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The Effect on the Colour of the Diarylazo Chromogen, and Electronic Substituent Constants, of the *N*-pyridinium Group

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ABSTRACT

Para- *and* meta-N-*pyridinium-substituted anilines have been synthesised by displacement of dinitroaniline from* N-*(2,4-dinitrophenyl)pyridinium chloride by* p-*phenylenediamine or* m-*acetylaminoaniline in hot DMF. Diazotisation and coupling with* N,N-*diethylaniline gave azo compounds, with visible absorption maxima:* p-*pyridinium isomer, 486 nm (neutral), and 504 nm (acid);* m-*pyridinium isomer, 456 nm (neutral), and 508 nm (acid). Dual-parameter relationships have been derived for a series of substituted azo compounds, connecting their halochromic shifts (difference in visible absorption maximum between neutral and protonated forms) and the electronic substituent constants,* σ_I *and* σ_R. *Via these relationships, values of* $\sigma_I = 1{\cdot}01$ *and* $\sigma_R = 0{\cdot}05$ *have been derived for the* N-*pyridinium substituent. Thus, this group is shown to be an exceedingly powerful electron-withdrawer, exerting its effect mainly by inductive/field effects. Its effect on the colour of azo dyes is roughly equivalent to that of the nitro group.*

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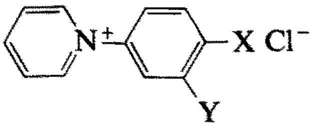
1 INTRODUCTION

Cationic dyes in commercial use have usually fallen into one of two classes. Firstly, a charged unit is appended to a conventional chromogen via a non-conjugated linking unit, where it has little effect on the colour of the dye. The opposite situation pertains in fully conjugated systems such as cyanines or hemicyanines. Here, the presence of the formal charge is a significant and determining influence on the colour of the molecule. However, there are dyes of a third, intermediate nature which are less well exemplified, where the cationic centre is attached directly to the chromogen, and therefore might be expected to affect the colour, but where it is not formally delocalised into the chromogen. In this paper, we report results relating to the *N*-pyridinium substituent, where the cationic centre, as formally drawn, is attached to the aryl ring of the ubiquitous arylazo chromogen, but no resonance forms can be drawn where the positive charge is delocalised into the chromogen.



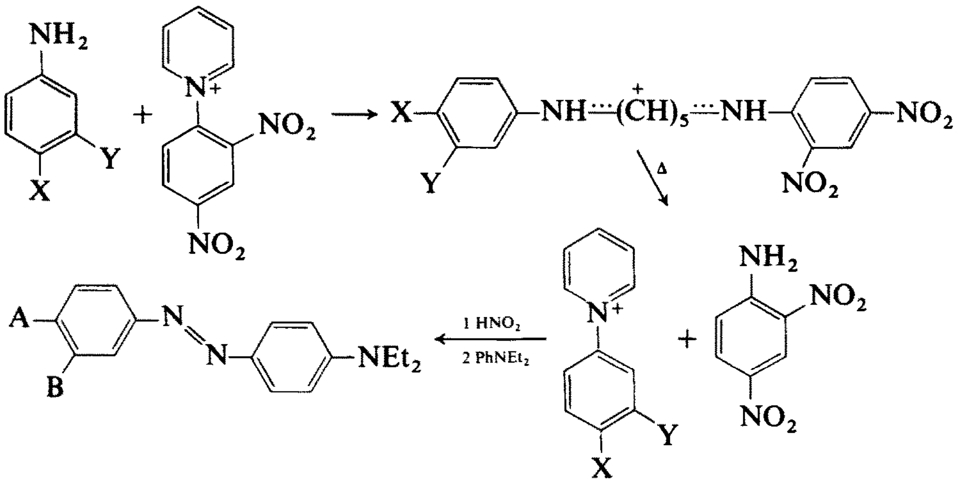
(**1**) $X = NH_2$, $Y = H$
(**2**) $X = H$, $Y = NH_2$

The results reported include: (i) syntheses of *para*- and *meta*-*N*-pyridinium-substituted anilines **1** and **2**; (ii) the visible spectral absorption maxima of derived azo compounds in both neutral and protonated forms; (iii) development of new dual-parameter correlations, relating halochromic shifts (change in visible absorption maximum on protonation) with inductive and resonance substituent constants, σ_I and σ_R;[1,2] and (iv) estimates of substituent constants for *N*-pyridinium based on the observed halochromism. Parameters which quantify the electronic properties of substituents are important data of use in reactivity and other physical studies, as well as in the design of molecules with specific properties, such as drugs or agrochemicals.[3] Substituents of extreme electronic character are particularly valuable in these contexts. As far as we are aware, values of σ-constants for *N*-pyridinium have not previously been published.

