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Quantitative Analysis of Azo–Quinonehydrazone Tautomeric Equilibrium

St. Stoyanov & L. Antonov

Department of Chemistry, University of Sofia, Sofia 1126, Bulgaria

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ABSTRACT

In order to evaluate the influence of various factors affecting the azo–quinonehydrazone tautomeric equilibrium, a quantitative spectrophotometric method for the analytical determination of this tautomerism was developed. The method can be utilised to obtain the values of percentage content for the two tautomeric species, the constant K_T of this equilibrium and the individual spectral curves for the pure tautomeric forms. These data were used for analysis of the influence of solvents, substituents and temperature on the position of the tautomeric equilibrium in 1-phenylazo-4-naphthol and its derivatives. The method may also be applied to the analysis of other tautomeric systems, in which the absorption spectra of the individual tautomeric species cannot be experimentally observed.

1 INTRODUCTION

The possibility of azo–quinonehydrazone tautomeric equilibrium in the case of 1-phenylazo-4-naphthol (Fig. 1) was shown for the first time by Zince & Bindenwald[1] more than 100 years ago. This phenomenon is still the subject of many investigations using various chemical and physical methods (e.g. Refs 2, 3).

Knowledge of which of the tautomeric structures is dominant under certain conditions is important in respect of the colouristic and

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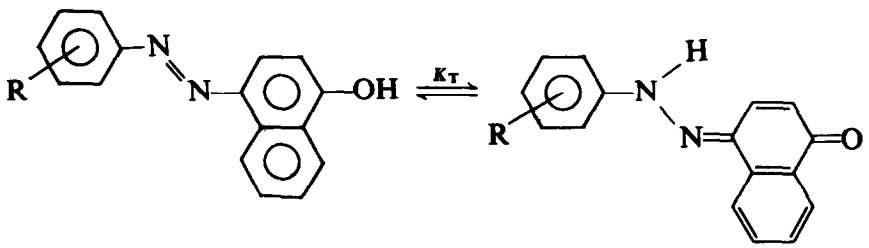

Fig. 1. Azo–quinonehydrazone tautomerism of 1-phenylazo-4-naphthols.

technological properties of dyes. About 50% of commercially disclosed structures of azo dyes contain a naphthol ring and therefore have a potential tautomeric structure.[4] Surprisingly, there are no quantitative data dealing with this tautomeric equilibrium. Usually semiquantitative approaches, based on various assumptions and approximations, are used. In some cases, however, these lead to contradictory results, due to the impossibility of determining directly from the absorption spectra the molar absorptivities of the pure tautomeric forms.[5-13] The most popular equation used is that of Ospenson:[5]

$$H\ (\%) = D_H/(D_A + D_H) \times 100 \qquad (1)$$

where D_A and D_H are the absorbances of the compound under investigation at the absorption maxima of the azo (A) and hydrazone (H) forms respectively. Similar equations were used by Sawicki[6,7] and Burawoy *et al.*[8] It should be noted that these equations are valid only in the case when the following two conditions are fulfilled.

(a) The A-form has no absorption at the absorption maximum of the H-form and vice versa, i.e. the molar absorptivities $\varepsilon_A^{\nu_H}$ and $\varepsilon_H^{\nu_A}$ are equal to 0.

(b) The molar absorptivities of the two tautomeric forms at their absorption maxima are equal, i.e. $\varepsilon_A^{\nu_A} = \varepsilon_H^{\nu_H}$.

Some authors[10,11] have used model compounds with fixed A and H forms in order to determine the values of $\varepsilon_A^{\nu_A}$ and $\varepsilon_H^{\nu_H}$ and to 'improve' eqn (1). The transfer of these values to the real tautomeric system may however lead to some uncertainties, due to possible noncoplanarity of the model H form, thus resulting in a significant decrease of the $\varepsilon_H^{\nu_H}$ value and a large discrepancy in the published values.[10,14-16]

The purpose of this investigation is to develop and apply a quantitative approach in determining the tautomeric equilibrium constants K_T and an analysis of the absorption spectra of the well-known tautomeric compounds 1-phenylazo-4-naphthol and its derivatives.

