Dyes and Pigments **5** (1984) 351–370

Substituent Effects on the Tautomerism and Photochromism Exhibited by a Series of Hydroxyazo Cationic Dyes for Polyester Fibres

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(Received: 4 July, 1983)

SUMMARY

A critical study of the substituent effects on different properties exhibited by a series of thirteen cationic dyes of the hydroxyazo type is presented. This series is well representative of the polarity scale (o, m, p: OCH_3, CH_3, *Cl,* NO_2*).*

The first part deals with the constant K = H/A, *the thermodynamic characteristics* ΔH, ΔS *of the azo–hydrazone equilibrium and the* pK, ε, $\bar{\nu}$ *of these tautomers. Some deviations encountered are explained.*

In a second part, the substituent effect on the kinetic relaxation of these photochromic dyes is easily accounted for by the empirical σ_T *constants. However, more advanced models are envisaged and comparison between the different results enables some considerations on the validity of the linear free energy relationships to be presented.*

1. INTRODUCTION

Numerous properties of the fundamental as well as of the excited states of a series of 13 new cationic azo-dyes (Fig. 1) have been established:[1,2] the dye molecules exhibit tautomerism and photochromism, these two properties being strongly interdependent. Moreover, the present series of dyes is very attractive since it involves four substituents covering the

Dyes and Pigments 0143-7208/84/$03·00

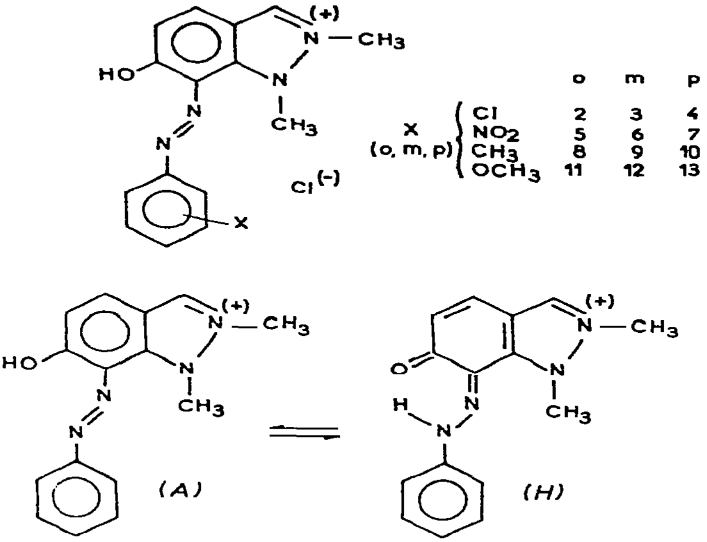


Fig. 1. The compounds studied and the azo-hydrazone tautomerism.

polarity scale and the three possible sites of substitution (cf. Fig. 1). On that account, our study is not restricted to the kinetic aspects only, but includes all the quantities at our disposal. In such studies we impinge on the choice of the procedure to be adopted, having at our disposal experimental data referring to different physico-chemical quantities for a series of compounds. Consideration has to be given to the choice of a set of parameters and the question of the need for it to be unique.

Empirical correlations between chemical reactivity and substituent effects are still of increasing interest since the initial works by Hammett.[3] At first, the purpose was to bring out a linear relationship between the logarithm of the equilibrium constant (the rate constant) of a given reaction and a parameter which should be specific to the substituent whatever the reaction studied.

From the following equations:

$$\Delta G^\circ = -RT \log K \tag{1}$$

$$\ln k = \ln A - \frac{\Delta G^\ddagger}{RT} - \frac{\Delta S^\ddagger}{R} \tag{2}$$

it turns out that, at a given temperature, the quantities of interest are respectively functions of the standard variation of free energy ΔG° and the free energy of activation.

Consequently such linear correlations are called Linear Free Energy Relationships (LFER) or Hammett's relations, the first terminology being in fact more correct. Gradually, it has emerged that many physico-chemical quantities obey LFER. As a result a proliferation of substituent constants has appeared which have been somewhat prejudicial to the essential idea underlying the initial work by Hammett. (A similar course of events is occurring with the empirical polarity parameter of a solvent.)

For convenience, eqns (1) and (2) can be rewritten as:

$$\log(K/K_0) = \sigma\rho \tag{3}$$

$$\log(k/k_0) = \sigma\rho' \tag{4}$$

where σ is the substituent constant; which denotes the polar effect of the substituent as compared with the hydrogen atom, and should not depend on the type of reaction; and ρ is the reaction constant, which depends on the reaction studied and the solvent, and measures the dependence of the reaction on the polar effect. (We have not considered multiple parameters correlation, the use of which is suspect.)

Dealing with LFER problems calls for some general considerations. From the mathematical point of view we are interested in testing the validity of a linear correlation. This is currently undertaken by considering the well-known statistical quantities:

r = correlation coefficient

s = standard deviation

which are obtained in the present paper from a least-squares fitting without weighting. However, the use of r has been questioned by Davis and Pryor[4] but unfortunately these authors did not propose any other statistic. Moreover, the extreme situations advanced in their paper were not encountered in our investigation.

Additionally, use of substituent constants is not compulsory for the study of substituent effects. Information can be obtained by plotting two quantities for each studied compound (*vide infra*).

