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STRUCTURE-COLOUR RELATIONSHIPS OF SOME NEW N-ARYLPYRIDINIUM HEMICYANINE DYES

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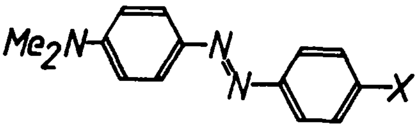
Abstract - N-aryl derivatives of 4-(p-dimethylamino)pyridine are novel examples of donor-acceptor dyes. Para-substituents in the N-aryl group influence the spectra, such that the more electron-withdrawing lead to more bathochromic shifts. However, a 2-nitro substituent in the N-aryl ring has surprisingly little influence on the absorption maximum. PPP-MO-CI calculations, and correlation and conformational analyses are applied to the study.

Many dyes can be classified as donor-acceptor systems, of generalised structure (1).[1a,2a] In (1), two aromatic or heteroaromatic groups are linked directly or via a conjugating chromophore, Y, and are substituted by electron-donor substituents, D, and electron-acceptors, A, respectively. The commonest and commercially most important example is the substituted azobenzene molecule (2). Modifications of the (hetero)aromatic ring systems as well as the D and A combinations has led to a plethora of coloured systems, but variation of the Y component in (1) is less common. One simple example along these lines involves the use of the pyridinium group as the interconnecting chromophore Y, leading to the novel hemicyanine[2b] structures (3; overleaf) which are the subject of this paper.

Although dyes (3) are new, substructures of (3) are known as coloured materials in their own right. N-Alkyl analogues (4; X = NAlkyl) are bright yellow, fluorescent salts,[3] and the corresponding pyrylium[4,5] and thiapyrylium[5] salts (4; X = O,S) have also been characterised. The other arylpyridinium unit of (3) is typified by the much-studied pyridinium betaines (5), whose strongly solvent-dependent absorption characteristics have been applied in defining the E_T scale of solvent polarity.[6]

$\ddot{D}$–(het)aryl–Y–(het)aryl–A

1



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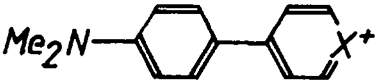

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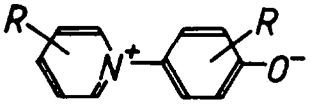

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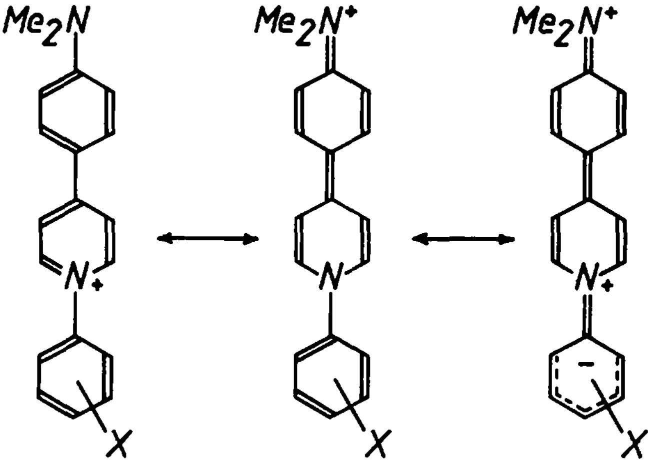
Table 1 Structures and absorption maxima of pyridinium derivatives (3).

	Substituents	Absorption Maximum (nm)				$\Delta\lambda$ (nm)
		10% HOAc	H_2O	MeOH	$CHCl_3$	($CHCl_3$ - H_2O)
(6)	(3); X = 4-OMe	445	440	446	456	16
(7)	(3); X = H	446	442	448	458	16
(8)	(3); X = 4-Cl	452	444	451	463	19
(9)	(3); X = 4-NO_2	471	465	468	479	14
(10)	(3); X = 2,4-$(NO_2)_2$	472	464	466	476	12
(11)	(3); X = 2,4-$(NO_2)_2$-6-Me	465	462	465	472	10
(12)	(3); X = 2,4-$(NO_2)_2$-5-Me	460	464	464	474	10
(13)	(3); X = 2,4-$(NO_2)_2$-5-NHAc	-	464	465	476	12
(14)	(4); X = NMe	-	414	421	435	21
(15)	(4); X = NCH_2Ph	424	424	431	437	13



a b c

3

Besides being on the one hand structurally novel, and on the other related to other dye types, (3) possesses several additional features of note. For instance, by opening up the possibility for extended conjugation (e.g. 3c) the N-aryl ring and its substituents can themselves play a part in the light-absorption process, thus potentially distinguishing them from the N-alkyl analogues (4; X = NAlkyl). Furthermore, the nonplanarity of (3) which results from the biphenyl-type substructures can also engender special effects on the colour properties. It is from all these viewpoints that the visible spectral properties of (3) are now discussed.