2 MATERIALS AND METHODS

The compounds used in this study were the following: 1-phenylazo-4-naphthol (**I**) and the 4′-methyl (**II**); 4′-chloro (**III**), 4′-methoxy (**IV**), 4′-acetyl (**V**), 3′-acephonamide (**VI**) and 4′-nitro derivatives (**VII**). They were prepared by the usual method of diazotising and coupling reactions, carefully purified free from the possible *o*-isomer and their purity was confirmed by TLC and m.p. The absorption spectra were recorded on a 'Specord UV–VIS' spectrophotometer. The computer program, written in BASIC, is available on request.

The quantitative method developed below is based on the general approach for the analysis of a closed two-component mixture with unknown molar absorptivities of the components, as used by Bernstein & Kaminskii.[17,18] Such a system could be analysed if areas of individual absorption for each tautomeric form exist. The essential part of the adopted method consists of the following consecutive procedures.

(a) An appropriate pair of solvents is selected in order to give a qualitative difference in the position of the tautomeric equilibrium, i.e. in their absorption spectra (Fig. 2).
(b) The absorption spectra are measured of a number, usually 5–10, of isomolar solutions, where the volume ratio of the solvents used is different but the total concentration C_0 is constant.
(c) A computer analysis of the experimental data is then made.

The values of the absorptions $D_i^{\nu_j}$ are used as starting data, where i is the

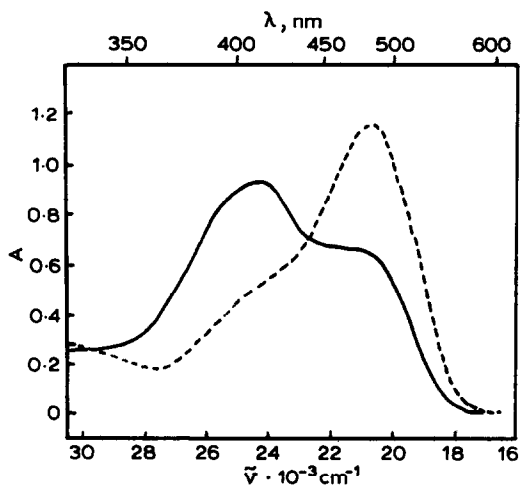

Fig. 2. Absorption spectra of **I** in ethanol, $C = 3{\cdot}03 \times 10^{-5}$ M, $l = 2$ cm (——) and in formamide, $C = 1{\cdot}61 \times 10^{-5}$ M, $l = 2$ cm (– – –).

number of the isomolar solution and ν_j is the jth wavenumber in cm^{-1} in the 330–600 nm range, where the two tautomeric species have the largest difference in absorption. In the general case $\nu_j - \nu_{j+1} = 500\,cm^{-1}$. The individual areas of absorption for the A and H forms are determined using eqn (2), which is valid for any closed two-component mixture:[17]

$$\frac{D_i^{\nu_j}}{\frac{(\varepsilon_A^{\nu_j}\varepsilon_H^{\nu_k} - \varepsilon_A^{\nu_k}\varepsilon_H^{\nu_j})}{\varepsilon_H^{\nu_k} - \varepsilon_A^{\nu_k}}} + \frac{D_i^{\nu_k}}{\frac{(\varepsilon_A^{\nu_j}\varepsilon_H^{\nu_k} - \varepsilon_A^{\nu_k}\varepsilon_H^{\nu_j})}{\varepsilon_A^{\nu_j} - \varepsilon_H^{\nu_j}}} = C_0 l \tag{2}$$

where ν_j and ν_k are any two wavenumbers in the measured range, C_0 is the total concentration of the components in the solutions and l is the path length. For all ν_j within the range of individual absorbance of the A form, the value of $\varepsilon_H^{\nu_j}$ is equal to 0 and the intercept $D_{max}^{\nu_k}$ is a constant, equal to $\varepsilon_H^{\nu_k} C_0 l$. If ν_k is in the region of individual absorbance of the H form, i.e. $\varepsilon_A^{\nu_k} = 0$, then the intercept $D_{max}^{\nu_j} = \varepsilon_A^{\nu_j} C_0 l$ has a constant value for any ν_k determining this region. The using of the least-squares method at this stage is much more efficient than the graphic determination used in the original work.[18] Further, the evaluation of K_T, C_A and C_H, according to eqn (3) proceeds at each ν_j and ν_k within the regions of individual absorption, as well as at their absorption maxima ν_A^{max} and ν_H^{max}.