In the present paper, resort to the constants σ_T proposed by Taft[5] was motivated by the presence of *ortho*-substituents. Nevertheless, the σ_0 set,[6] though not designed for *ortho*-substituents, has been considered also in some cases: this σ_0 set, which does not significantly differ from the σ_T set, has proved to be convenient when dealing with azo-compounds.[7]

For clarity, we judged it more convenient to present successively the results relative to the fundamental states and then those referring to

TABLE 1

Substituent Effects on the Equilibrium Constant, Ultraviolet Transitions and pK

Dye no.	X	σ_r	σ_0	K^a (25°C)	*log K* (25°C)	ΔH^b	ΔG^b	ΔS^b	$\tilde{\nu}_H$ (cm^{-1})	$\tilde{\nu}_A$ (cm^{-1})	$\tilde{\nu}_D$ (cm^{-1})	ε_H	ε_A	ε_D	pK_{app}	pK_H	pK_A
1	—	0	0	6·1	0·79	−2·0	−1·07	−3·01	21 790	26040	25 000	20600	13900	14200	8·85	8·80	8·0
2	*o*-Cl	0·200		6·45	0·81	−1·82	−1·10	−2·38	21 690	25 320	24 690	19000	13700	11 400	9·05	8·90	8·2
3	*m*-Cl	0·373	0·37	5·65	0·75	−1·76	−1·02	−2·44	21 930	25975	24 690	22000	16200	14800	8·25	8·20	7·45
4	*p*-Cl	0·112	0·27	7·05	0·85	−1·72	−1·15	−1·86	21 600	25910	24 750	21 300	17000	14700	8·45	8·40	7·55
5	*o*-NO$_2$	0·780		7·1	0·85	−1·82	−1·15	−2·20	21 460	25770	24 510	21 800	11 700	10700	8·95	8·90	8·05
6	*m*-NO$_2$	0·662	0·70	6·0	0·78	−1·84	−1·06	−2·60	22 220	25910	24 390	18 100	13700	13 500	7·80	7·80	7·0
7	*p*-NO$_2$	0·777	0·82	8·35	0·92	−1·76	−1·25	−1·66	21 740	24690	22470	26 200	19000	15 900	8·10	8·05	7·1
8	*o*-CH$_3$	−0·17		5·3	0·72	−1·80	−0·98	−2·70	21 415	25770	25 125	20 500	11 200	11 600	9·65	9·60	8·85
9	*m*-CH$_3$	−0·07	−0·07	6·5	0·81	−1·76	−1·10	−2·16	21 645	25640	25 000	22 300	15000	14 500	8·80	8·75	7·90
10	*p*-CH$_3$	−0·306	−0·15	6·8	0·83	−1·90	−1·13	−2·54	21 320	26040	25 125	22 600	17000	14 300	8·80	8·75	7·90
11	*o*-OCH$_3$	−0·48		9·0	0·95	−1·64	−1·30	−1·10	20 700	23255	24 875	19000	14000	11 000	10	9·95	9·0
12	*m*-OCH$_3$	0·04	0·08	7·2	0·86	−1·88	−1·16	−2·36	21 550	25 770	24 750	19400	14000	14 600	8·75	8·70	7·85
13	*p*-OCH$_3$	−0·764	−0·12	6·2	0·79	−1·80	−1·08	−2·39	20 750	25640	25 000	21 100	16800	15 300	8·70	8·65	7·85
Average experimental uncertainties				±0·4		±0·2		±0·3	±150	±350	±100	±1 000	±1 500	±500	±0·03	±0·06	±0·06

[a] $K = [H]/[A]$, equilibrium constant of the azo⇄hydrazone tautomerism.

[b] ΔH, ΔG (kcal/mol) and ΔS (e.u.): thermodynamic characteristics of the azo⇄hydrazone equilibrium.

the kinetic behaviour. Relevant data are given in Tables 1 and 2. The temperature is 25 °C unless otherwise specified. Terminology and experimental items are to be found in refs 1 and 2.

2. PROPERTIES OF THE FUNDAMENTAL STATES

2.1. Azo–hydrazone equilibrium $K = [H]/[A]$

From Fig. 2 and Table 1 it seems that no linear correlation between log K and σ_T or σ_0 holds. However, we have to exclude the *o*-substituted dyes

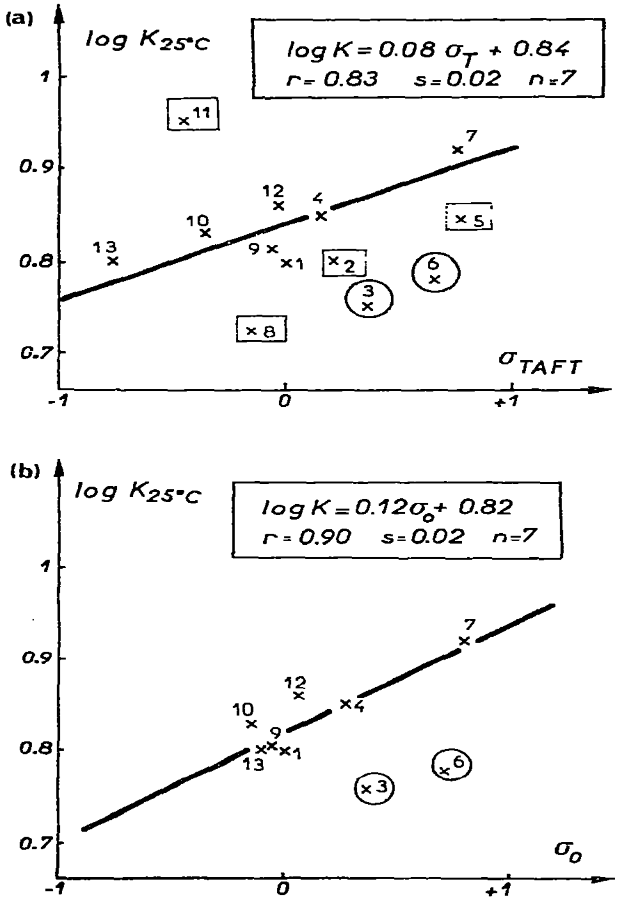


Fig. 2. Tentative correlation of log $K_{25\,°C}$ with σ_T and σ_0.

(curve a, **2**, **5**, **8**, **11**) since there is a hydrogen bond in the H tautomer[1] (such specific interaction cannot be accounted for by the σ constants), and a steric effect is certainly occurring. Additionally, **3** and **6** appear to be clearly different from the others; we are not able to put forward a satisfactory explanation for this deviation, but can only mention two plausible explanations: (i) there is a modification of the geometry, possibly a rotation of the ϕ—X part of the molecule; (ii) the participation of two or more conformers is deduced from the conformational analysis performed in ref. 1.

