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COLOUR AND CONSTITUTION OF AZO COMPOUNDS DERIVED FROM DIAMINOAZINES

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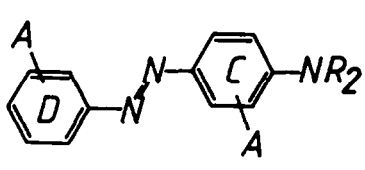
Abstract - Visible absorption spectra have been recorded for azo compounds derived from 2,5-dichlorosulphanilic acid azo-coupled with N,N-diethyl-m-phenylenediamine, and with azine analogues. The effects of the ring-aza substituents as well as cyano on the spectra indicate a surprising difference in sensitivity of the two ring positions meta to the azo group. M.O. calculations show that the amino group ortho to the azo linkage introduces asymmetry into the HOMO, and this is responsible for the differing effects of substitution.

The colours of the commercially important aminoazobenzene dyes (1) have been manipulated by the introduction of combinations of electron-withdrawing and -accepting substituents, A, into either of the two rings, C and D (Coupling and Diazo components, respectively). The usual effect of pi-electron-donors, such as amino, alkoxy, or acylamino, as substituents A in ring C of (1) is to induce bathochromic shifts in the visible absorption maximum (shifts to longer wavelength; lower energy transitions).[1a] Conversely, electron acceptors in ring C result in hypsochromic shifts.[1b] It is sometimes technically advantageous to substitute the nuclear CH units of the azobenzene skeleton by heteroatoms, and on the basis of the above generalisations, substitution of CH in ring C by aza-nitrogen might be anticipated to result in hypsochromic shifts. Since aza substitution decreases the ease of azo coupling, in practice most derivatives of this type simultaneously include more than one donor group to activate formation of the azo compound, this in turn tending to counteract the expected hypsochromic shift introduced by the ring aza-nitrogen. The subject of this paper is the visible spectral behaviour of the series of molecules which is obtained when one or more of the ring positions X, Y, and Z in (2) is occupied by nuclear N atoms to give azoaminoazines.



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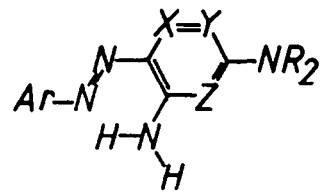

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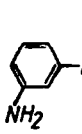
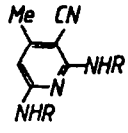
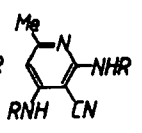
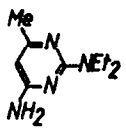
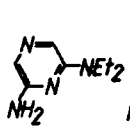
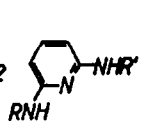
Besides the homobenzenoid parent, there are seven possible derivatives of (2). Some of these have already been described, especially in the patent literature, while others are unknown.[2] We report experimental data for the parent benzenoid system, two of the three pyridines (2; Y or Z =

Table. Absorption Maxima of Dyes (3) - (8), Ar-N=N-Ar' (Ar = 2,5-dichloro-4-sulphophenyl)[a]

Ar'[b]	 (3)	 (4)	 (5)	 (6)	 (7)	 (8)
λ_{max}	493	457	410	415	476	485
λ'[c]	493	465	418	415	476	493
λ(PPP)	439	438	404	402	471	438
λ(CNDO/S)	527	524	509	499	582	524

a Recorded in 50% aqueous methanol solvent. Values are in nm.
b The Ar-N=N- unit is attached to the leftmost atom of the diamino substituted ring in each case. R = $HO(C_2H_4)$-; R' = $MeO(C_3H_6)$-.
c These values correspond to structures based on (2; R = Et), and including CN in the case of (4) and (5). See text for details.

N), the pyrimidine (2; Y = Z = N), and the pyrazine (2; X = Z = N). The other aromatic ring of (2) is held constant throughout, and is derived from 2,5-dichlorosulphanilic acid (4-amino-2,5-dichlorobenzenesulphonic acid, abbreviated as Ar in this paper). Monoacid azo compounds of this type are commercially important dyes for basic fibres such as nylon, and the biological activity of analogues has also been investigated.[3]

After the visible spectral properties of these molecules have been discussed, the conclusions will be compared with results of theoretical calculations with the aim of defining how the colour variations within (2) are related to the structural modifications.