2 RESULTS AND DISCUSSION

2.1 Syntheses and spectral properties

Although the syntheses of both *para*- and *meta*-*N*-pyridinium-substituted anilines have been reported previously,[4] we were not able to duplicate successfully the described procedures. We have now found that *N*-(4-aminophenyl)pyridinium chloride (**1**) can be prepared from *p*-phenylenediamine and *N*-(2,4-dinitrophenyl)pyridinium chloride by a nucleophilic



(4) A = py$^+$, B = H
(5) A = H, B = py$^+$

(1) X = NH$_2$, Y = H
(3) X = H, Y = NHAc
(2) X = H, Y = NH$_2$ $\xleftarrow{H_3O^+}$

Scheme 1

ring-opening, ring-closure sequence[5] as summarised in Scheme 1. Use of DMF containing a little ethanol as solvent gives acceptable yields of clean material. Application of this procedure to the *m*-diamine failed, polymeric material being the main product. However, *m*-acetylaminoaniline reacted satisfactorily to give **3**. Acid-catalysed hydrolysis then led to the required *N*-(3-aminophenyl)pyridinium chloride (**2**), isolated as the hydrochloride. Diazotisation of **1** and **2** in aqueous acidic nitrite solution at 0°C, and subsequent coupling with *N*,*N*-dialkylanilines, as well as other conventional coupling components, proceeded readily. The visible absorption maximum of the derived *p*-*N*-pyridinium azo compound (**4**) is 486 nm in aqueous alcohol solution. Protonation of the azo-linkage of **4** shifted the absorption maximum to 504 nm. The *m*-isomer (**5**) had λ_{max} 456 nm in neutral solution, and λ_{max} 508 nm after protonation. (Amino-substituted azobenzenes are protonated on both the azo group and the amino group. In the former case, the visible absorption maximum frequently changes appreciably and it is to this that the data reported here refer. In the latter case, the electron-donor property of the amino group is removed, and the main absorption reverts to the UV region, and is approximately constant at *c*. 325 nm for all azo compounds.[6])

2.2 Correlation analyses

Because substituents on the azobenzene skeleton can themselves take part in the light-absorption process, it is not usually possible to correlate absorption maxima with electronic substituent parameters, such as Hammett's σ.[7] Furthermore, σ-constants refer to, and are derived from, ground-state properties, so their inapplicability to an excited-state property is not surprising. However, an empirical linear correlation has been reported between the *differences* in absorption maxima of the neutral azo and protonated azonium compounds (halochromic shift, $\Delta\lambda$) and Hammett σ-constants of substituents.[8] We have checked these correlations with the quoted σ-constants (as well as with more recent values[2,3]). The coefficients of the regression equations are unchanged from those published by the Russian workers, although the statistics are different. Thus, for *para*-substituted azo compounds:

$$\Delta\lambda(para) = 124{\cdot}4 - 106{\cdot}5\sigma_p \qquad n = 22;\ s = 8{\cdot}1\ \text{nm};\ R^2 = 0{\cdot}971 \tag{1}$$

and for the *meta*-isomers:

$$\Delta\lambda(meta) = 114{\cdot}3 - 62{\cdot}9\sigma_m \qquad n = 12;\ s = 4{\cdot}5\ \text{nm};\ R^2 = 0{\cdot}943 \tag{2}$$

where n = number of compounds; s = standard deviation; R^2 = square of (multiple) correlation coefficient. Statistical analyses were done using the commercial SAS package; see Ref. 9.

