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Colour–Constitution Relationships in 2-Acylamino-4-*N*,*N*-Diethylaminoazobenzene Disperse Dyes

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ABSTRACT

Nitration of N,N-*diethylaniline in concentrated sulphuric acid afforded a readily separable mixture of the 3- and 4-nitro derivatives, the former being the major product. Reduction and subsequent reaction of 3-amino-*N,N-*diethylaniline with acid chlorides, chloroformates, isocyanates and sulphonylchlorides gave a range of coupling components suitable for the synthesis of blue azo disperse, using 2-bromo-4-nitro-6-cyanoaniline as diazo component.*

The colour of the dyes is discussed with respect to electronic and steric effects in the acylamino (and analogous) substituents; depending on the acylamino substituent, positive or negative solvatochromic effects were apparent in ethanol with respect to benzene and/or cyclohexane.

1 INTRODUCTION

An important class of industrially utilised blue azo dyes for synthetic-polymer fibres is based on the use of 3-acylamino-*N*,*N*-dialkylanilines as coupling component, and typically, 2-bromo-4-nitro-6-cyanoaniline as diazo component. The problems associated with traditional blue disperse dyes based on anthraquinone have been well documented,[1,2] and many

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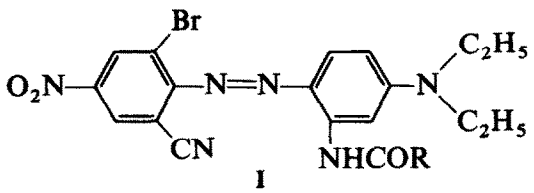
4-aminoazobenzene derivatives have been found to exhibit similar technological properties to the anthraquinonoid dyes. 3-Acylamino-*N,N*-dialkylanilines in which the acyl group contains an alkyl substituent have been extensively cited, particularly in respect of reddish to neutral blue dyes, e.g. Refs 3–6 and variants stated to improve fastness to sublimation have also been reported, e.g. 3-benzoylamino,[7] 3-phthalimido,[8] and 3-aryloxyarylthio- and arylamino acetylamino.[9] The influence of both diazo and coupling component on colour–structure relationships in blue 4-aminoazobenzene derivatives has been described,[10] including those derived from a limited number of 3-acylamino-*N,N*-dialkylanilines in which the acyl substituent carries a lower alkyl or phenyl group. Electronic and steric



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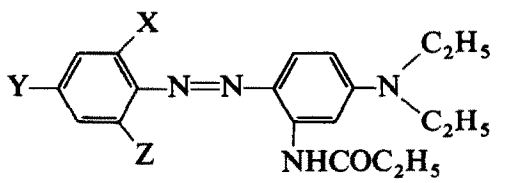


II

influences of a range of 2-substituents, including amino and substituted amino, in 4-nitro-4-*N,N*-diethylaminoazobenzene have also been reported.[11] Whilst a variety of derivatives of 3-amino-*N,N*-dialkylanilines in which the 3-amino group contains, e.g. alkyl-, alkoxy-, aryl-, aryloxy- and *N*-substituted aminocarbonyl or alkyl- and arylsulphonyl moieties, have been described in patent specifications,[6] more detailed information on the influence of the nature of substituents in the 3-acylamino and related groups is limited and we report here the synthesis of a range of appropriate coupling components and their use in the synthesis of blue dyes of general formula **I**, together with related yellow to red dyes **II**, and an evaluation of colour–constitution relationships in such dyes.

2 EXPERIMENTAL

2.1 3-Nitro-*N,N*-diethylaniline

N,N-Diethylaniline (149 g, 1 mol) was nitrated in concentrated sulphuric acid following the procedure described for the nitration of *N,N*-

dimethylaniline.[12] The initial precipitate on addition of ammonium hydroxide to the nitration liquor afforded crude 4-nitro isomer (54 g) as essentially solid material (TLC indicating an approximate content of 80% 4-nitro derivative and 20% 3-nitro derivative). Subsequent addition of ammonium hydroxide gave 3-nitro-*N,N*-diethylaniline as a deep orange oil (133 g) (TLC indicating only minor contamination with the 4-nitro isomer). The crude 4-nitro product required repeated crystallisation from ethanol to obtain homogeneous material (8 g final recovery) and was more readily purified (on a 2–3 g scale) by column chromatography on silica gel, applying from solution in toluene and eluting with the same solvent. The 3-nitro isomer eluted rapidly from a deep orange zone, allowing facile later elution of pure 4-nitro derivative from a lower R_f clear yellow zone; bright yellow prisms, m.p. 73–74°C, *m/z* (EI) 194, M^+, 23%; 179, M—CH_3, 100%. ^{1}H-NMR, d_6-DMSO: δ 8·06–8·00, 2H, pseudo-dd, $J = 9{\cdot}53$ Hz and 2·20 Hz. H-3, 5; δ 6·77–6·72, 2H, dd, $J = 9{\cdot}53$ Hz and 2·2· Hz, H-2, 6: δ 3·47, 4H, q, CH_2, $J = 6{\cdot}96$ Hz; δ 1·14, 6H, t, CH_3, $J = 6{\cdot}96$ Hz.