With the seven compounds that remain (**1**, **4**, **7**, **9**, **10**, **12**, **13**) the two following relations are obtained:

$$\log K = 0{\cdot}12\sigma_0 + 0{\cdot}82 \qquad r = 0{\cdot}90 \qquad s = 0{\cdot}02 \qquad n = 7 \qquad (5)$$

$$\log K = 0{\cdot}08\sigma_T + 0{\cdot}84 \qquad r = 0{\cdot}83 \qquad s = 0{\cdot}02 \qquad n = 7 \qquad (6)$$

Here σ_0 seems to be more convenient (as expected) but the value of the correlation coefficient is poor. Again, results of the conformational analysis could account, at least partly, for the bad correlation observed. Moreover, the experimental determination of K was not straightforward.[1] However, the trend of variation is clearly established and agrees with the observations reported on azo–hydrazone tautomerism:[8] ρ is positive. Moreover, its low value is of practical importance: it shows that in the case of this series of new dyes the tautomeric equilibrium is slightly dependent on the nature of the substituent, hence a well-defined hue for the series.

2.2. Acid–Base Equilibrium

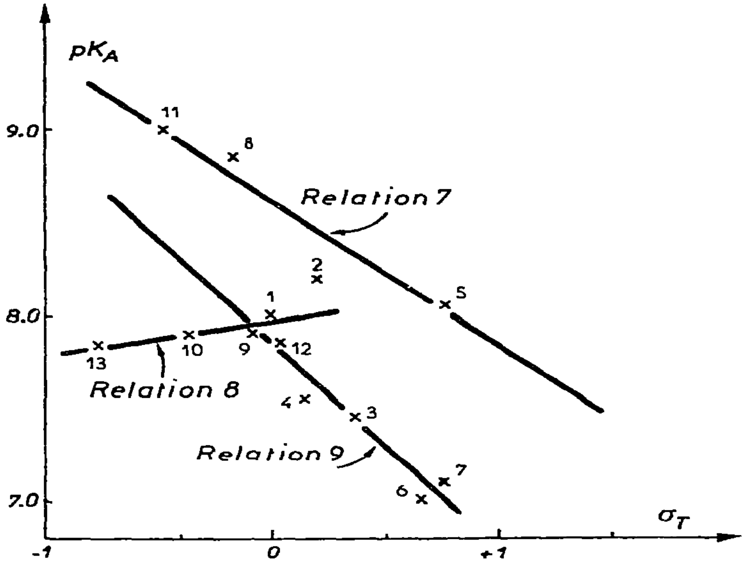
From Table 1, it can be seen that *o*-substituted azo-tautomers display too high a pK_A. It is of interest to note that these compounds (**2**, **5**, **8**, **11**) are very well correlated by the σ_T constants but independently of the other compounds (cf. Fig. 3):

$$\mathrm{p}K_A(\mathit{ortho}) = -0{\cdot}82\sigma_T + 8{\cdot}60 \qquad r = 0{\cdot}94 \qquad s = 0{\cdot}2 \qquad n = 4 \quad (7)$$

However, for the remaining compounds the tentative correlation with σ_T leads clearly to two regression lines, one corresponding to the *donor* substituents $\sigma_T < 0$, the other to the *acceptor* substituents ($\sigma_T > 0$):

$$\mathrm{p}K_A = 0{\cdot}14\sigma_T + 7{\cdot}95 \qquad r = 0{\cdot}96 \qquad s = 0{\cdot}05 \qquad n = 4 \qquad (8)$$

$$\mathrm{p}K_A = -1{\cdot}13\sigma_T + 7{\cdot}86 \qquad r = 0{\cdot}95 \qquad s = 0{\cdot}11 \qquad n = 6 \qquad (9)$$



$$\text{ortho }\sigma_T : pK_A = -0.82\,\sigma_T + 8.6 \quad r = 0.94 \quad n = 4 \quad (7)$$

$$\text{donor }\sigma_T : pK_A = 0.14\,\sigma_T + 7.95 \quad r = 0.96 \quad n = 4 \quad (8)$$

$$\text{acceptor }\sigma_T : pK_A = -1.13\,\sigma_T + 7.86 \quad r = 0.95 \quad n = 6 \quad (9)$$

Fig. 3. Complex correlation of pK_A with σ_T. All the studies compounds are taken into account.

It is worth noting that pK_A decreases whatever the nature of the substituent, in contradiction with the expected variation. Such an influence of the substituent (two lines) is not unknown. Herkstroeter,[9] and Wendt and co-workers[10] while dealing with benzylidene aniline derivatives observed a decrease of the rate constants of the *cis–trans* relaxation for every substituent. Zollinger and co-workers[11] quoted dyes the pK of which was decreased through substitution by electron donor substituents. The unusual thing is that the pK_A of these compounds correlates well (except the *o*-substituted) with the σ_0 set according to (Fig. 4):

$$pK_A = -1{\cdot}0\sigma_0 + 7{\cdot}83 \qquad r = 0{\cdot}96 \qquad s = 0{\cdot}09 \qquad n = 9 \qquad (10)$$

The same difficulties were encountered with the hydrazone tautomer. Again, the most appropriate correlation was obtained with σ_0 as:

$$pK_H = -0{\cdot}95\sigma_0 + 8{\cdot}65 \qquad r = 0{\cdot}94 \qquad s = 0{\cdot}12 \qquad n = 9 \qquad (11)$$

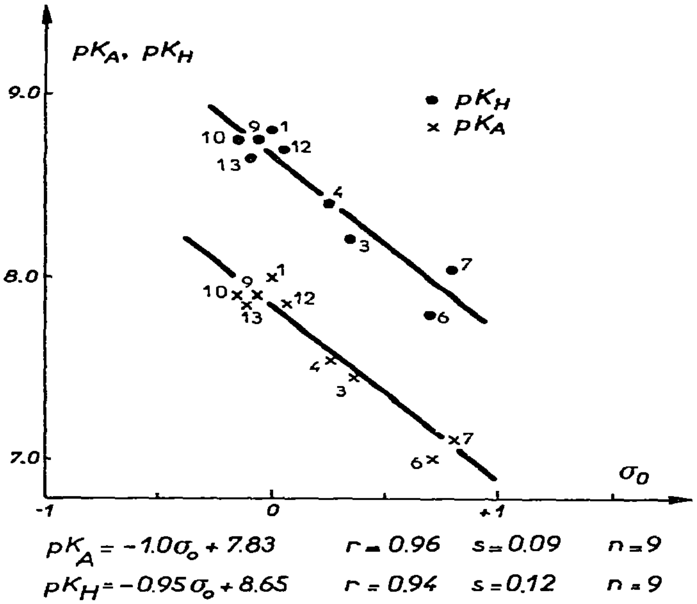


Fig. 4. Linear correlation of pK_A and pK_H with σ_0. The *o*-substituted dyes are not considered.