RESULTS AND DISCUSSION

Syntheses and Spectra. - The representative dyes (3) - (7) of type (2) are collected together in the Table. Their syntheses followed conventional routes, although some of the dyes and their intermediates are novel. In general, if the diaminoazine precursor was not available, it was prepared by displacement of halogen from an appropriate precursor, itself derived by the action of phosphorous oxychloride on the hydroxy derivative. Azo coupling with diazonium salt proceeded in unexceptional manner in most cases. The parent diaminoazobenzene (3) was most cleanly prepared by basic hydrolysis of its acetylamino derivative.

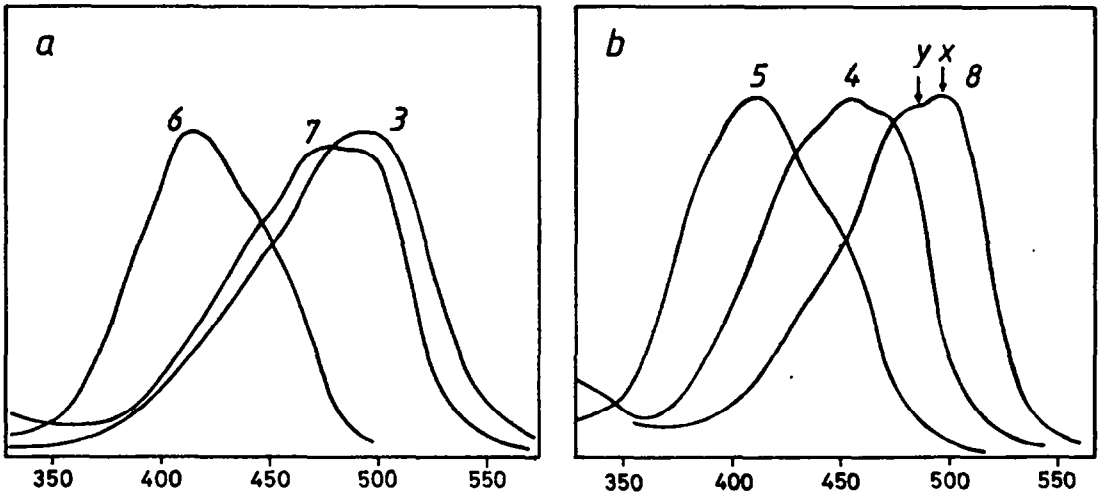


Figure 1 Visible absorption spectra of: (a) (3), (6) and (7); (b) (4), (5) and (8). The significance of the arrows over the spectrum of (8) is discussed in the text.

Visible spectral data are recorded in the Table, and Figure 1. The colours range from yellow through to red. Careful examination of all five spectra for (3) - (7) reveals that the absorption envelopes are composed of at least three peaks, probably deriving from vibrational effects. The M.O. results which follow suggest that there is only one electronic transition in this energy range. In each case, the λ_{max} value recorded in the Table corresponds to the central peak. The higher and lower energy shoulders are of differing intensities, leading to the band asymmetries characteristic for each compound, as is apparent in Figure 1.

Qualitative differences between 2,5- and 3,5-diaza substitution (pyrazine (7) and pyrimidine (6), respectively), and the benzenoid parent (3), are immediately apparent from Figure 1(a). The most notable feature is the similarity between the pyrazine and benzene derivatives, whereas the alternative diaza configuration of the pyrimidine is markedly hypsochromic. It thus appears that ring-nitrogen substitution meta to the azo group in the pyrimidine (6) (cf. Y in (2)) has a much greater hypsochromic influence than analogous substitution ortho to azo in pyrazine (7) (cf. X in (2)). Figure 1(b) demonstrates that the 2,6-diaminopyridine-derived azo compound (4) is considerably more bathochromic than the 2,4-diamino analogue (5).