RESULTS AND DISCUSSION

The pyridinium derivatives (6)-(15) of this study are listed in Table 1. Those derived from methyl and benzyl halides,[7] and from dinitro-activated aryl chlorides, were prepared in unexceptional manner by direct quaternisation of 4-(p-dimethylaminophenyl)pyridine (16). p-Chloronitrobenzene was not sufficiently activated by electron-withdrawing groups to undergo analogous reaction, but the corresponding p-fluoro derivative gave the pyridinium salt (9) in hot DMSO. Other N-aryl derivatives were prepared by indirect displacement of 2,4-dinitroaniline from (10) by a more basic aniline. These reactions proceed via the well-precedented nucleophilic attack, ring-opening, ring-closing reaction.[8] However, only relatively basic anilines were found to react in this way, any less basic than p-chloroaniline failing to yield any sign of ring-opening of the pyridinium nucleus.

Table 2
Absorption Maxima of 4-Substituted N-Arylpyridinium Dyes (3) Calculated by the PPP-MO-CI Method, Values Predicted by Equation 2, and Values for σ-constants.[11]

4-Substituent	λ(PPP)	λ(eq.2)	Δλ	σ_I	σ_R
CN	500.7	495.8	4.9	0.57	0.13
NO_2	499.2	502.5	-3.3	0.70	0.15
COMe	483.9	486.5	-2.6	0.28	0.16
CO_2Me	477.6	478.4	-0.8	0.32	0.03
$CONH_2$	473.0	475.4	-2.4	0.30	0.00
Cl	470.4	465.0	5.4	0.47	-0.23
$CH=CH_2$	465.6	462.9	2.7	0.08	-0.05
2-furyl	464.8	463.6	1.2	0.04	-0.02
H	464.8	463.5	1.3	0.00	0.00
OCOMe	460.0	461.8	-1.8	0.39	-0.23
NHCOMe	450.3	454.8	-4.5	0.25	-0.25
OMe	443.7	441.8	1.9	0.30	-0.45
NH_2	432.3	433.6	-1.3	0.15	-0.48
Et_2N	426.6	427.3	-0.7	0.16	-0.57

Table 1 also records the absorption maxima of the visible spectra measured in solvents ranging in polarity from chloroform to water. The difference between the values recorded in these latter two solvents gives an indication of the relative solvatochromic behaviour of (3).

Semi-empirical MO calculations based on the Pariser-Parr-Pople (PPP) approximation with configuration interaction,[9] gave theoretical information on the photoexcitation behaviour of dyes (3) (Table 2). Standard parameters were employed.[9] The PPP model assumes a planar conformation for the molecule calculated, whereas this is definitely not the case for (3) (below). However, justification for use of the technique in such circumstances has been presented elsewhere, where PPP calculations on the equally nonplanar triarylcarbenium ion-dyes proved satisfactory in describing their colour properties.[10]

Para-substituted N-Phenyl Derivatives (6)-(9). The pyridinium hemicyanines (6)-(9) are somewhat more bathochromic and less fluorescent than the simple alkyl analogues (14) and (15) (Table 1), and range through shades of yellow to the bright orange of the 4-nitro derivative (9). The trend in absorption maxima clearly shows that increase in the electron-withdrawing power of the 4-substituent induces more bathochromic shifts. In fact, a quantitative relationship exists between the λ_{max} values and the Hammett σ_p-constants of the 4-substituents (eq. 1, methanol values).