The interpretation of the substituent effects on p*K* is not straightforward but we can deduce that the p*K* of the two tautomers are affected strongly and identically by the substituents.

2.3. Ultraviolet transitions

The absorption coefficients of either the azo (ε_A), the hydrazone (ε_H) or the basic (ε_B) structures cannot be correlated either with σ_T or σ_0. In the case of the basic form for which intramolecular hydrogen bonds do not exist, the dispersion of the points prevents any correlation (Fig. 5). But interesting information can be drawn from the plot, for instance, of ε_H against ε_A (except for **5** and **8**, which are *o*-substituted) (Fig. 5):

$$\varepsilon_H = 1{\cdot}1\varepsilon_A + 3970 \qquad r = 0{\cdot}88 \qquad s = 1030 \qquad n = 11 \qquad (12)$$

The slope is nearly unity: as observed for p*K*, the molecular extinction coefficients are equally affected by substitution.

As regards the wavenumber $\tilde{\nu}$ we were interested by the relationship

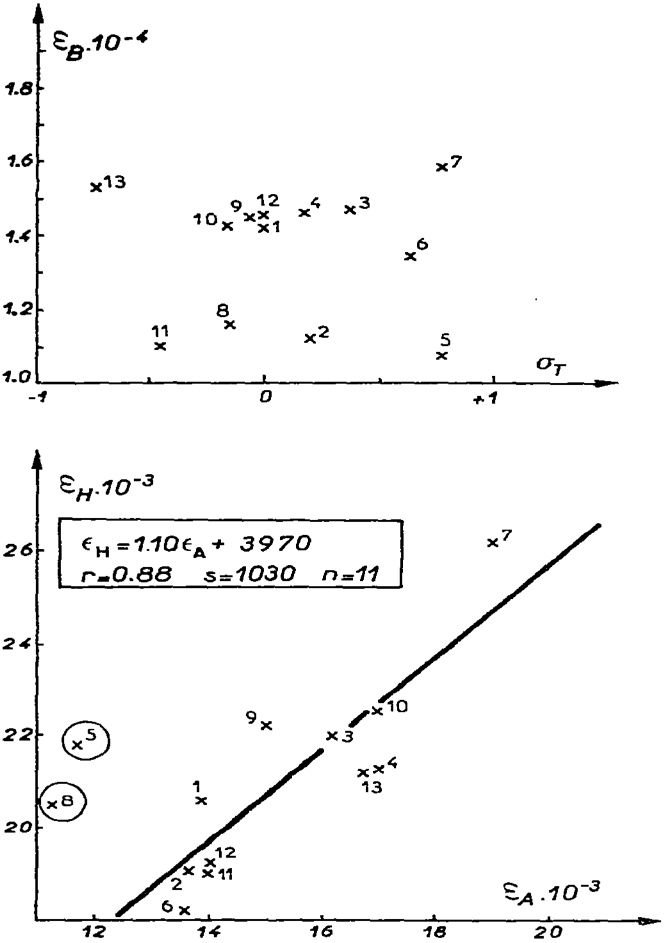


Fig. 5. Substituent effects on molar extinction coefficients of the basic, azo and hydrazone structures.

established by Hancock and co-workers[12] from general considerations of thermodynamics:

$$\tilde{\nu}_{\text{base}} - \tilde{\nu}_{\text{acid}} = -(0{\cdot}8RT)\text{p}K_{\text{acid}} + \frac{\Delta E^* - T\Delta S^\circ}{2{\cdot}86} \qquad (13)$$

where ΔE^* is the energy gap between the excited states in basic and acidic media. Effectively, we found linear correlations poor but significant (reported in Fig. 6). With the azo-tautomer, excluding **11**:

$$\tilde{\nu}_B - \tilde{\nu}_A = 712\text{p}K_A - 6645 \qquad r = 0{\cdot}86 \qquad s = 290 \qquad n = 12 \qquad (14)$$

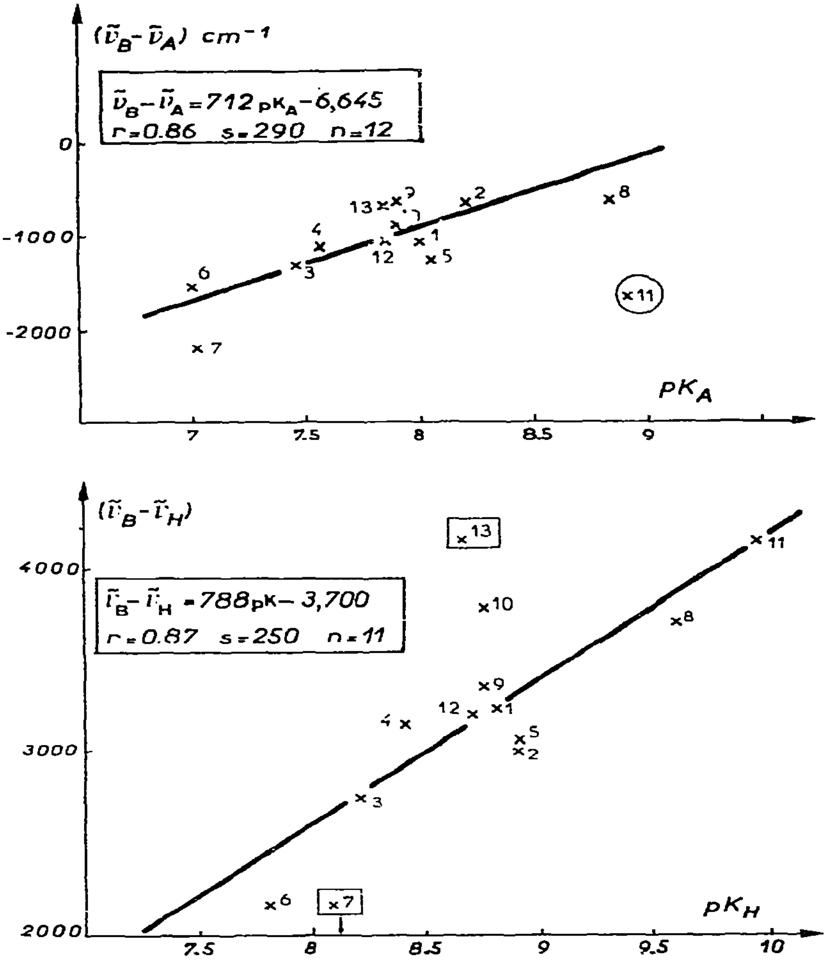


Fig. 6. Application of eqn (13) to both tautomers.