Substitution of the $\Delta\lambda$ values for **4** and **5** (18 and 52 nm, respectively) into eqns (1) and (2) yields σ_p and σ_m values for the *N*-pyridinium group of 1·00 and 0·99, respectively.

More recent treatments of electronic substituent constants have attempted to quantify separately the different mechanisms of electronic interaction. The best-established formalism replaces the all-encompassing Hammett σ-constant by two parameters which reflect firstly the resonance effect (σ_R), and secondly inductive and/or through-space field effects (σ_I).[1,2] A major advantage of such a treatment is a better understanding of the underlying modes of behaviour of the particular substituents in the system under study. We have applied these two parameters to the literature data[8] already described by eqns (1) and (2). Thus, dual-parameter analyses have led to the equations (3) and (4), where now the differences in absorption maxima are described in terms of the separate resonance and inductive/field parameters.

$$\begin{gathered}\Delta\lambda(para) = \underset{(\pm 4{\cdot}5)}{117{\cdot}4} - \underset{(\pm 9{\cdot}2)}{92{\cdot}3}\sigma_I - \underset{(\pm 6{\cdot}2)}{114{\cdot}5}\sigma_R \\ n = 20;\ s = 7{\cdot}9\ \text{nm};\ \mathrm{R}^2 = 0{\cdot}976\end{gathered} \tag{3}$$

$$\begin{gathered}\Delta\lambda(meta) = \underset{(\pm 2{\cdot}4)}{111{\cdot}2} - \underset{(\pm 5{\cdot}0)}{58{\cdot}6}\sigma_I - \underset{(\pm 4{\cdot}7)}{33{\cdot}7}\sigma_R \\ n = 12;\ s = 3{\cdot}9\ \text{nm};\ R^2 = 0{\cdot}962\end{gathered} \tag{4}$$

The statistics[9] of these dual-parameter relationships indicate that they are not significantly better than those dependent on Hammett σ-constants alone. Importantly, though, they now allow estimation of the σ_R and σ_I

constants for the *N*-pyridinium group. Substitution of the halochromic shifts for the *p*- and *m*-derivatives, **4** and **5**, into eqns (3) and (4) gave estimates of $\sigma_R(py^+) = 0{\cdot}05$, and $\sigma_I(py^+) = 1{\cdot}01$. Thus, the *N*-pyridinium group exerts its electron-withdrawing effect mainly by inductive/field mechanisms. Its resonance interaction is weak, but also electron-withdrawing.

Comparison of these values with those of better-established substituents is instructive. The isoelectronic phenyl substituent is a weak electron *donor* by resonance ($\sigma_R = -0{\cdot}11$), and a weak acceptor as reflected by its inductive/field effect ($\sigma_I = 0{\cdot}12$).[2] Only strongly electron-withdrawing groups lead to bathochromic visible maxima comparable with those exhibited by structures **4** and **5**. Thus, in systems comparable with **4** but containing a nitro group at position A, $\lambda_{max} = 485$ nm,[10] $\sigma_R = 0{\cdot}10$, and $\sigma_I = 0{\cdot}67$;[2] and for similar cyano substitution $\lambda_{max} = 466$ nm,[10] $\sigma_R = 0{\cdot}08$, and $\sigma_I = 0{\cdot}57$.[2] Whilst the resonance interaction of *N*-pyridinium is marginally less than that for these substituents, not surprisingly it is a much stronger electron-withdrawer by inductive/field effects. In fact, it is a more powerful electron-withdrawer than any known uncharged substituent, and is only approximated by other cationic groups. Thus, the σ-constants for Me_3N^+ are $\sigma_p = 0{\cdot}97$, $\sigma_I = 1{\cdot}07$, and $\sigma_R = -0{\cdot}11$.[2] Significantly, the latter value indicates that this group is a weak electron-*donor* by resonance effects. *N*-Pyridinium cannot therefore be considered merely an equivalent to Me_3N^+. It is nearer in electronic effect to the chemically less stable substituent, Me_2S^+ ($\sigma_p = 1{\cdot}14$, $\sigma_I = 0{\cdot}90$, $\sigma_R = 0{\cdot}24$).[2] However, none of these substituents approaches the electron-withdrawing power of an *endo*cyclic protonated aza atom. Protonated pyridinium substituent constants have been reported to be 2·18 (*meta*) and 2·42 (*para*).[11]

A series of σ_I values has recently been published for a range of neutral heterocyclic substituents.[12] However, these do not include *N*-pyridinium, and none of the σ_I values is as high as that estimated for *N*-pyridinium.