A more quantitative comparison of (3) - (7) is complicated by three factors: the methyl group in (4), (5), and (6); the additional cyano group in (4) and (5); and the nonequivalence of the amino group substituents. We have approached this problem by making the following assumptions.

(a) The methyl group ortho to the azo group is known from comparative studies on other pyridine and pyrimidine derivatives to have very little influence on the absorption maximum,[4] and its effect was therefore assumed to be zero.

(b) Aza substitution in a given position in (2) (i.e. X or Y or Z) has a constant effect on the visible spectrum, whatever other substituents are present. Thus, it is assumed that Y = N, for instance, has the same effect in the pyridine (5) as in the pyrimidine (6). Transferability of exocyclic substituent effects is a feature of many azobenzene systems.[5]

(c) From studies on analogous pyrimidine derivatives,[4] the effect of replacing NHC_2H_4OH ortho to the azo group by NH_2 is a hypsochromic shift of -4nm. By extrapolation from published data,[5] NHC_2H_4OH para to the azo group is about -12nm more hypsochromic than NEt_2.

No presumptions were made regarding the influence of the cyano substituents in (4) and (5). The above allowances lead to estimates for the absorption maxima for analogues of (4), (5) and (6) based on the general structure (2; R = Et) (and including the cyano groups in the cases of (4) and (5)). These values are recorded in the second row of the Table.

It is now possible to construct the four equations (1) to (4) (Scheme) between the shifts in absorption maxima with reference to the benzenoid parent system, and the five aza and cyano substituent effects. To enable solution for these effects, a fifth equation is needed. This is derived from the 2,6-diaminopyridine azo compound (8) which contains no cyano group (Table and Fig. 1(b)).[6] In fact, the true λ_{max} for this species (arrowed x in Figure 1(b)) corresponds to the low energy peak of the three which comprise the absorption envelope. In order to maintain consistency with the other data, the value recorded in the Table is the wavelength of the central absorption (arrowed y in Figure 1(b)). Equation 5 of the Scheme now permits solution for the five substituent effects, the results for which are recorded in the Scheme.

The magnitudes of these effects substantiate and extend the qualitative conclusions already given. Ring-nitrogen substitution ortho to the azo group (X in (2)) has a hypsochromic influence

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Scheme[a]

$\lambda'(4) - \lambda'(3)$	=	-28	=	CCN(Y) + N(Z)	(1)	N(X)	= -17nm
$\lambda'(5) - \lambda'(3)$	=	-75	=	N(Y) + CCN(Z)	(2)	N(Y)	= -78nm
$\lambda'(6) - \lambda'(3)$	=	-78	=	N(Y) + N(Z)	(3)	N(Z)	= 0nm
$\lambda'(7) - \lambda'(3)$	=	-17	=	N(X) + N(Z)	(4)	CCN(Y)	= -28nm
$\lambda'(8) - \lambda'(3)$	=	0	=	N(Z)	(5)	CCN(Z)	= 3nm

a CCN(Y) implies position Y in (2) is carbon substituted by cyano; N(Z) implies that position Z is nitrogen; etc.

of -17nm compared with the unsubstituted (3). Introduction of nitrogen in position Z of (2) has no effect at all. In contrast, the aza substituent in the other position meta to azo in (2), Y, has a substantial hypsochromic shift of -78nm. Substitution of the electronegative N atom in this position is therefore responsible for the much more hypsochromic shades of the pyrimidine and 2,4-diaminopyridine compounds.

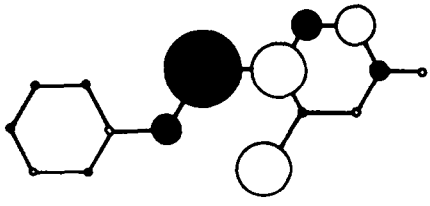
The substituent effects estimated for the two distinct cyano orientations are consistent with the conclusion that the Y position of (2) is much more sensitive than Z to substitution by electronegative groups. In the latter position, cyano has a marginal bathochromic influence on the absorption maximum (3nm), while in the former it causes a substantial -28nm hypsochromic shift.