$$\lambda_{max} = 447.7 + 24.0\,\sigma_p \qquad (1)$$

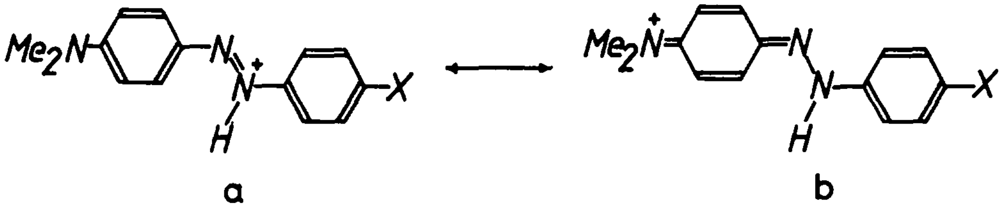
$$= 447.7 + 24.0\,\sigma_I + 24.0\,\sigma_R \qquad (1a)$$

(correlation coefficient, $r = 0.986$; standard deviation, $s = 2$ nm)

The use of substituent constants, which are derived from ground state data, in excited state correlations is unusual, but nevertheless not without precedent.[1b] Where such correlations are observed, the substituents are not part of the chromogen, but rather act mainly as perturbing influences on the chromogen itself. This implies in the current context that the electron excitation does not extend to the substituents on the N-aryl ring.

The experimental observation of negative solvatochromism - that is, hypsochromic shift with increased solvent polarity (Table 1) - is comparatively uncommon, and indicates that the lowest excited state of (3) is less polar than the ground state.[1c,2c] Negative charge donation by the dimethylamino substituent during excitation results in the pyridinium positive charge being more evenly distributed over the molecule. Thus, while the ground state is most accurately represented by (3a), the excited state contains a greater resonance contribution from (3b). The ^1H nmr chemical shifts corroborate this conclusion, in that they are wholly consistent with the dimethylaminophenyl ring being neutral in the ground state (high field shift for the 3' and 5' protons, see experimental section), while the pyridinium ring protons are well downfield, typical for a charge-localised pyridinium system, rather than the delocalised (3b).

These observations can be compared with the behaviour of azo and azonium systems (2) and (17), respectively, each of which bears formal resemblance to (3). Azo dyes (2) also become more bathochromic as the electron-withdrawing ability of the substituent X increases. On the other hand, they exhibit positive solvatochromism. In this case, charge is transferred on excitation from the amino donor group into the azo linkage and C_6H_4X, and the excited state has more charge separation than the ground state. The reverse is true for the azonium dyes (17), where for electron-withdrawing X, a hypsochromic shift results. The spectra of (17) are rationalised in valence bond terms by assuming the major ground state resonance contributor is (17b).[1d,2d] Electronegative substituents X thus decrease the donor ability of the central NH, rather than act as auxochromes as in (2).[1d,2d] The pyridinium dyes (6)-(9) clearly resemble (2) rather than (17) in behaviour. Again, the conclusion is that the positive charge remains localised on the pyridinium ring in the ground state (3a), and that (3b) is not an important contributor to the ground state.



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Turning now to the MO theoretical results (Table 2), the trend of the PPP-calculated absorption maxima is similar to the experimental, and is well-described by the dual substituent parameter relationship of eq. 2, derived by multilinear regression analysis.

$$\lambda(\mathrm{PPP}) = 463.5 + 39.8\,\sigma_I + 74.6\,\sigma_R \qquad (2)$$
$$(\underline{r} = 0.991;\ \underline{s} = 3.3\ \mathrm{nm})$$

The two parameters σ_R and σ_I are the conventional resonance and nonresonance substituent constants, respectively.[11] The coefficients show that the resonance effect is significantly more important than the nonresonance effect in influencing the PPP-calculated maxima.

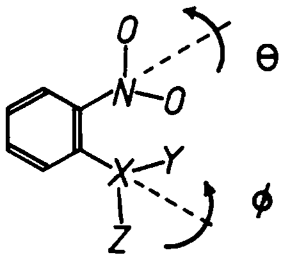
According to the PPP calculations, the excitation corresponds to promotion of an electron from the HOMO, best described by the lone pair of the dimethylamino group, into the LUMO, centred on the pyridinium, and to a lesser extent the N-aryl, rings. Consistent with this, the bathochromic shift induced by more electronegative substituents is due more to the latter's effect on the LUMO energies, rather than the HOMO energies. This MO interpretation matches well that already given above based on qualitative valence bond arguments.

There are significant differences of magnitude in the relative shifts in experimental absorption maxima, compared with the calculated. The Hammett σ_p-constant is related to σ_I and σ_R by $\sigma_p = \sigma_I + \sigma_R$. Equation 1 can therefore be rewritten as eq. 1a, with the implication that the resonance and nonresonance effects are contributing equally to the observed shifts in absorption maxima.[12] This difference between the calculated and experimental results can be related to the nonplanar actual geometry of (3), compared with the idealised planar one which is calculated, as follows.