In the case of the hydrazone tautomer, 7 has to be excluded:

$$\tilde{\nu}_B - \tilde{\nu}_H = 745pK_H - 3230 \qquad r = 0{\cdot}71 \qquad s = 400 \qquad n = 12 \quad (15)$$

and probably 13:

$$\tilde{\nu}_B - \tilde{\nu}_H = 788pK_H - 3700 \qquad r = 0{\cdot}87 \qquad s = 250 \qquad n = 11 \quad (16)$$

These two substituents are known to give strong mesomeric effects. However, eqn (13) shows that in so far as the term $(\Delta E^* - T\Delta S°)/2{\cdot}86$ can be considered constant or varies significantly less than pK_A the slope

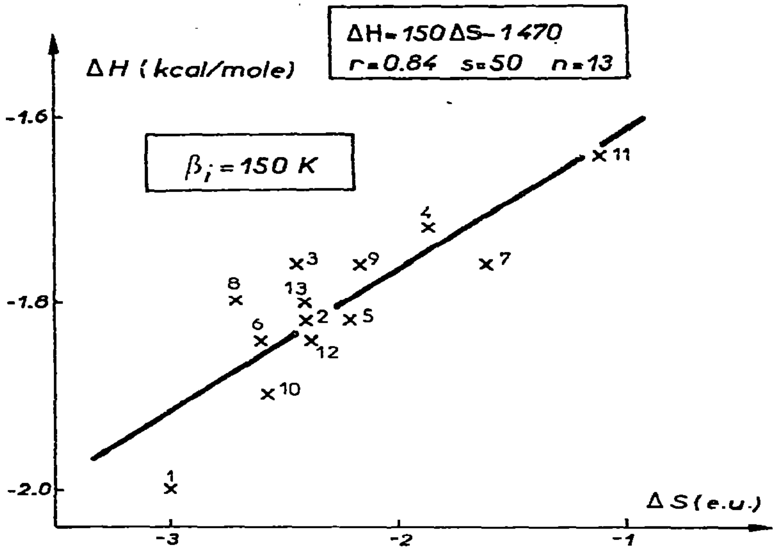


Fig. 7. Linear enthalpy–entropy relationship in the case of the azo ⇄ hydrazone equilibrium.

should be negative and equal to $-480\,\mathrm{cm}^{-1}$. We find here a different value and, what is more, of the opposite sign, as was the case in an earlier paper.[12] Probably the entropic term ΔS° is not constant at all.

The search for correlating ε and $\tilde{\nu}$ with empirical substituent constants thus showed limitations. Throughout the literature, very few attempts have been successful and it can be asked whether the reason for these failures is the fact that the substituent parameters were not originally intended for this purpose.

2.4. ΔH–ΔS correlation

Figure 7 shows that ΔH and ΔS, the thermodynamic characteristics of the azo–hydrazone equilibrium, are not independent but obey the relation:

$$\Delta H = 150\Delta S - 1470 \qquad r = 0{\cdot}84 \qquad s = 50 \qquad n = 13 \qquad (17)$$

Moreover, the correlation factor is better than the one obtained by Hepler in his detailed investigation on the ionization of benzoic acids.[13] This is an important result for investigators involved in LFER since to the best of our knowledge such a correlation has never been reported when dealing with tautomerism. The practical interest of relation (17) is to give the

TABLE 2

Experimental Data on the Relaxation Kinetics

Dye no.	$log\,k^{25°C}_{expt}$ *pH 1·1*	$log\,k^{25°C}_{expt}$ *pH 12·9*	σ_T	E ($kcal\,mol^{-1}$)	$E_{H'}$ ($kcal\,mol^{-1}$)	$log\,A$	$log\,A_{H'}$	$k_{H'}$ ($\times 10^{-9}$) ($M^{-1}\,s^{-1}$)[a]	α (*slope*)	$pK(H^+B_c)$
1	3·43	−3·02	0	13·7	11·6	13·5	17·7	1·45	0·95	6·05
2	3·87	−2·82	0·200	12·6	10·7	13·1	17·3	1·35	0·92	5·70
3	3·82	−2·48	0·373	11·9	11·6	12·4	17·2	0·4	0·86	5·55
4	3·44	−3·15	0·112	10·6	9·6	11·0	16·2	1·10	0·94	6·00
6	4·38	−2·40	0·662	14·5	9·6	15·0	16·2	1·30	0·89	5·30
8	2·91	−3·61	−0·17	14·6	6·0	13·3	13·7	1·85	0·99	6·35
9	3·25	−3·13	−0·07	11·9	10·8	11·9	17·6	4·90	0·99	6·45
10	2·90	−3·55	−0·306	11·8	6·0	13·5	13·6	1·50	0·99	6·40
11	2·64	−3·25	−0·48	15·2	13·0	13·6	21·0	3·50	0·99	6·90
12	3·48	−2·87	−0·04	10·6	14·7	11·0	19·4	2·50	0·95	6·20
13	2·44	−3·88	−0·764	15·8	4·8	14·0	11·7	0·13	0·93	6·10
Standard deviation				±1	±0·5	±1	±0·5			±0·3

[a] From eqn (19).

iso-equilibrium temperature β_i through the slope:[14,15] $\beta_i = 150\,\mathrm{K}$. At this temperature ΔH and ΔS theoretically would not depend on the substituent. Unfortunately the present value is too low to allow any experimental verification.