The effect of aza substitution in position X of (2) is about the same as that of cyano or nitro (-14, and -16nm, respectively) ortho to the azo group in the monoamino-substituted azo dyes (1).[1b,7] The average value for the effect of aza and cyano in positions Y and Z of (2) are -39 and -12nm, respectively, compared with a value of -45nm for NO_2 ortho to R_2N (R = H) in (1).[1b,7]

The precision of the derived substituent increments should not be overestimated, particularly in view of both the impossibility of accounting for differential solvent effects, and the approximations inherent in the assumptions (a) to (c) necessary to permit quantitative comparison across the series. However, the difference between substituents in the two "meta" positions (2, Y and Z) for both ring-nitrogen and cyano is significant and, to us, surprising. We probe this point more thoroughly in the light of theoretical calculations.

Calculations of electronic spectra. Molecular orbital calculations were carried out using three methods: the pi-electron-only Parr-Pariser-Pople (PPP) approximation with a configuration interaction (CI) treatment;[8] the screened complete neglect of differential overlap method of Jaffe and coworkers (CNDO/S), again including CI;[9] and Dewar's MNDO method.[10] The first two calculate electronic excitation energies and associated electronic redistributions. The MNDO method gave comparisons of calculated ground state properties using a different theoretical approximation. For convenience, R in (2) was taken as Me for the calculation, rather than Et as in the experimental comparisons. Planar geometries with standard bond lengths and angles were assumed for the molecules, and no geometry optimisation was attempted. It was also assumed that the NH_2 group H-bonds to the more remote of the two azo group nitrogen atoms, holding the diamino-substituted ring in a fixed conformation with respect to the remainder of the molecule (i.e. as shown for (2)). There is ample precedent for 6-membered ring intramolecular H-bonding of this type.[11]

The electronic reorganisation after the lowest energy $\pi\rightarrow\pi^*$ excitation in the benzenoid derivative (3) as calculated by the PPP method is given in (9). Filled circles correspond to build-up of electron density on excitation, while empty circles represent centres which donate electron density. In most respects the CNDO/S calculation gives the same pattern of electron redistribution.



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Very little charge is transferred into the dichlorosulphonic-substituted benzene ring (Ar). The major centres of charge build-up are the nitrogen atoms of the azo group, particularly the nitrogen atom not formally conjugated with the amino group electron donors. This is entirely consistent with many other calculations on azobenzene systems.[1c] According to the PPP calculation, of the two donors the NH_2 group releases most charge on excitation, rather than the NMe_2 group although the latter is expected to be the better donor. In this respect, the CNDO/S results differ,

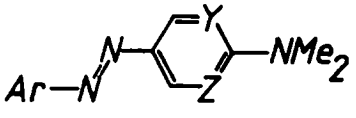
in that they suggest the NMe_2 group is indeed the better donor. The main point of current interest relates to the benzenoid carbon atoms of the amino-substituted ring. Three positions act as electron donors: the carbon atom directly attached to the azo group, and the two ortho to the amino-substituted positions, Y rather strongly, and Z much less so. In contrast, the carbon atom ortho to the azo group (X in (2)) is a mild electron acceptor on excitation. A simple perturbational treatment suggests that substitution by the more electronegative nitrogen atom for the latter CH group would stabilise the excited state and therefore lead to a bathochromic shift in the visible absorption. On the other hand, a hypsochromic shift should result from N-substitution in position Y. Finally, N-substitution at Z would be expected if anything to have a much smaller hypsochromic effect.

PPP and CNDO/S calculations on the aza-derivatives themselves are consistent with all these conclusions. The calculated absorption maxima are recorded in the Table, and the values obtained bear out quantitatively the qualitative conclusions just derived. Furthermore, the results for the pyrimidine (6) and the pyrazine (7) show that additivity of effects is indeed roughly followed (cf. assumption (b) above), although there does seem to be a slight synergetic effect between two aza substituents, when present. Only one strong $\pi \rightarrow \pi^*$ absorption is calculated in the visible spectrum. It thus appears that the asymmetry of the experimental absorption bands (Figure 1) is not due to separate, closely-spaced $\pi \rightarrow \pi^*$ transitions, but rather results from vibrational splitting of one main absorption.