Nonbonded H...H repulsive interaction between the two rings of biphenyl is relieved by torsion of about 35° about the inter-ring bond.[13] Similar behaviour for (3) results in a nonplanar molecule, anticipated to be less sensitive overall to substituent influences. This is in fact reflected by the decreased coefficients of σ_I and σ_R in eq. 1a as compared with those of eq. 2. The relatively greater decrease in importance of the resonance effect is also a result of the nonplanarity of the pyridinium and N-aryl rings. Thus as the torsional angle between the rings increases so the degree of pi-interaction between them is lessened, and the influence on the spectra due to resonance effects correspondingly decreases. The decrease in the σ_R coefficient by a relative factor of 0.53 (= 39.8/74.6; cf. eq. 1a and 2) allows an estimate of the torsional angle (α). If the transmission of resonance effects across nonplanar systems is dependent on the cosine of the torsional angle, then $\alpha = 58^o$ ($\cos^{-1}0.53$); if a cosine^2 dependence is followed, then $\alpha = 43^o$ ($\cos^{-1}\sqrt{0.53}$). These estimates are in line with expectation, given that α for Ph-Ph is about 35^o and the Ph-pyridinium torsional angle should be somewhat more since the inter-ring bond is shorter than the Ph-Ph bond.[14,15]

<u>N-2,4-Dinitrophenyl derivatives</u> (10)-(13). - The observed colours and measured absorption spectra (Table 1) of all these dinitro derivatives do not differ much from the 4-nitro analogue (9), which at first sight is most surprising. For the hypothetical case of least (zero) resonance interaction between the 4-nitro group and the pyridinium system (i.e. the 4-nitrophenyl unit of (9) orthogonal to pyridinium), eq. 1a predicts a λ_{max} of <u>no less</u> than 463 nm in methanol. When this result is applied to the 2,4-dinitro analogue (10), and if transferability of substituent increments is assumed, introduction of the 2-nitro substituent induces a bathochromic shift of <u>at most</u> 3 nm. Such a very small influence is surprising in view of the marked bathochromic effect of nitro in the 4-position in this system and the known appreciable bathochromic influence of 2-nitro in analogous dye classes (e.g. diarylazo (2)). The question is thus raised: what are the underlying reasons for the 2-nitro group's relatively hypsochromic influence?

The stereochemistry of the 2,4-dinitro derivatives is ill-defined. A survey of the solid phase conformations of systems of general type (18) has recently been published, from which a few conclusions of relevance can be extracted.[16] In the current case, X in (18) is the pyridinium nitrogen atom, and Y and Z are the α-carbon atoms and remainder of the pyridinium ring. A range of conformations is energetically feasible, but all are based on the relationship $\theta + \phi = 90^o$, where θ and ϕ are the torsional angles depicted in (18), and each group is rotated in the same sense. The most likely conformation is one with θ and ϕ in the range $30\text{-}60^o$.[15,17] Thus, the introduction of a 2-nitro group into (9) to give (10) does <u>not</u> necessarily induce much greater torsion about the N-arylpyridinium C-N bond over and above that of $35\text{-}55^o$ derived above for simple 4-substituted derivatives.



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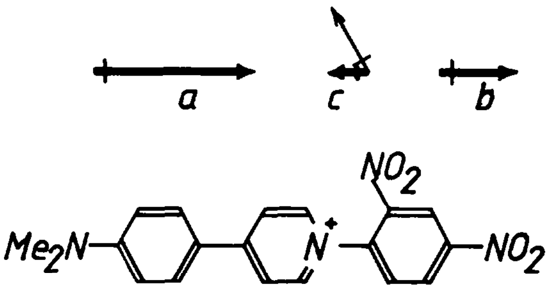
As there is little extra torsion induced by the 2-nitro group, its lack of a bathochromic effect is <u>not purely steric</u> in origin. The spectrum of (11), where an additional 6-methyl group has been introduced, supports this assertion. Here, the conformation is indeed radically changed to the extent that the pyridinium and N-aryl rings will be almost orthogonal.[14] Despite this, (11) exhibits an additional hypsochromic shift of only -2 nm compared with (10).