$$K_T = C_H / C_A \tag{3}$$

The advantage of this procedure is the possibility of determining the values of K_T, C_A and C_H at least at eight analytical wavenumbers, since the minimal range of individual absorbance consists of three ν_j, ν_k. The statistical evaluation of K_T gives standard error of a mean (S.E.M.) usually less than 1%. The individual values of the molar absorptivities for the pure A and H forms, in the whole range investigated, are computed at each ν_j using eqns (4) and (5):

$$D_i^{\nu_j} = C_i^H (D_H^{\nu_j} - D_A^{\nu_j}) + D_A^{\nu_j} \tag{4}$$

$$D_i^{\nu_j} = C_i^A (D_A^{\nu_j} - D_H^{\nu_j}) + D_H^{\nu_j} \tag{5}$$

Following this procedure the spectral curves of the pure tautomeric species are constructed and plotted along with the starting experimental absorption curves.[19]

3 RESULTS AND DISCUSSION

The quantitative determination of the factors affecting the tautomeric equilibrium, as well as the analysis of the semiquantitative approaches used

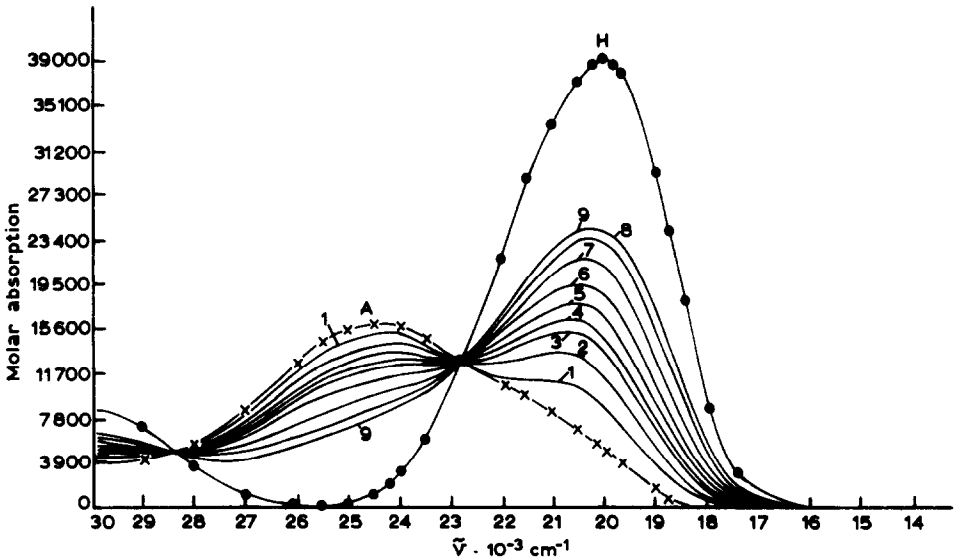

Fig. 3. Absorption spectra of **I** in different volume ratios of ethanol/H_2O. The calculated absorption spectra of the pure A and H forms are also given. The percentages of water for the curves 1–9 are given in Table 1.

in the literature for this purpose, are of theoretical and practical importance. The absorption spectra of **I** at different volume ratios of the applied pair of solvents ethanol/water, together with the computed individual absorption curves of the pure tautomeric forms, are shown in Fig. 3. With the increase of the volume content of water, the absorption of the H form increases, while that of the A form decreases. The main results obtained are listed in Table 1. When the solubility in the added solvent is not sufficient, the relationship