The calculated effects across the series compare with experiment as follows. Calculation predicts correctly the observed hypsochromic effect of N in position Y of (2), but underestimates its magnitude. The lack of effect observed in position Z is reproduced accurately. There is a discrepancy for N-substitution in position X ortho to the azo group. While both MO methods suggest there should be a notable bathochromic shift, a hypsochromic shift is implied by the experimental data. (In the same way, calculations on (1) suggest that electronegative substituents ortho to the azo group should lead to bathochromic shifts (cf. Figure 2, below), whereas in practice the opposite is the case, as discussed above.[1b])

Reasons for the discrepancy between experiment and calculation could lie on either side of the comparison. On the one hand, the experimental aza-substituent effects have been derived from limited data by way of assumptions which might not be wholly justified. Furthermore, the experimental data refer to species heavily solvated by dipolar protic solvent, whereas the calculated values apply to isolated molecules. Thus, solvent may be perturbing the inherent effects of ring-substitution. On the other hand, the calculations themselves are based on approximate theories of molecular bonding, and may not be as accurate as desirable. Unfortunately, higher levels of theory are inapplicable due to the increased and prohibitive demands on computation time. The CI treatment itself only considered single electron excited configurations, whereas inclusion of double excitations might be necessary to give optimum results.

Despite the inexact correspondence between experiment and theory, we believe the calculations are sufficiently consistent and of adequate quality to apply them to the problem of determining how the structural features present in the systems are responsible for the observed effects, especially the difference in N-substitution at positions Y and Z. The possibility of a purely conformational effect was eliminated by calculations on the two model systems (10) and (11). The calculated λ_{max} values were essentially the same.



10 Y = N Z = CH λ(PPP) = 420nm

11 Y = CH Z = N λ(PPP) = 419 nm

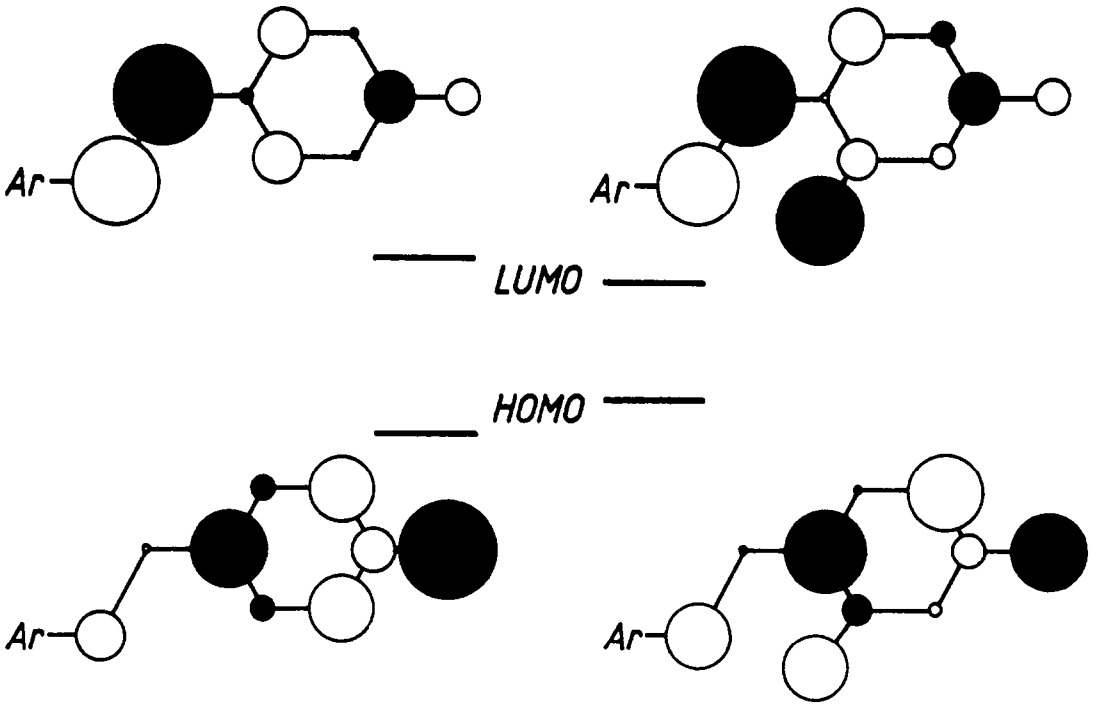


Figure 2 HOMOs and LUMOs of (1) and (3). The vertical energy scale is qualitative.