Even if the resonance effect of the 2-nitro group in (10) were minimal because of sterically induced torsion about the C-nitro bond - and we repeat this is not inevitably so - its nonresonance effect would still be operative. Moreover, in the case of nitro the nonresonance effect is inherently stronger than the resonance effect, as reflected by the σ-constants ($\sigma_I(NO_2) = 0.7$; $\sigma_R(NO_2) = 0.15$).[11] Thus, an appreciable bathochromic shift might still be anticipated. However, σ_I is itself a measure of at least two effects. One is the classical through-bond inductive mechanism which is independent of geometry and consequently bathochromic in this instance, just as for 4-nitro. A second is the through-space field effect which is electrostatic in nature and operates by a dipole-(di)pole mechanism. In fact, it is this effect that we believe underlies the spectral behaviour of these dyes.

The electron transfer during the excitation implies a transition dipole as indicated by *a* in (19). The MO calculations support this conclusion. The orientation of the 4-nitro group dipole (19*b*) is such as to stabilise the transition dipole, leading to a bathochromic shift, as observed. In contrast, the component of the 2-nitro group's dipole (*c* in 19) which acts in the direction of the transition dipole, is *opposed* to the latter. The consequent effect is therefore relatively hypsochromic. These conclusions apply regardless of the overall conformation of the molecule.



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In effect, the 2-nitro group is acting to solvate the ground state molecule *intra*molecularly. A consequence of this is that less negative solvatochromism is expected - external solvent molecules would have less opportunity, or need, to solvate the molecule and thus to influence the spectrum. In fact, experiment bears this out: the four 2,4-dinitro derivatives (10)-(13) have an average $\Delta\lambda$(CHCl$_3$ - H$_2$O) 33% less than that for the remaining derivatives where such internal solvation is not possible (Table 1).

Although we believe there is no precedent for such unexpected behaviour by an electronegative substituent in influencing excited state spectral properties in comparable systems, there is precedent for the anomalous behaviour of adjacent substituents, including nitro, in influencing electronic ground state reactivity. For instance, the basicity of 2'-nitro-4-aminobiphenyl is greater than expected;[18] the acidity of 2'-nitro-4-carboxybiphenyl is less than anticipated;[19] and a similar relative acid-weakening effect by 8-nitro is observed in 1-naphthylcarboxylic acid.[20]

A methyl group in the 5-position of (12) only results in a lessening of the resonance effect of the 4-nitro group due to sterically-induced torsion. However, as already noted, the nitro group exerts its influence more via nonresonance effects than resonance with the consequence that the hypsochromic shift is minimal (-2 nm). The acetylamino group of (13) is able to H-bond to its *ortho*-nitro group thus maintaining the latter's coplanarity with the phenyl nucleus, with no reduction of resonance effect. Acetylamino itself is inductively electron-withdrawing, but is a resonance donor, with the consequence that there is little effect on the spectrum compared with (10).

CONCLUSIONS

All the observations and calculations discussed in this paper support the classification of the *N*-arylpyridinium hemicyanines of structure (3) as donor-acceptor dyestuff systems. The excitation responsible for their colour is a simple charge-transfer from dimethylamino to pyridinium, modified by substituents in the 4-position of the *N*-aryl ring. However, the lack of influence by a 2-nitro group is notable. The relative importance of field effects compared with other mechanisms of electronic interaction in colour-structure studies is being further investigated.

ACKNOWLEDGMENTS

Some of the experimental work was carried out by D.P. Devonald and B.H. Meyrick, to whom I am grateful.

EXPERIMENTAL

UV/visible spectra were recorded on a Unicam SP8000 instrument in purified solvents, and were calibrated with a holmium filter. ^1H nmr spectra were recorded in d_6-DMSO using TMS as internal standard on a Perkin-Elmer R-24A instrument. Starting materials were either commercially available or were obtained from the I.C.I. specimen collection. It was necessary to pump most of the products at 100°C under high vacuum over P_2O_5 for at least 24 h to obtain satisfactory elemental analyses. Despite this treatment, most retained water of crystallisation. Integration of the ^1H nmr spectra confirmed the proportion of water present.