TABLE 1

Values of C_A, C_H, K_T and Standard Error of the Mean (S.E.M.) for Each Isomolar Solution of **I** in Ethanol/H_2O

H_2O (%)	*No.*	C_A (%)	C_H (%)	K_T	*S.E.M.* (%)
0	1	90·7	9·3	0·10	1·9
10	2	83·7	16·3	0·19	0·5
20	3	79·2	20·8	0·26	0·4
30	4	75·4	24·6	0·33	0·7
40	5	70·8	29·2	0·41	0·6
50	6	65·8	34·2	0·52	0·5
60	7	58·4	41·6	0·71	0·6
70	8	47·9	52·1	1·09	0·4
80	9	39·6	60·4	1·52	1·4

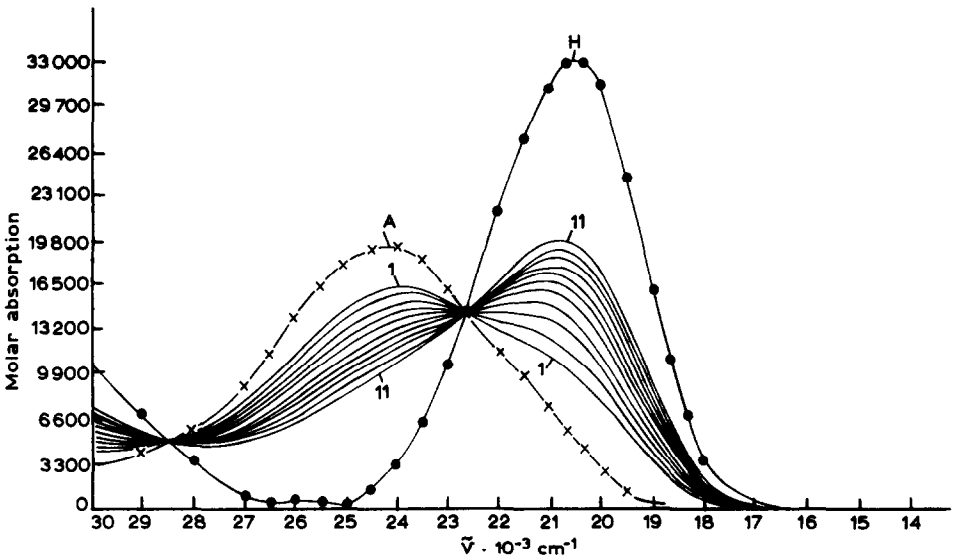

Fig. 4. Absorption spectra of **II** in different volume ratios of methanol/formamide, where 1 corresponds to the spectrum in 100% methanol and for each curve to 11 the volume content of formamide is increased by 10%. The calculated absorption spectra of A and H forms are also presented.

between K_T and the mole fraction of the added solvent could be approximated to obtain its value of K_T. A similar approach was used for all other compounds and pairs of solvents investigated. Another example for the applied procedure is given in Fig. 4.

It must be noted that the two conditions determining Ospenson's equation are not valid for all cases. In general, eqn (6) gives the value of C_H when $C_H + C_A = C_0 = \text{constant}$.

$$C_H\,(\%) = \frac{(\varepsilon_{obs}^{\nu H} - \varepsilon_A^{\nu H})/(\varepsilon_H^{\nu H} - \varepsilon_A^{\nu H})}{((\varepsilon_{obs}^{\nu A} - \varepsilon_H^{\nu A})/(\varepsilon_A^{\nu A} - \varepsilon_H^{\nu A})) + ((\varepsilon_{obs}^{\nu H} - \varepsilon_A^{\nu H})/(\varepsilon_H^{\nu H} - \varepsilon_A^{\nu H}))} \times 100 \qquad (6)$$

If $\varepsilon_A^{\nu H} = 0$ and $\varepsilon_H^{\nu A} = 0$, eqn (6) takes its simpler form (7):

$$C_H\,(\%) = \frac{\varepsilon_{obs}^{\nu H}}{\varepsilon_{obs}^{\nu H} + \varepsilon_{obs}^{\nu A}(\varepsilon_H^{\nu H}/\varepsilon_A^{\nu A})} \times 100 \qquad (7)$$