According to the calculations on (3) and derivatives, the visible absorption maxima correspond most closely to a single electron excitation from the HOMO to the LUMO. Figure 2 compares the HOMO/LUMO structures for the monoaminoazobenzene (1) with the diamino system (3). The PPP, CNDO/S, and MNDO methods all give essentially the same structures to the HOMOs and LUMOs. The LUMO of the arylazo system is dominated by the electronegative azo group, and the addition of one more donor group in going from (1) to (3) has little effect: the LUMOs of (1) and (3) have almost the same overall composition. In contrast, the HOMO of (1) is typical of a mono-donor substituted benzenoid system, being centred largely on the lone pair of the donor group, as expected. When a second donor group is added, as in (3), the structure of the HOMO is radically changed. The asymmetry induced by the NH_2 group with respect to the azo group is clearly apparent from Figure 2. To be explicit, the atomic orbital coefficient of Y is much higher than that of Z in the diamino series (3), whereas they are about the same in the monoamino derivative (1). Since the charge transferred on excitation is largely dependent on the structures of the corresponding HOMOs and LUMOs, the difference in HOMO structure resulting from NH_2-induced asymmetry appears to be the source of the different substituent effects for Y and Z.

We can devise no satisfactory corresponding valence bond rationale.

ACKNOWLEDGMENTS

Thanks are due to D.P.Devonald for carrying out some of the experimental work and to P.Gregory for discussions.

EXPERIMENTAL

UV/visible spectra were recorded on a Unicam SP8000 instrument in purified solvents, and were calibrated with a holmium filter. ^{1}H nmr spectra were recorded at ambient probe temperature in d_6-DMSO (unless otherwise stated) using TMS as internal standard on a Perkin-Elmer R-24A instrument. ^{13}C nmr spectra were recorded on a Bruker WH-90 spectrometer. Ir spectra were recorded as thin films or nujol mulls on a Perkin-Elmer 297 instrument. Starting materials were either commercially available or were obtained from the I.C.I. specimen collection. Dye (4) was a purified commercial sample.

Diazotisation of 4-amino-2,5-dichlorobenzenesulphonic acid - 2,5-Dichlorosulphanilic acid (9.3g) was dissolved in water (250ml) containing sodium hydroxide solution (10ml 2N), cooled to 0-5°C, and sodium nitrite solution (18ml 2N) was added, followed by concentrated HCl (10ml). The off-white suspension which formed was stirred for 1.5h, excess nitrous acid was removed with sulphamic acid solution (2ml 10% w/v), and the diazonium salt coupled as follows.

Sodium 4-amino-2-N,N-diethylamino-6-methyl-5-(2',5'-dichloro-4'-sulphonatophenylazo)-pyrimidine (6) - 4-Amino-2-N,N-diethylamino-6-methylpyrimidine (5.4g) was dissolved in acetic acid (25ml) and ice (ca. 30g), and Dispersol OG (10ml 10% solution) added. To this emulsion was added the diazonium salt suspension prepared above. The pH was raised to 7.0 by the careful addition of aqueous NaOH solution, and the mixture was allowed to stir for 0.5h. The pH was then further raised to 11.0 to remove residual stabilised diazonium salt, whereupon complete solution occurred. The pH was then adjusted back to 8.0 by addition of acetic acid, and the product precipitated as a yellow powder which was filtered, washed with cold water, and dried (12.2g, 92%). The material obtained in this way was pure as determined by tlc in a variety of systems, by microanalysis, and by nmr. Found: C 38.7, H 3.7, N 17.7%. $C_{15}H_{17}N_6O_5Cl_2SNa.0.5H_2O$ requires C 38.8, H 3.9, N 18.1%. ^{1}H nmr: δ 1.17 (tr, 6H, J = 7, CH_2CH_3), 2.62 (s, 3H, CH_3C), 3.65 (q, 4H, J = 7, CH_2), 7.64 (s, 1H, CH), 7.99 (s, 1H, CH), 8.13 (bs, NH), 9.49 (bs, NH).