1-(4'-Methoxyphenyl)-4-(4"-dimethylaminophenyl)pyridinium chloride (6). p-Anisidine (3g) and pyridinium salt (10) (2g) were stirred together overnight at 20°C in DMF (15ml). Crude product was filtered off and dissolved in hot ethanol. Successive crops of impurities were filtered off and the remaining mother liquors were concentrated and diluted hot with water. Pure yellow microcrystalline product was obtained by fractional crystallisation, m.p. 214-215°C. (Found: C, 67.0; H, 6.5; N, 7.6%. $C_{20}H_{21}N_2OCl.H_2O$ requires C, 66.9; H, 6.8; N, 7.8%).

1-Phenyl-4-(4'-dimethylaminophenyl)pyridinium chloride (7). Essentially the same method as for (6) with aniline as nucleophile (130°C for 20 min) gave orange microcrystalline product, purified by recrystallisation from water (50% yield), m.p. 242°C. (Found: C, 67.5; H, 6.3; N, 8.3%. $C_{19}H_{19}N_2Cl$. $1.5H_2O$ requires C, 67.5; H, 6.6; N, 8.3%.)

1-(4'-Chlorophenyl)-4-(4"-dimethylaminophenyl)pyridinium chloride (8). Essentially the same method as for (6) with p-chloroaniline as nucleophile (130°C for 3.5 h) gave crude product (61% yield). A sample was dissolved in water, washed with chloroform, and allowed to crystallise as orange microcrystals, m.p. 250°C dec. (Found: C, 59.6; H, 5.5; N, 7.3%. $C_{19}H_{18}N_2Cl_2.2H_2O$ requires C, 58.9; H, 5.8; N, 7.4%.)

1-(4'-Nitrophenyl)-4-(4"-dimethylaminophenyl)pyridinium iodide (9). Arylpyridine (16) (0.5g) and p-nitrofluorobenzene (1.7g) were stirred at 130°C for 8 h in DMSO (5ml). After cooling, the salt was precipitated with excess acetone, filtered, and washed with more acetone. This was dissolved in boiling water and reprecipitated as the iodide by the addition of aqueous KI solution. The brown product was filtered and purified by elution through a silica column with chloroform/methanol. The orange brown fraction was evaporated and the dark brown product recrystallised from aqueous ethanol (0.13g, 10%) m.p. 220-223°C. (Found: C, 51.0; H, 3.9; N, 9.3%. $C_{19}H_{18}N_3O_2I$ requires C, 51.0; H, 4.1; N, 9.4%. ^1H nmr: δ 3.13 (s, 6H, $(CH_3)_2N$), 6.94 (d, J=8.5, 2H, 3"(5")-CH), 8.14 (d, J=8.5, 2H, 2"(6")-CH), 8.43 (d, J=7, 2H, 3(5)-CH), 9.00 (d, J=7, 2H, 2(6)-CH), 8.14 (d, J=9, 2H, 2'(4')-CH), 8.55 (d, J=9, 2H, 3'(5')-CH.)

1-(2',4'-Dinitrophenyl)-4-(4"-dimethylaminophenyl)pyridinium chloride (10). Arylpyridine (16) (0.99g) and 2,4-dinitrochlorobenzene (1.3g) were dissolved in DMF (20ml) and heated for a total of 5.5h at 80°C, an intense red colour soon developing. On standing on ice, dark red crystals formed. These were filtered, and washed with ether to give analytically pure material (1.65g, 80%) m.p. 210-212.5°C. (Found: C, 55.5; H, 4.5; N, 13.7%. $C_{19}H_{17}N_4O_4Cl.0.5H_2O$ requires C, 55.7; H, 4.8; N, 13.8%. ^1H nmr: δ 3.14 (s, 6H, $(CH_3)_2N$), 6.95 (d, J=9, 2H, 3"(5")-CH), 8.28 (d, J=9, 2H, 2"(6")-CH), 8.4-9.1 (m, 7H).)

1-(2',4'-Dinitro-6'-methylphenyl)-4-(4"-dimethylaminophenyl)pyridinium chloride (11). Arylpyridine (16) (0.5g) and 2-chloro-3,5-dinitro-toluene (0.67g) were heated for 4h in DMF (10ml). Crude product precipitated after cooling and quenching with acetone. This was purified by chromatography on silica using chloroform containing successively greater concentrations of methanol as eluent. Concentration of the orange eluates resulted in crystallisation of pure product as red platelets m.p. 226-228°C. (Found: C, 55.7; H, 4.6; N, 12.9%. $C_{20}H_{19}N_4O_4Cl.H_2O$ requires C, 55.5; H, 4.8; N, 12.9%. ^1H nmr: δ 2.29 (s, 3H, 6'-CH_3), 3.07 (s, 6H, $(CH_3)_2N$), 6.82 (d, J=9, 2H, 3"(5")- CH), 8.10 (d, J=9, 2H, 2"(6")-CH), 8.45 (d, J=7, 2H, 3(5)-CH), 8.85 (d, J=7, 2H, 2(6)-CH), 8.79 (s, 2H, 3-CH, 5-CH).)

