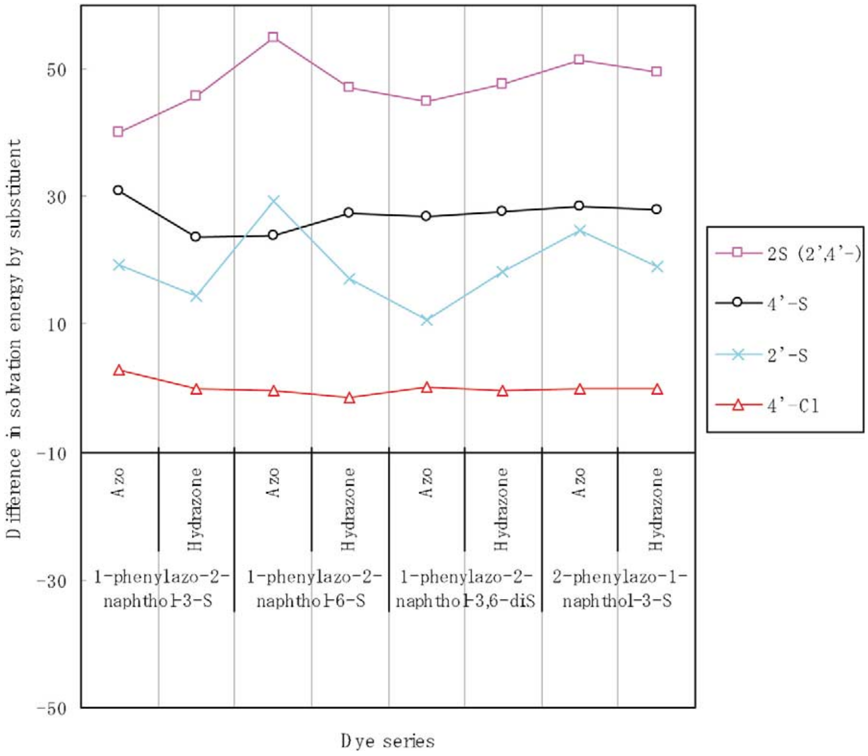


Fig. 2. Effects of substituents on $\Delta\Delta H_{sol}$, differences in ΔH_{sol} by substituents, estimated by MOPAC 2002, PM5 and COSMO methods (cf. Tables 6 and 7).

and Schumacher [76–79] investigated the properties such as light fastness as well as reactivities to hydrogen peroxide and hypochlorite for a series of derivatives of C.I. Reactive Red 227. The substituent effects of diazo components for the derivatives of C.I. Reactive Red 227 on AHT were also re-examined. 2′-Sulfonate, 4′-sulfonate and hydrogen were selected to re-examine substituent effects of diazo compounds. The enthalpy of formation in the gaseous phase and in water and the solvation energies are shown in the lower part of Table 9. Clearly, 2′-sulfonate substituent was exceptional in that the ATs of the dye carrying this substituent resulted in higher stability in water than HT's.

According to Bredereck and Schumacher [76–78], *o*-sulfonate derivative of this dye showed exceptional behaviour in terms of the relationship between λ_{max} and Hammett σ-constant [76] and in the relationship between pK_a and the relative rate constant of reaction with hypochlorite [77] and hydrogen peroxide [78], although this dye alone was not always exceptional. The present authors suspect that the predominant reason why this dye was the exception is because it exists as the AT's in water. However, a detailed explanation is still required.

4. Summary

In the field of heterocyclic chemistry, there are various tautomeric equilibria of model heterocyclic compounds such as nucleic acid bases and heterocycles of amino acids. The equilibria have been shown to be quite sensitive to solvation effects. The enthalpy of formation of the A & H Ts of hydroxyazo dyes in both the gaseous phase and water and the solvation energies as a result were estimated by semi-empirical molecular orbital PM5 and COSMO methods.