3. SUBSTITUENT EFFECTS ON THE PHOTOCHROMIC BEHAVIOUR

On the basis of our kinetic study on the unsubstituted dye **1**,[2] we proposed a mechanism which can be summarized as follows. The main consequence of a photon absorption for both tautomers is a rapid deprotonation and a subsequent *trans–cis* isomerization of the resulting azoic base (B_{cis}). Moreover, the experimental kinetic constant of relaxation k_{expt} was demonstrated to be strongly pH-dependent. At low pH the relaxation is governed by the *cis–trans* isomerization of the protonated *cis*-base:

$$\mathrm{HB}_c \xrightarrow{k_1} \mathrm{HB}_t \qquad k_{\mathrm{expt}} = k_1 \tag{18}$$

At high pH the relaxation corresponds to a bimolecular reaction:

$$\mathrm{B}_c + \mathrm{H}^+ \rightarrow \mathbf{1}$$

and it was shown[2] that least-squares analysis indicates a linear dependence of k_{expt} on pH according to the following equation:

$$\log k_{\mathrm{expt}} = \log k_{\mathrm{H}^+} - \alpha\,.\,\mathrm{pH} \qquad k_{\mathrm{expt}} \simeq K_{\mathrm{H}^+}[\mathrm{H}^+] \tag{19}$$

It should be noted that for some dyes (**3**, **6**) the slope α is significantly different from unity, which may be due to a more complicated scheme or again to the participation of more than one conformer. Such a description was found to apply to all the dyes under study except compounds **5** and **7**: surprisingly, we have failed to detect any transient species with these two dyes and we discuss an explanation later.

As regards the lightfastness, these relaxation mechanisms are of critical importance since a rapid relaxation is expected to lead to low degradation yield.

We now present a detailed interpretation of the substituent effects upon the kinetics accounted for by eqns (18) and (19). Moreover, as shown in ref. 4 it is possible to determine the pK of the transient species $\mathrm{H^+B}_c$ and we will also consider this quantity.

3.1. Classical treatment

Figure 8(a) shows the excellent linear correlations obtained with the same set, σ_T, of substituent constants as used previously. The substituent effect is dramatic and is different at the two pH values of interest, a fact which shows that the mechanisms are not the same at these two pH values, in agreement with our previous conclusions:[2]

$$\mathrm{pH} = 1{\cdot}1 \quad \log k = 1{\cdot}42\sigma_T + 3{\cdot}38 \qquad r = 0{\cdot}98 \qquad s = 0{\cdot}11 \qquad n = 11 \tag{20}$$

$$\mathrm{pH} = 12{\cdot}9 \quad \log k = 1{\cdot}06\sigma_T + 3{\cdot}07 \qquad r = 0{\cdot}91 \qquad s = 0{\cdot}18 \qquad n = 11 \tag{21}$$

Two significant inferences can be drawn:

(i) at pH = 12·9 the sign of ρ is positive, supporting the view that the reaction is nucleophilic in agreement with the mechanism proposed by eqn (19).
(ii) the *ortho*-substituent compounds obey eqns (20) and (21).

At first sight, this result is surprising if one considers the deviations presented by these compounds while trying to correlate their pK. Probably, hydrogen bonds do not play any part in the determining kinetic process. Because of this, the substituent effects are well accounted for and in turn, confirm *a postiori* the kinetic scheme proposed.[2] However, the unique set of substituents at our disposal prompted us to investigate in more detail the substituent effects by more advanced approaches: the results presented are likely to interest workers involved in the study of linear energy relationships.

3.2. Another approach to substituent effects

Our purpose is not to present here a detailed statement; we will mention only the review of this question by Exner.[16] Two possibilities are offered to the experimentalist.

(i) $\log k_2(T_2)$ is reported as a function of $\log k_1(T_1)$ for each compound. If a linear relationship:

$$\log k_2 = a + b \log k_1 \tag{22}$$

is fulfilled it is concluded that an isokinetic relationship is valid. According to Exner[16] the interest of such a procedure is to indicate the