If $\varepsilon_A^{\nu A} = \varepsilon_H^{\nu H}$, then eqn (7) becomes equivalent to eqn (1). In Table 2 the values of $\varepsilon_{max}^{\nu A}$, $\varepsilon_{max}^{\nu H}$, λ_{max}^{A}, λ_{max}^{H} and the ratio $\varepsilon_{max}^{\nu H}/\varepsilon_{max}^{\nu A}$, calculated for **II** in all pairs of solvents, are given. Analysis of these data shows a relatively small variation of $\varepsilon_{max}^{\nu A}$ and $\varepsilon_{max}^{\nu H}$ values, which suggests even smaller variation within the given pair of solvents.

The data obtained in this work on the percentage content of the H form

TABLE 2
Spectral Characteristics, Calculated for the Pure Tautomeric Forms of **II**

Solvents	λ^{A}_{max} (*nm*)	$\varepsilon^{\nu A}_{max}$	λ^{H}_{max} (*nm*)	$\varepsilon^{\nu H}_{max}$	$\varepsilon^{\nu H}_{max}/\varepsilon^{\nu A}_{max}$
Ethanol/H_2O	410	18 000	500	30 500	1·70
DMSO/H_2O	417	19 800	500	27 800	1·41
DMFA/H_2O	414	19 900	500	26 700	1·34
Acetone/$CHCl_3$	410	20 300	488	23 200	1·14
Iso-octane/CH_2Cl_2	385	16 600	476	27 200	1·64
Ethyl acetate/CH_3CN	405	20 600	473	33 700	1·64
CH_3OH/formamide	400	20 800	500	27 000	1·30

for compounds **I–III** are compared with those reported in the literature[7,9–11,13,20] and are collected in Table 3. In most cases, the values of C_H obtained by us are smaller than those derived by using eqns (1) and (7). Evidently the second condition, i.e. $\varepsilon^{\nu A}_{max} = \varepsilon^{\nu H}_{max}$, is the main reason for this difference since the calculated ratio $\varepsilon^{\nu H}_{max}/\varepsilon^{\nu A}_{max}$ in most cases is between 1·5 and 2·0, leading to smaller values of C_H.

TABLE 3
Values (%) of C_H for the Compounds I–III Found in the Literature, Compared with Those Determined in this Work

Solvent	*R = H*		*R = 4′-CH₃*		*R = 4′-Cl*	
	Lit.	*Our data*	*Lit.*	*Our data*	*Lit.*	*Our data*
Iso-octane	33·0 (8) 21·0 (10)	10·4	18·0 (10)	3·0	23·0 (10)	6·0
CH_2Cl_2	—	61·1	—	48·0	—	56·2
$CHCl_3$	79·0 (9)	57·2	62·0 (9)	40·5	67·0 (9)	45·0
Ethyl acetate	—	20·5	—	10·0	—	20·6
CH_3CN	22·0 (12)	36·5	—	23·0	—	38·2
Acetone	22·0 (12) 30·0 (9)	27·1	11·0 (9)	11·5	33·0 (9)	18·0
MeOH	40·0 (9)	20·3	19·0 (9)	16·0	38·0 (9)	22·5
EtOH	42·0 (19)		12·0 (9)		29·0 (9)	
	43·0 (6)	9·3	31·0 (6)	8·7	35·0 (10)	7·5
	31·0 (9) 35·0 (10)		28·0 (10)			
50% EtOH/H_2O	62·0 (8)	34·2	47·3 (8)	25·0	69·4 (8)	36·8
Formamide	—	59·5	—	47·0	—	51·7
DMFA	29·0 (8)	8·0	—	7·0	30·0 (10)	15·0
DMSO	77·0 (8)	11·1	74·0 (8)	9·9	77·0 (8)	11·7
CH_3COOH	50·0 (12)	—	77·0 (9)	—	89·0 (9)	—

TABLE 4
Values of K_T for Compounds I–IV, Determined in Different Solvent Mixtures