From quantum-mechanical analyses of substituent effects on the enthalpies of formation of hydroxyazo dyes, the following conclusions were derived:

1. Enthalpy differences between two tautomers were less than 20 kcal mol^{-1} and in almost cases smaller than 4 kcal mol^{-1},

Table 9
Enthalpy of formation, H_f (kcal mol^{-1}) and energy of solvation, ΔH_{sol} (kcal mol^{-1}), of A & H T's for 8*N*-arylamino-2-(substituted phenylazo)-1-naphthol-3,6-disulfonic acids, estimated by semiempirical MO (PM5 and COSMO) method

Substituent	M.W.	Azo tautomer			Hydrazone tautomer		
		H_f		$-\Delta H_{sol}$	H_f		$-\Delta H_{sol}$
		Gas phase	Water		Gas phase	Water	
8*N*-Substituted amino-2-(2′-sulfophenylazo)-1-Naphthol-3,6-disulfonic acid							
8*N*-2,4-Dioxy-6-triazinyl	614.533	−332.51	−451.06	118.55	−331.24	−443.19	111.95
8*N*-2,4-Dichloro-6-triazinyl[a]	651.424	−249.58	−351.63	102.05	−244.28	−354.74	110.46
8*N*-2-Chloro-4-oxy-6-triazinyl	632.978	−291.08	−392.51	101.43	−290.40	−398.51	108.11
8*N*-2-(3-β-Oxyethylsulfonylanilino)-4-oxy-6-triazinyl	797.757	−381.24	−505.47	124.23	−378.86	−501.73	122.87
8*N*-2-(3-β-Oxyethylsulfonylanilino)-4-chloro-6-triazinyl	816.203	−344.19	−485.08	140.89	−337.46	−474.36	136.90
8*N*-2-(3-Vinylsulfonylanilino)-4-chloro-6-triazinyl[b]	798.188	−283.47	−395.52	112.05	−273.67	−388.17	114.50
8*N*-2-(4-β-Oxyethylsulfonylanilino)-4-oxy-6-triazinyl	797.757	−387.17	−518.93	131.76	−379.96	−506.45	126.49
8*N*-2-(4-β-Oxyethylsulfonylanilino)-4-chloro-6-triazinyl	816.203	−347.28	−468.06	120.78	−337.87	−464.29	126.72
8*N*-2-(4-Vinylsulfonylanilino)-4-chloro-6-triazinylamino-2-(substituted phenylazo)-1-naphthol-3,6-disulfonic acid							
No substituent	718.129	−161.15	−267.57	106.42	−157.25	−268.75	111.50
2′-Sulfo[c]	798.188	−283.47	−395.52	112.05	−273.67	−388.17	114.50
4′-Sulfo	798.188	−279.98	−410.03	130.05	−276.05	−419.97	143.92

[a] C.I. Reactive Red 1.

[b] C.I. Reactive Red 194.

[c] C.I. Reactive Red 227.

which corresponds to the population ratio of larger than 10^{-3} at 25 °C;

2. Enthalpies of formation for ATs are in many cases larger than those for HTs in the gas phase, while in water the former become smaller than the latter, with some exceptions;
3. The general principles of heterocyclic tautomerism hold in AHT. The position of the mobile equilibrium of AHT is attributed to the solvation energy or solvent effects as in the case of heterocyclic tautomerism;
4. Substituent effects on AHT are not controlled by the electron-withdrawing property of a substituent but instead by solvation energies imparted by the substituents;
5. Sulfonic acid groups in the diazo component have a great deal of solvation energy, but the specific position such as *o*- to the azo group results in ATs, which possess higher stability than HTs in water;
6. Sulfonate groups at specific positions in the naphthalene ring have special effects in terms of solvation of ATs in water;
7. Besides sulfonate groups at the *o*′-position in the diazo component and at specific positions in naphthols, various substituents especially *o*′- and *p*′-carboxy, *p*′-nitro, *o*′-methoxy have some effect on solvation, although less than that of sulfonate groups;
8. Commercial reactive azo dyes, such as C.I. Reactive Red 1, Red 194 and Red 227, which possess *o*-sulfonate groups, exhibit specific behaviour that is different from that of other usual dyes which exist as HTs in water.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research by the Minister of Education, Science and Culture, Japan.

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