The 3-nitro derivative was purified by vacuum distillation, clear yellow oil, b.p. 116–118°C (0·2 mm Hg) (122 g, 63%) (lit.[10] b.p. 115°C, 11 Pa); *m/z* (EI) 194, M^+, 26%; 179, M—CH_3, 100%; ^{1}H-NMR, d_6-DMSO: δ 7·43–7·34, 3H, m, H-2, 4, 5; δ 7·10–7·05, 1H, dt, H-6, $J = 7{\cdot}32$ Hz and 2·20 Hz; δ 3·41, 4H, q, CH_2, $J = 6{\cdot}96$ Hz; δ 1·12, 6H, t, CH_3, $J = 6{\cdot}96$ Hz.

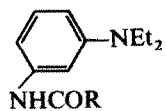
2.2 3-Amino-*N,N*-diethylaniline

3-Nitro-*N,N*-diethylaniline was reduced using hydrazine hydrate and 10% Pd on charcoal following the procedure reported for the reduction of 5-nitroacenaphthene.[13] The 3-amino derivative was obtained as a brownish-yellow oil (92%), used without further purification in the preparation of the 3-acylamino derivatives. Vacuum distillation of a small sample gave a pale yellow oil, b.p. 105–108°C (0·2 mm Hg), rapidly darkening on exposure to light/air. *M/z* (EI) 164, M^+, 49%; 149, M—CH_3, 100%. ^{1}H-NMR, d_6-DMSO: δ 6·77, 1H, t, H-5; δ 5·93–5·82, 3H, m, H-2, 4, 6; δ 4·70, 2H, s, NH_2 (D_2O exchangeable); δ 3·22, 4H, q, CH_2, $J = 6{\cdot}96$ Hz; δ 1·05, 6H, t, CH_3, $J = 6{\cdot}96$ Hz.

2.3 3-Acylamino-*N,N*-diethylanilines (and related intermediates)

3-Amino-*N,N*-diethylaniline (3·3 g, 0·02 mol) was stirred at room temperature in toluene (or ethyl acetate) (25 ml) and the solution warmed to 40–45°C. The appropriate acid chloride, chloroformate, isocyanate or sulphonyl chloride (0·04 mol) dissolved in the same solvent (10 ml) was added portionwise over 30 min. After addition was complete, the mixture was stirred at 60–65°C for 10 min, the solvent removed *in vacuo* and the residue

TABLE 1
Characterisation Data for 3-Substituted-*N*,*N*-Diethylanilines



Reactant	*R*	*M.p.* (°C)	*Mass spectra*		*IR spectra* ν (C=O) (cm^{-1})
			M^+ (%)	$[M-(CH_3)]^+$ (%)	
Formic acid	H	68–69	192 (37)	177 (100)	1 660
Acetyl chloride	CH_3	72–73[a]	206 (35)	191 (100)	1 661
Propionyl chloride	CH_2CH_3	76–77[a]	220 (30)	205 (100)	1 663
Butyryl chloride	$(CH_2)_2CH_3$	65–66[a]	234 (30)	219 (100)	1 657
Valeryl chloride	$(CH_2)_3CH_3$	57–58[a]	248 (28)	233 (100)	1 658
Hexanoyl chloride	$(CH_2)_4CH_3$	69–70	262 (25)	247 (100)	1 654
Dodecanoyl chloride	$(CH_2)_8CH_3$	67–68	318 (24)	303 (100)	1 659
Lauroyl chloride	$(CH_2)_{10}CH_3$	137–138	346 (30)	331 (100)	1 659
Iso-butyryl chloride	$CH(CH_3)_2$	85–86	234 (30)	219 (100)	1 660
Iso-valeryl chloride	$CH_2CH(CH_3)_2$	71–72	248 (24)	233 (100)	1 659