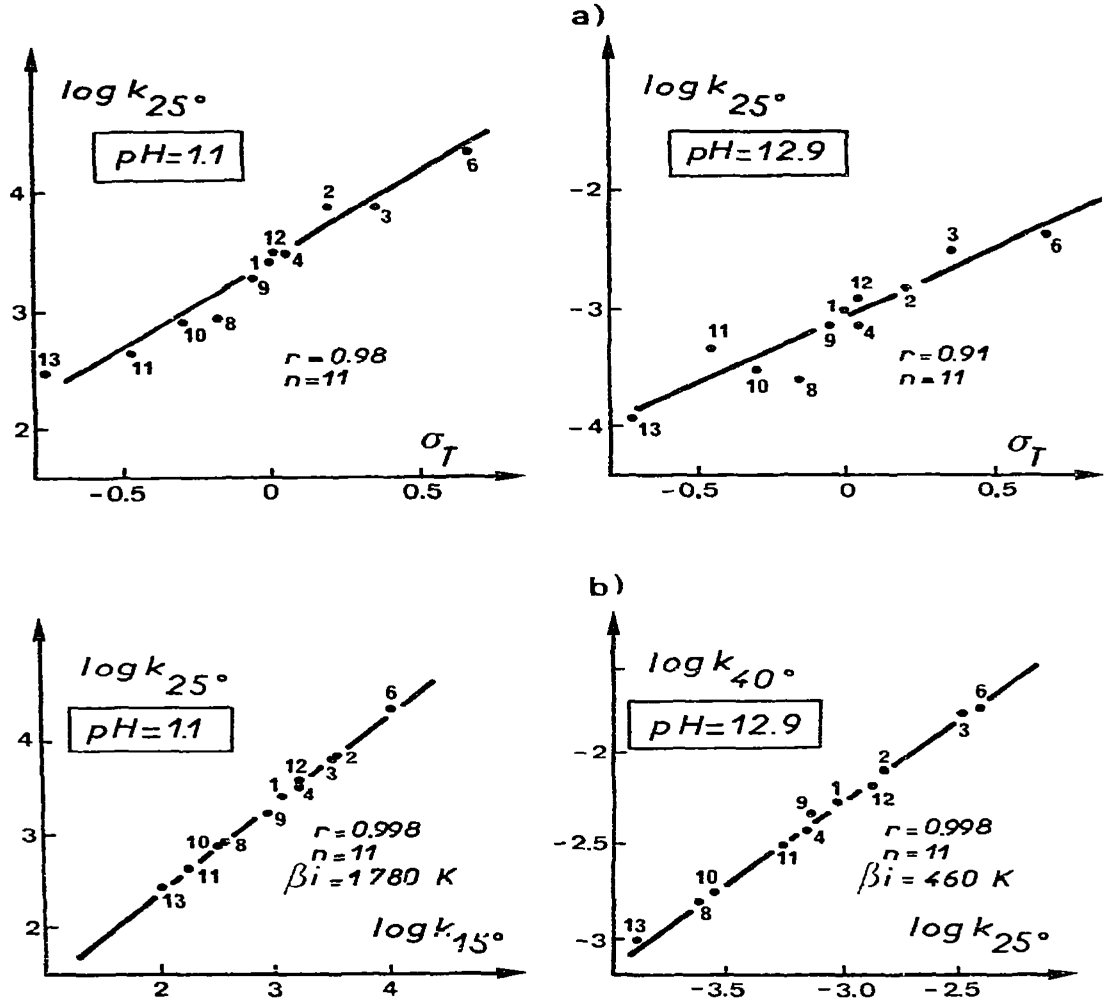


Fig. 8. Substituent effects on relaxation kinetics: (a) classical treatment; (b) more advanced approach using rank correlation.

correct value of the isokinetic temperature β_i (the theoretical temperature at which the substituent effect is reversed) by the relation:

$$\beta_i = T_1 T_2 \frac{1-b}{T_1 - bT_2} \tag{23}$$

In fact, it can be seen from Fig. 8(b) that such a relationship is actually obeyed for both acidic and basic pH and with a high correlation level.

$$\text{pH} = 1{\cdot}1 \quad \log k_{25^\circ} = 0{\cdot}96 \quad \log k_{15^\circ} + 0{\cdot}45 \quad r = 0{\cdot}998 \quad s = 0{\cdot}04 \quad n = 11 \tag{24}$$

$$\text{pH} = 12{\cdot}9 \quad \log k_{40^\circ} = 0{\cdot}86 \quad \log k_{25^\circ} + 0{\cdot}32 \quad r = 0{\cdot}998 \quad s = 0{\cdot}03 \quad n = 11 \tag{25}$$

The corresponding isokinetic temperatures are $\beta_i = 1780\,\text{K}$ (pH = 1·1) and $\beta_i = 460\,\text{K}$ (pH = 12·9), both values excluding any experimental verifications (as in most cases).

It is worth pointing out that in such an approach each substituent is characterized by a rank in a sequence and not by a numerical value of a parameter. However, it is striking that the substituents are classed nearly in the same order as when using σ_T. Since linear correlations were observed for each one of the pH values investigated, the important question arises whether the rank of a given substituent is pH-independent?

In order to answer this question one can resort to Spearman's test on rank correlation:[17]

$$r = 1 - \sum 6 \frac{\sum (x_i - y_i)}{n(n^2 - 1)} \tag{26}$$

where x_i, y_i are the ranks of the substituent in two experiments.

From Table 3 and tables relating to Spearman's test[17] it can be

TABLE 3

Correlation of $\log k_1 \leftrightarrow \log k_2$ and Spearman's Test

	log k₂₅° →										
	Rank										
pH	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
1·1	13	11	10	8	9	1	4	12	3	2	6
6·85	13	8	10	11	1	9	4	2	12	3	6
9·2	13	8	10	4	11	1	9	2	12	3	6
11·1	13	10	8	4	11	1	9	12	2	3	6
12·9	13	8	10	11	4	1	9	12	2	3	6
$(x_i - y_i)^2$*	0	4	0	4	1	1	0	1	1	4	0
$(x_i - y_i)^2$**	0	1	1	1	1	0	0	0	0	0	0

* Spearman's test applied to pH 1·1 and 6·85 ($r = 0{\cdot}93$).

** Spearman's test applied to pH 11 and 12·9 ($r = 0{\cdot}98$).

asserted that the hypothesis 'the rank of a substituent is pH-independent' is acceptable to a high level of confidence.

(ii) A second possibility consists in expressing the activation energy, E, in terms of the logarithm of the pre-exponential factor, $\log A$, as reported in Fig. 9. The linear correlations observed are slightly less good than in the previous case:

$$\text{pH} = 1{\cdot}1 \qquad E = 1{\cdot}21 \log A - 2{\cdot}7 \qquad r = 0{\cdot}82 \qquad s = 1{\cdot}0 \qquad n = 11 \tag{27}$$

$$\text{pH} = 12{\cdot}9 \qquad E_{\text{H}^*} = 1{\cdot}11 \log A_{\text{H}^*} - 8{\cdot}42 \qquad r = 0{\cdot}96 \qquad s = 0{\cdot}87 \qquad n = 11 \tag{28}$$

According to Good *et al.*,[18] the best procedure consists of a mixing of procedures (i) and (ii): first establish the graph of E vs. $\log A$ as in (ii) and join together the experimental points in the same order as in (i). In fact, Good[18] confesses that the resulting relationship may be very complex. Therefore, accounting for the substituent effect and as a consequence getting information on the mechanism of the reaction studied is no longer straightforward (as in section 3.1). Hence, the very poor use of these approaches among organic chemists.