Other azo compounds were prepared in analogous fashion.

Sodium 4-(2'-Amino-4'-N,N-diethylaminophenylazo)-2,5-dichlorobenzenesulphonate (3) - Reflux of the acetylamino precursor in aqueous ethanolic NaOH solution for 24h led to the deacetylated product. This was isolated by filtration and recrystallised from aqueous 2-methoxyethanol. The purity was verified by tlc (silica; ethyl acetate/acetone/water) and hplc (lichrosorb RP8, 200 mm x 4.6 mm, 10μ, 20% acetonitrile, 80% 0.25% acetic acid in water), as well as microanalysis and nmr spectroscopy. Found: C 41.6, H 4.1, N 12.0%. $C_{16}H_{17}N_4O_5Cl_2SNa.H_2O$ requires C 42.0, H 4.2, N 12.25%. ^{1}H nmr: δ 1.15 (tr, 6H, J = 7, CH_3C), 3.4 (q, 4H, J = 7, CH_2), 6.0 (bs, 1H), 6.3 (d, 1H, J = 10), 7.5 (d, 1H, J = 10), 7.75 (s, 1H), 7.9 (s, 2H, exch D_2O, NH_2), 8.02 (s, 1H). ^{13}C nmr: δ 12.8 (q), 44.1 (tr), 93.8 (d), 104.6 (d), 117.5 (d), 127.4 (s), 129.9 (d), 130.4 (s, 2C), 134.2 (d), 143.2 (s), 146.6 (s), 149.1 (s), 151.6 (s).

3-Cyano-2,4-di(2'-hydroxyethylamino)-6-methylpyridine - 3-Cyano-2,4-dichloro-6-methylpyridine (2.8g, prepared by the method of ref 12) was added in portions to 2-ethanolamine (6.1g), and the mixture stirred and warmed at 130°C for 0.5h. After cooling, water was added, the resulting solid was filtered, washed with ice-water and dried to give product (2.5g, 71%). A sample was recrystallised from water. m.p. 158-159°C. Found: C 56.1, H 6.8, N 23.5%. $C_{11}H_{16}N_4O_2$ requires C 55.9, H 6.8, N 23.7%. Ir (nujol): 3360, 2200, 1600 cm^{-1}. ^{1}H nmr: δ 2.15 (s, 3H, CH_3), 3.43 (m, 8H, C_2H_4) 4.7 (bs, 2H), 5.83 (s, 1H, CH), 6.03 (t, 2H).

4-Amino-2-N,N-diethylamino-6-methylpyrimidine - 4-Chloro-2-N,N-diethylamino-6-methylpyrimidine (20g; prepared by the method of ref 13) was heated at 180°C for 56h with concentrated aqueous NH_3 (80ml) in a Carius tube. The white solid which formed was collected by filtration, washed well with water and dried (17.2g, 95%). A sample was recrystallised from petroleum ether. m.p. 85.5°C. Found: C 59.2, H 9.0, N 30.3%; $C_9H_{16}N_4$ requires C 59.9, H 8.9, N 31.0%. Ir (nujol): 3450, 3330, 3200, 1620cm^{-1}. ^{1}H nmr ($CDCl_3$): δ 1.12 (tr, 6H, J = 7, CH_3), 2.15 (s, 3H, CH_3), 3.56 (q, 4H, J = 7, CH_2), 4.45 (bs, 2H exch D_2O, NH_2), 5.55 (s, 1H, CH).