Solvent	*R = H*	*4'-CH₃*	*4'-Cl*	*4'-OCH₃*
EtOH	0·10	0·10	0·08	0·06
MeOH	0·25	0·20	0·27	0·10
Acetone	0·37	0·12	0·22	0·09
Ethyl acetate	0·26	0·13	0·27	—
CH_3CN	0·58	0·30	0·62	—
Iso-octane	0·12	0·03	0·06	—
$CHCl_3$	1·33	0·68	0·82	0·27
CH_2Cl_2	1·57	0·86	1·16	—
Formamide	1·47	0·89	1·07	0·36
DMFA	0·09	0·07	0·20	—
DMSO	0·13	0·11	0·15	—
H_2O	2·35	1·38	1·80	0·82

The values of K_T obtained for compounds I–IV in different solvents are shown in Table 4. According to the order of increasing values of K_T, the solvents investigated can be placed in the following order:

$$\text{iso-octane} < \text{DMFA} \simeq \text{ethanol} < \text{DMSO} < \text{MeOH} \simeq \text{ethyl acetate} \simeq \text{acetone} < \text{acetonitrile} < 50\%\ \text{ethanol/H}_2\text{O} < \text{CHCl}_3 < \text{CH}_2\text{Cl}_2 \simeq \text{formamide} < \text{H}_2\text{O}$$

It should be noted that this order is valid for all compounds studied, indicating that the reasons determining this order are little influenced by the substituent in the phenyl ring.

In accordance with the results published by Reeves & Kaiser[21] on 4-arylazo-1-naphtholsulphonates, there is no correlation between empirical parameters reflecting the solvent polarity[22] and the position of the tautomeric equilibrium. Solvents such as EtOH, MeOH, acetone, DMFA and DMSO shift the equilibrium towards the A form and their action is similar to that of the non-polar solvents iso-octane and hexane. On the other hand, solvents such as CH_2Cl_2, $CHCl_3$, formamide and particularly H_2O, lead to an increase of the H form. We suggest that two factors are mainly responsible for this tautomeric shift, viz.

(a) selective solvation, depending on the two- or three-dimensional structure of the solvent;[21,23]
(b) the solvent's ability to form stronger intermolecular H bonds with a particular tautomeric form.

It is therefore possible to achieve stronger stabilisation of the less polar A form, in spite of increased solvent polarity.

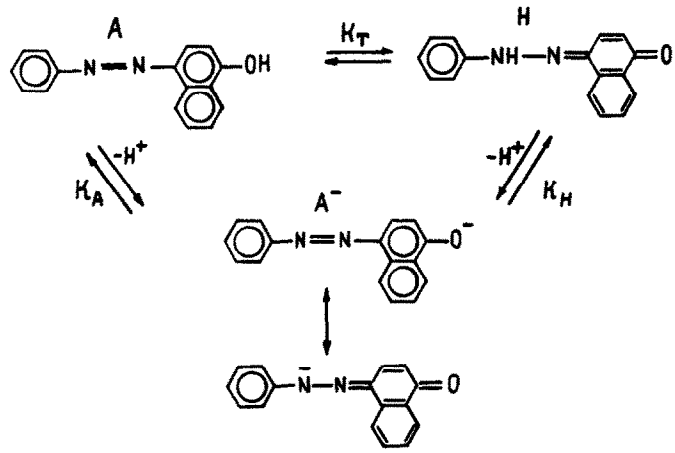

Fig. 5. Possible equilibrium processes of **I** in alkaline medium.