3.3. pK(H$^+$B$_c$)

From Fig. 2 in ref. 4 it can be deduced that the pK of H$^+$B$_c$—a transient species—is given by:

$$\text{p}K(\text{H}^+\text{B}_c) = \frac{\log k_{\text{H}^*} - \log k_1}{\alpha} \tag{29}$$

From Fig. 10 it is apparent that a good linear correlation of pK(H$^+$B$_c$) with σ_T is observed if **13** is excluded (this anomaly can be attributed to the specific mesomeric effect: $\text{CH}_3\text{O}\!-\!\!- \leftrightarrow \text{CH}_3\text{O}^+\!\!=$).

$$\text{p}K(\text{H}^+\text{B}_c) = -1{\cdot}4\sigma_\text{T} + 6{\cdot}15 \qquad r = 0{\cdot}96 \qquad s = 0{\cdot}12 \qquad n = 10 \tag{30}$$

In contrast to the effect observed on the pK of the azo and hydrazone tautomers (cf. section 2.2) the substituents with negative σ_T values (inducing **13**) increase pK(H$^+$B$_c$). Since the *ortho*-substituents obey eqn (30), it can be inferred that intramolecular hydrogen bonds do not occur, a conclusion which confirms the structure proposed for the species H$^+$B$_c$.[2] This shows all the information we can obtain from a study of the substituent effects.

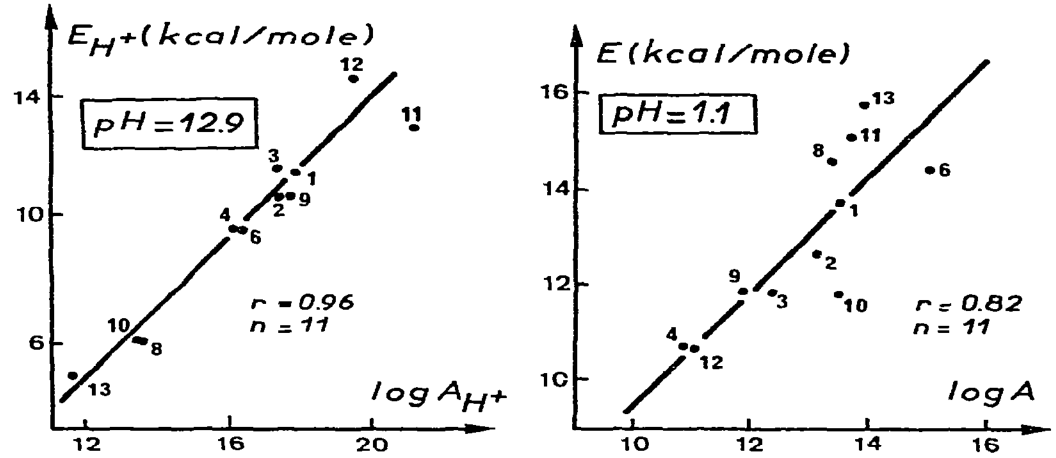


Fig. 9. Treatment of the substituent effect on the relaxation kinetics by using the activation energy and the pre-exponential factor.

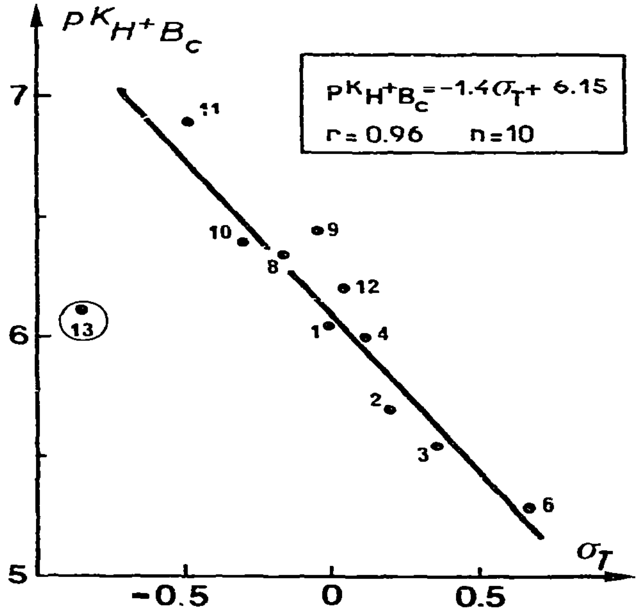
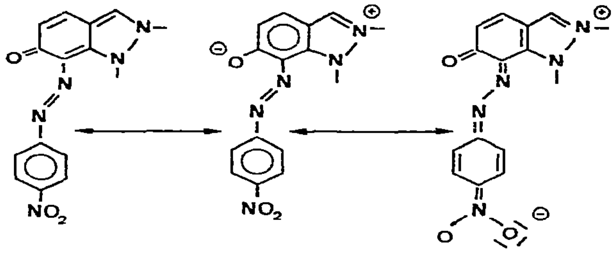


Fig. 10. Linear correlation of the pK of the transient species H^+B_c with σ_T.



7 a) neutral form

7 b) dipolar form

7 c) dipolar form

Fig. 11. The strong mesomeric effect of the nitro-group in the basic form of dye 7.

Now we have to account for the lack of transient in **5** and **7**. According to eqn (30) one could reasonably expect these compounds ($\sigma_T \simeq 0{\cdot}8$) to have a lifetime in the range 20–50 μs at the most unfavourable case of $pH = 1{\cdot}1$. This lifetime range is easily attainable with our apparatus. The non-existence of a transient signal could be caused by the strong mesomeric effect of the nitro-group in the *o*- and *p*-positions which results in a N—N bond with highly single character (form c in Fig. 11) and which excludes in every way *cis–trans* isomerization. This mesomeric effect is not possible for **6** and in fact this compound presents a normal transient.

4. CONCLUSION

We have investigated a series of molecules which constitutes a severe test for the validity of linear free energy relationships. The interpretation of the substituent effects presents some difficulties when dealing with properties of the ground state of the investigated compounds. Some of the observed deviations can be simply related to well-known specific effects such as hydrogen bonds. We conclude that the contribution of more than one conformer—as deduced from the conformational analysis—has to be taken into account. The interpretation of the substituent effect on the relaxation kinetics is less intricate and moreover it confirms the proposed kinetic model. Obviously, the existence of several conformers does not induce such important deviations as observed when dealing with the p*K* correlations. The experimental data enabled us to deal with more advanced approaches than are usually made and to point out their limits.

From a practical point of view the slight dependence of the tautomer composition (a constant hue) combined with the dramatic dependence of the relaxation kinetics on the substituent are of interest in assessing the best substituent as regards the lightfastness.

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