2-Amino-6-chloropyrazine. - 2,6-Dichloropyrazine (10g ex Aldrich) was heated at 140°C for 15h in concentrated aqueous ammonia in a Carius tube. After cooling, the solid material which had formed was filtered, washed with water, and dried (6.53g, 76%). m.p. 152°C. Found: C 37.0, H 3.1, N 31.9%. $C_4H_4N_3Cl$ requires C 37.1, H 3.1, N 32.4%. Ir (nujol): 3300, 3180, 1640cm^{-1}. ^{1}H nmr: δ 8.05 (s, 2H), 8.25 (s, 2H, exch D_2O, NH_2).

2-Acetylamino-6-chloropyrazine. - 2-Amino-6-chloropyrazine (2.5g) was mixed with acetic acid (5ml) and acetic anhydride (7ml) and heated at 95°C for 2.5h, after which time tlc showed complete reaction. The mixture was cooled to 10°C and the product filtered off, washed with acetic acid, and pumped dry (1.8g, 55%). m.p. 171.5°C. Found: C 40.9, H 3.6, N 24.1%. $C_6H_6N_3OCl$ requires C 40.6, H 3.4, N 23.7%. Ir (nujol): 3200, 3040, 1700cm^{-1}. ^{1}H nmr: δ 2.13 (s, 3H, CH_3), 8.25 (s, 1H, CH), 9.15 (s, 1H, CH), 10.7 (s, 1H exch D_2O, NH).

2-Acetylamino-6-N,N-diethylaminopyrazine. - 2-Acetylamino-6-chloropyrazine (1.2g) was heated in a Carius tube with diethylamine (6ml) for 18h at 200°C. The crude product was warmed with acetic anhydride to give pure material after cooling, crystallisation, ether washing, and drying (0.94g, 68%). m.p. 182°C. Found: C 57.7, H 7.8, N 26.3%. $C_{10}H_{16}N_4O$ requires C 57.7, H 7.7, N 26.9%. Ir (nujol): 3200, 1690, 1590cm^{-1}. ^{1}H nmr: δ 1.10 (tr, 6H, J = 7, CH_2CH_3), 2.05 (s, 3H, CH_3CO), 3.48 (q, 4H, J = 7, CH_2), 7.68 (s, 1H, CH), 8.36 (s, 1H, CH), 10.5 (s, 1H exch D_2O, NH).

2-Amino-6-diethylaminopyrazine. - 2-Amino-6-chloropyrazine (2.5g) was heated with diethylamine (20ml) in a Carius tube at 210°C for 18h, then cooled to room temperature. Attempts to isolate the product resulted in progressive and rapid decomposition as judged by tlc and nmr. Although the ^{1}H nmr spectrum was consistent with formation of the desired material, it was best characterised by acetylation of the crude reaction product, the acetyl derivative being identical to that prepared above. A subsequent preparation gave material which was immediately dissolved in HCl acid (pH 1.0-1.5) and azo coupled directly.

2-(3-Methoxypropylamino)-6-(2-hydroxyethylamino)pyridine. - The product was prepared as a brown oil by successive replacement of the fluorine atoms of 2,6-difluoropyridine by ethanolamine and 3-methoxypropylamine by routes analogous to those described above. The purity was confirmed by glc and the product was characterised via its ^{1}H nmr spectrum ($CDCl_3$): δ 1.8(m), 3.25(s), 3.5(m), 5.55 (d, 2H, 3(5)-CH), 7.0 (t, 1H, 4-CH).

REFERENCES AND FOOTNOTES

1. (a) P.F.Gordon and P.Gregory, "Organic Chemistry in Colour", Springer-Verlag, Berlin, 1983, p.129; (b) p.127; (c) p.138; (d) p.102.
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3. Arylazoaminopyrimidines have a range of biological activities, cf. D.Sen, S.R.Bhowmik, and P.Sengupta, Indian J.Chem., 22, 388 (1983) and references cited. Phenazopyridine hydrochloride ((2); Ar = phenyl, R = H, X = Y = CH, Z = N) is an analgesic for the urinary tract, although it has now been found to be carcinogenic ("The Merck Index", ed. M.Windholz, Merck and Co., Rahway, N.J., U.S.A., 10th edn., 1983).
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