Two caveats are in order. Firstly, charged substituents interact strongly with solvent, so their substituent 'constants' are not strictly constant under different physical conditions.[13] Secondly, the σ-values for *N*-pyridinium have been derived from just one data source. Reliable values are only obtained by analysis of several correlation studies on different chemical systems. Therefore the above values should only be considered estimates and applied with caution.

3 EXPERIMENTAL

All materials were available either commercially, or from the ICI specimen collection.

3.1 *N*-(4-aminophenyl)pyridinium chloride (1)

2,4-Dinitrochlorobenzene (50·6 g, 0·25 mol) was heated in pyridine (25 ml) and DMF (200 ml) for $2\frac{1}{2}$ h on a steam bath. *p*-Phenylenediamine (54 g, 0·5 mol) in DMF (200 ml) was added at room temperature to the suspension of *N*-(2,4-dinitrophenyl)pyridinium chloride which had formed, giving an immediate purple colouration and total solution. After 2 h on a steam bath, the purple colour had disappeared. The solution was cooled, poured into ether (200 ml), and cooled further to 0°C. The crude product was filtered off, washed with toluene and ether, and isolated as a brown powder (25·4 g, 49%). A sample was recrystallised from damp MeOH to give pale yellow needles, m.p. 256–259°C (lit. m.p. 252°C). $\delta_H^{DSS}(D_2O)$ 4·75 (s, 4H, —$NH_2 + H_2O$), 6·96 [d, 2H, $J = 8$, CH(ar)], 7·52 [d, 2H, $J = 8$, CH(ar)], 8·26 [tr, 2H, $J = 7$, β-H(py)], 8·74 [tr, 1H, $J = 7$, γ-H(py)], 8·94 [d, 2H, $J = 7$, α-H(py)].

3.2 *N*-[4-(4′-diethylaminophenylazo)phenyl]pyridinium chloride (4)

The pyridinium salt (1) (1·03 g, 5 mmol) was dissolved in dilute HCl (10 ml 2M) and diazotised with $NaNO_2$ solution (10·0 ml 0·5M, 5 mmol) at 0–5°C. The slight excess of nitrite was destroyed with sulphamic acid. *N*,*N*-Diethylaniline (0·8 ml, 5 mmol) was added with stirring and the solution brought to, and maintained at, pH 6·0 by addition of caustic soda solution. The mixture was stirred at room temperature for 1 h and the precipitated azo dye filtered off and washed (1·39 g, 85%; m.p. 253–255°C). Found: C, 64·4; H, 6·6; N, 14·3. $C_{21}H_{23}N_4Cl.1{\cdot}5H_2O$ requires: C, 64·0; H, 6·6; N, 14·2%. $\delta_H^{TMS}(d_6\text{-DMSO})$ 1·18 (tr, 6H, $J = 7$, $2 \times CH_3$), 3·4 (m, $2 \times CH_2 + H_2O$), 6·88 (d, 2H, $J = 9$), 7·71 (d, 2H, $J = 9$), 8·38 (s, 1H), 8·4 (m, 2H), 8·9 (tr, 2H, $J = 8$), 9·09 (s, 1H), 9·39 (d, 2H, $J = 7$). λ_{max} 486, 275 nm; $\lambda_{max}(H^+)$ 504, 319 nm.