The possible equilibria processes of **I** in alkaline medium are presented in Fig. 5. Using eqns (8) and (9), reflecting the relationships between K_T, K_A and K_H, valid for any two-component tautomeric system,[2] as well as the values of pK_a^{obs} in 50% EtOH/H_2O listed by Schreiber *et al.*,[24] we calculated the values of K_A and K_H as pK_a^A and pK_a^H respectively. The K_T values used were determined for the same solvent mixture and are presented in Table 5.

$$K_A = K_a^{obs}(1 + K_T) \tag{8}$$

$$K_H = K_a^{obs}\left(\frac{1}{K_T} + 1\right) \tag{9}$$

The dependence between pK_a^A and σ_0 is shown in Fig. 6, together with the respective values of pK_a^{obs}, shown with open circles. As Schreiber *et al.*[24] noted, the poor correlation between the pK_a^{obs} and σ_0 is due to the presence

TABLE 5

Observed and Calculated Equilibrium Constants for **I** and its Derivatives in 50% (v/v) Ethanol/H_2O

R	K_T	pK_a^{obs}	pK_a^A	pK_a^H	σ_0
H	0·52	9·18	8·99	8·71	0
4′-CH_3	0·33	9·14	9·02	8·53	−0·07
4′-Cl	0·58	8·89	8·69	8·45	0·25
4′-OCH_3	0·25	9·15	9·05	8·45	−0·12
4′-$COCH_3$	1·15	9·05	8·72	8·78	0·46
3′-SO_2CH_3	0·64	8·60	8·39	8·19	0·66
4′-NO_2	4·55	8·91	8·16	8·82	0·82

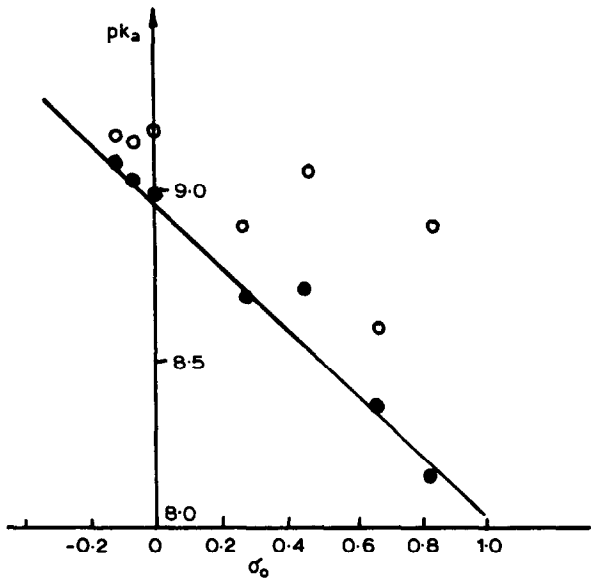

Fig. 6. Relation between pK_a^A(●) and σ_0 values. The values of pK_a^{obs} (○) are given for comparison.

of A⇌H tautomeric equilibrium. Taking into account the quantitative K_T values leads to a significant improvement of this relationship. According to the values of K_T it is possible to evaluate the influence of the substituents in the phenyl ring, leading to an increase of H form:

$$4'\text{-}OCH_3 < 4'\text{-}CH_3 < H < 4'\text{-}Cl < 3'\text{-}SO_2CH_3 < 4'\text{-}COCH_3 < 4'\text{-}NO_2$$

Our data are in accord with literature conclusions[5-10] about the influence of the substituents on this tautomeric equilibrium. Using eqn (10), connecting the calculated values of K_A and K_H with K_T and the opposite direction of the charge migration during the electronic transition $S_0 \rightarrow S_1$ for the pure A and H forms, it is possible to explain more correctly the observed influence of the substituents.[19,26]

$$K_T = K_A/K_H \tag{10}$$

The difference between the calculated π-electron density $\Delta Q_i = Q_i^{S_1} - Q_i^{S_0}$ for each atom i of both the tautomeric structures is shown in Fig. 7, where the overall area of circles is proportional to ΔQ_i. The shaded circles correspond to an increase, and empty ones to a decrease, of π-electronic density upon the excitation of the molecule. The existence of an electron-donor substituent in the phenyl ring of the tautomeric system will lead to an increase of K_H, since it enhances the polarisation of the molecule, and also to a decrease of K_A, since the acidic character of the OH proton decreases. The