1-(2',4'-Dinitro-5'-methylphenyl)-4-(4"-dimethylaminophenyl)pyridinium chloride (12). This was prepared from arylpyridine (16) (1.0g) and 3-chloro-4,6-dinitrotoluene (1.35g) exactly as (10). The product was precipitated from the crude reaction mixture on standing overnight. Recrystallisation from chloroform gave pure material as red platelets, m.p. 235°C dec. (Found: C, 57.6; H, 4.6; N, 13.6%. $C_{20}H_{19}N_4O_4Cl$ requires C, 57.9; H, 4.6; N, 13.5%. ^1H nmr: δ 2.61 (s, 3H, 5'-CH_3), 3.02 (s, 6H, $(CH_3)_2N$), 6.74 (d, J=9, 2H, 3"(5")-CH), 8.02 (d, J=9, 2H, 2"(6")-CH), 8.25 (s, 1H, 6'-CH), 8.38 (d, J=7, 2H, 3(5)-CH), 8.79 (s, 1H, 3-CH), 8.88 (d, J=7, 2H, 2(6)-CH).)

1-(2',4'-Dinitro-5'-acetylaminophenyl)-4-(4"-dimethylaminophenyl)pyridinium chloride (13). Arylpyridine (16) (1.98g) was heated at 135°C for 1h with N-acetyl-2,4-dinitro-5-chloroaniline (2.6g) in DMF (30ml). After cooling to 0°C, the dark red crystallised product was filtered and washed with ether. A further analytically pure crop was obtained by dilution of the mother liquors with ether (4.0g, 88%) m.p. 238-240°C. (Found: C, 55.4; H, 4.1; N, 14.9%. $C_{21}H_{20}N_5O_5Cl$ requires C, 55.1; H, 4.4; N, 15.3%. ^1H nmr: δ 2.21 (s, 3H, CH_3CO), 3.12 (s, 6H, $(CH_3)_2N$), 6.90 (d, J=9, 2H, 3"(5")-CH), 8.17 (d, J=9, 2H, 2"(6")-CH), 8.38 (s, 1H, 6'-CH), 8.51 (d, J=7, 2H, 3(5)-CH), 8.89 (d, J=7, 2H, 2(6)-CH), 8.93 (s, 1H, 3'-CH).)

1-Methyl-4-(4'-dimethylaminophenyl)pyridinium iodide (14). The method of ref. 7 gave the product in 65% yield after crystallisation from water m.p. 203-205°C. (Found: C, 49.4; H, 5.2; N, 8.3%. $C_{14}H_{17}N_2I$ requires C, 49.4; H, 5.0; N, 8.2%.)

1-Benzyl-4-(4'-Dimethylaminophenyl)pyridinium bromide (15). The method of ref. 7 gave large orange crystals of the product in 93% yield after crystallisation from water m.p. 226-228°C (lit.[7] m.p. 218-219°C.) (Found: C, 64.7; H, 5.8; N, 7.5%. $C_{20}H_{21}N_2Br$ requires C, 65.0; H 5.7; N, 7.6%.)

4-(4'-Dimethylaminophenyl)pyridine (16). This was prepared in 15% yield from pyridine and N,N-dimethylaniline by the method given in ref. 7. The product was isolated analytically pure as glistening colourless platelets after recrystallisation from hot DMF m.p. 235- 236°C (lit.[7] m.p. 233-234°C).

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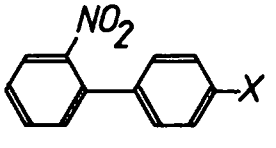
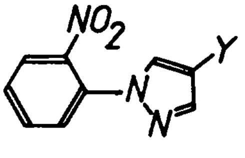


I $X = NH_2$

II $X = MeCO$



III $Y = Cl$

IV $Y = Br$