3.3 *N*-(3-acetylaminophenyl)pyridinium chloride (3)

To 3-aminoacetanilide (0·9 g, 6 mmol) in DMF (20 ml) was added dropwise *N*-(2,4-dinitrophenyl)pyridinium chloride (0·84 g, 3 mmol) in warm DMF/EtOH (30 ml/3 ml). The deep red solution was stirred at room temperature overnight, after which TLC analysis showed the solution was primarily the ring-opened intermediate. The solution was then heated at 100°C (oil-bath temperature) for $4\frac{1}{2}$ h. The pale red solution was poured in Et_2O (100 ml) and allowed to stand overnight. The yellowish-brown oil which separated out was washed several times with Et_2O until it was a pale yellow solid (0·55 g, 72%; m.p. 140–142°C). The hygroscopic nature of the material prevented microanalysis. $\delta_H^{TMS}(d_6\text{-DMSO})$ 2·12 (s, 3H, CH_3), 3·12 (s, 3H, $NH + H_2O$), 6·8–8·3 [m, 6H, CH(ar) + CH(py$^+$)], 9·38 [d, 2H, α-CH(py$^+$)]. δ_C^{TMS}(d$_6$-DMSO) 23·87(q), 114·47(d), 118·85(d), 121·07(d), 128·31(d), 130·44(d), 140·72(s), 142·84(s), 144·65(d), 146·72(d), 169·22(s). ν_{max}(KBr) 3430, 1697, 1610 cm^{-1}. *m/e*: 213(M$^+$), 150, 108(100%), 80.

3.4 *N*-(3-aminophenyl)pyridinium chloride (2)

The acetanilide **3** (0·39 g, 1·5 mmol) was refluxed in EtOH (10 ml) for 10 min and conc. HCl (2 ml) was then added. Reflux was continued for 3 h. After cooling, the reaction mixture was concentrated to dryness on a rotary evaporator to give a brown solid (0·29 g, 76%), which was diazotised as described below without further purification. ^{1}H-NMR at this stage revealed absence of the acetyl group.

3.5 *N*-(3-(4′-diethylaminophenylazo)phenyl)pyridinium chloride (5)

The pyridinium salt **2** (0·36 g, 1·5 mmol of the hydrochloride salt) was dissolved in aqueous HCl (19 ml, 0·4M, 5 equiv.). Sodium nitrite solution (10 ml, 0·6M, 4 equiv.) was then added dropwise at 0–5°C. Excess nitrite was destroyed by addition of sulphamic acid solution (negative starch–iodide end-point). *N*,*N*-Diethylaniline (0·23 ml, 1·5 mmol) was added dropwise with stirring at 0–5°C, followed by 2M-NaOH solution until the pH was stabilised at 6 (pH-meter). The red reaction mixture was stirred for 1 h at room temperature and was then extracted with $CHCl_3$ (5 × 20 ml), dried ($MgSO_4$) and concentrated to a red oil. This was purified by redissolving in water and continuous extraction with Et_2O for several hours. The aqueous layer was then concentrated to dryness giving a red oil (0·28 g, 52%). The hygroscopic nature of the material prevented microanalysis. δ_H^{TMS}(CD_3OD) 1·12 (tr, 6H, $J = 7$, 2 × CH_3), 3·37 (q, 4H, $J = 7$, 2 × CH_2), 4·64 (s, H_2O?), 6·64 [d, 2H, $J = 7$, CH(ar)], 7·6–8·05 [m, 6H, CH(ar)], 8·21 [tr, 2H, $J = 7$, β-CH(py$^+$)], 8·70 (tr, 1H, $J = 8$, γ-CH(py$^+$)), 9·19 (d, 2H, $J = 6$, α-CH(py$^+$)). δ_C^{TMS}(CD_3OD) 12·90(q), 45·40(tr), 112·00(d), 117·55(d), 124·84(d), 125·83(d), 126·89(d), 129·36(d), 132·03(d), 143·37(s), 144·45(s), 145·27(d), 147·55(d), 152·13(s), 155·09(s). *m/e* 331(M^+), 280, 149(100%), 136, 119, 116, 91, 78, 69. λ_{max}458, 266 nm; λ_{max}(H$^+$) 510, 350, 314, 270 nm.

4 CONCLUSION

As far as application in colour chemistry is concerned, *N*-pyridinium as a substituent in the diazo component of azo compounds is a charged alternative to conventional groups such as nitro, with about the same bathochromic influence. Furthermore, the pyridinium-substituted anilines are prepared much more conveniently than analogous anilines containing other cationic substituents, such as trialkylammonium. In the more general context of molecular design, pyridinium has about the same shape and size as phenyl, but has significantly different electronic and hydrophilic properties. It might therefore find use in breaking up collinearities in correlation analyses.

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