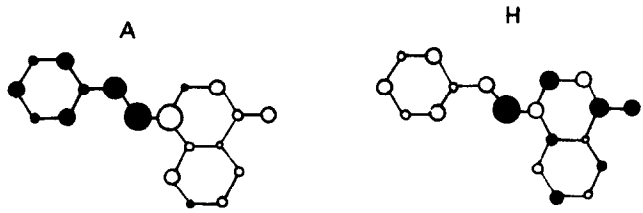

Fig. 7. Schematic presentation of ΔQ_i for the two tautomeric A and H forms.

total effect evidently will be a decrease of the K_T value or a shift of the tautomeric equilibrium towards the A form. The introduction of an electron acceptor substituent will cause a relatively stronger increase of K_A due to enhanced charge transfer and formation of a donor–acceptor conjugated system. A smaller change in the value of K_H might be expected. The direction of this change depends on the relative strength and position of the substituent, since the conjugated system formed has at both ends two substituents of similar nature. Therefore we can expect an increase of K_T and shift of the tautomeric equilibrium towards the H form.

The absorption spectra of I in formamide in the temperature range 293–353K are shown in Fig. 8. The values of K_T at each measured

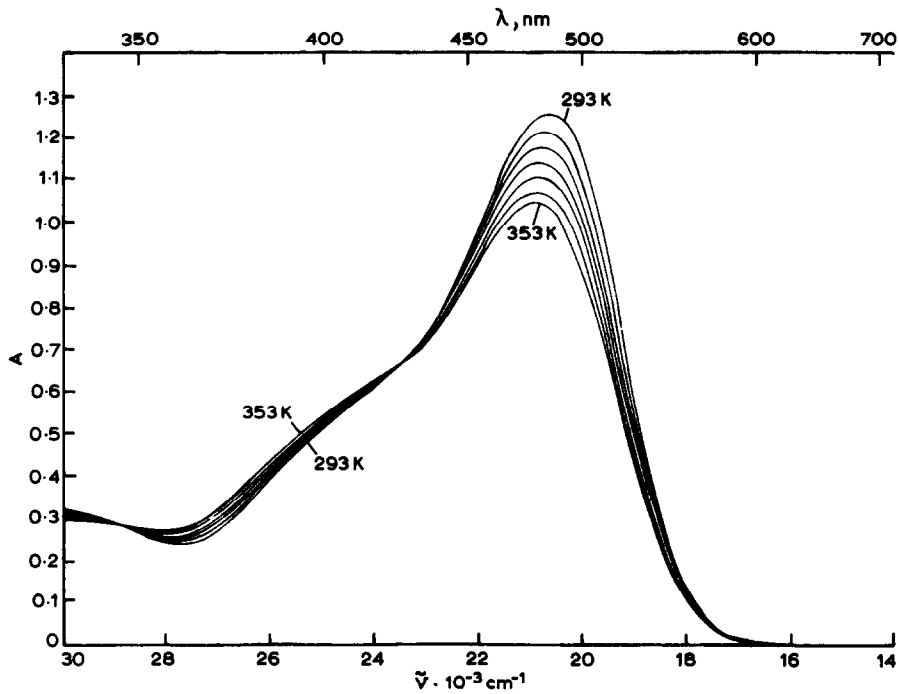

Fig. 8. Absorption spectra of I in formamide in the range 293–353 K, $C = 3{\cdot}28 \times 10^{-5}$ M, $l = 0{\cdot}5$ cm.

temperature and the thermodynamic parameters ΔG (293K) = $-0{\cdot}94\,\text{kJ mol}^{-1}$, $\Delta H = -10{\cdot}5\,\text{kJ mol}^{-1}$ and $\Delta S = -7{\cdot}8$ e.u. were calculated. These data suggest that the process A → H is exothermic and the entropy increase and enthalpy decrease will favour it, in agreement with published data.[27-29]

The quantitative approach for the analysis of the tautomeric azo–quinonehydrazone equilibrium of 1-phenylazo-4-naphthol and its derivatives is applicable to other potentially tautomeric systems. The isomeric 1-phenylazo-2-naphthols are of special interest, since they exhibit also tautomeric properties.[8,25,30-32] A quantitative investigation is in progress and the results obtained will be reported later.

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