Trimethyl acetyl chloride	$C(CH_3)_3$	214–215	248 (26)	233 (78)	1 681
Tert-butyl acetyl chloride	$CH_2C(CH_3)_3$	220–221	262 (29)	247 (100	1 679
Chloroacetyl chloride	CH_2Cl	64–65	240 (29)	225 (100)	1 665
Trichloroacetyl chloride	CCl_3	94–95	308 (30)	293 (100)	1 695
Trifluoroacetyl chloride	CF_3	103–104	260 (29)	245 (100)	1 732
3-Chloropropionyl chloride	CH_2CH_2Cl	96–97	254 (34)	239 (100)	1 664
2-Chloropropionyl chloride	$CHClCH_3$	76–77	254 (30)	239 (100)	1 662
Phenylacetyl chloride	$CH_2C_6H_5$	129–130	282 (38)	267 (100)	1 656
Cyclohexane carbonyl chloride	C_6H_{11}	231–233	274 (27)	259 (100)	1 658
Benzoyl chloride	C_6H_5	92–93[a]	268 (38)	253 (100)	1 646
4-Methoxybenzoyl chloride	$C_6H_4OCH_3$-*p*	174–175	298 (24)	283 (100)	1 686
4-Nitrobenzoyl chloride	$C_6H_4NO_2$-*p*	129–130	313 (29)	298 (100)	1 654
Ethyl chloroformate	OC_2H_5	61–62	236 (39)	221 (100)	1 698
Phenyl chloroformate	OC_6H_5	171–172	284 (26)	269 (46)	1 738
Ethyl isocyanate	NHC_2H_5	93–94	235 (54)	220 (85)	1 646
Phenyl isocyanate	NHC_6H_5	131–132	283 (48)	268 (86)	1 656
Benzene sulphonyl chloride	$SO_2C_6H_5$[b]	226–227	304 (35)	289 (100)	—

[a] Lit.[11], R = CH_3, m.p. 77–79°C; R = C_2H_5, m.p. 77–79°C; R = $(CH_2)_2CH_3$, m.p. 62–65°C; R = $(CH_2)_3CH_3$, oil; R = C_6H_5, m.p. 83–85°C.
[b] 3-Substituent is $HNSO_2C_6H_5$; $\nu(SO_2)$ 1336 and 1346, 1171 and 1185 cm^{-1}.

stirred in 10% ammonium hydroxide. The formyl derivative was prepared by heating the amine in excess formic acid at 70°C for 20 min, diluting with water and basifying with ammonia. Products were filtered and recrystallised from ethanol or aqueous ethanol as appropriate.

Alternatively, the amino derivative was stirred at 50–60°C for 10–30 min in excess of the appropriate reactant; after addition to ice-water, products were precipitated with ammonia, and, where necessary, the liquor refrigerated overnight to obtain solid material prior to filtration.

Several derivatives showed high solubility in alcohol and aqueous alcohol and required concentration to low volume during recrystallisation, and refrigerating to induce effective crystallisation. In such cases, rapid filtration of the cooled liquor was necessary to inhibit redissolution of the product as the liquor rose to ambient temperature.

Characterisation data for all products are shown in Table 1. All products showed, in their mass spectrum, molecular ion peaks in the general region of 30% RA; base peak in most spectra corresponding to loss of one methyl group, exceptions being the trimethylacetyl derivative, with base peak at m/z 57, corresponding to the *t*-butyl species, and the chloroformate and isocyanate derivatives. The latter tended to show a base peak due to the well established thermal or electron-impact induced formation of the isocyanate ion (m/z 190, generally low RA; m/z 175 at 100%). Absence of isocyanate impurity in the parent compound was confirmed by lack of any ν(N=C=O) (2240–2270 cm^{-1}) in the IR spectra.

2.4 Dye synthesis and purification

2-Bromo-4-nitro-6-cyanoaniline (2·4 g, 0·01 mol) was stirred vigorously at 0–5°C into concentrated sulphuric acid (10 ml) and the liquor diluted by gradual addition of glacial acetic acid (8 ml). Diazotisation was affected by addition of nitrosylsulphuric acid (prepared from 0·011 mol, sodium nitrite and 5 ml concentrated sulphuric, diluted with 5 ml glacial acetic acid) and after stirring for 3 h at 0–5°C, excess nitrite was removed with sulphamic acid and the diazo liquor stirred gradually into a solution of the appropriate coupling component (0·01 mol) in ice-cold 50% acetic acid (20 ml). After 2 h the liquor was diluted with ice-water (200 ml) and, where necessary, partially neutralised with sodium acetate to effect dye precipitation (yields generally around 90%).

The above method was also used for the dyes (Table 2) obtained from 6-chloro-2,4-dinitroaniline and 2,6-dibromo-4-nitroaniline; other dyes in Table 2 were prepared using conventional aqueous nitrite-hydrochloric acid procedures.

Dyes were purified by column chromatography on silica gel (for column

TABLE 2
Visible Absorption Spectral Data for Dyes **II** (λ in nm, ε in litres mol^{-1} cm^{-1})

Ref.	*X*	*Y*	*Z*	*M.p.* (°C)	*Absolute ethanol* λ_{max}, $\varepsilon_{max} \times 10^{-3}$		*Dichloromethane* λ_{max}, $\varepsilon_{max} \times 10^{-3}$				*Cyclohexane* λ_{max}			*Benzene* λ_{max}	
II.1	H	H	H	82–84	451	31·9	432*	30·4	459	35·3	427*	440	456*	456	—
II.2	H	NO_2	H	180–181	510	44·8	490*	36·3	520	45·8	490*	507	—	516	—
II.3	Cl	NO_2	H	193–194	529	45·5	—	—	539	46·3	505	527	—	535	—
II.4	NO_2	NO_2	H	208–210	545	46·0	—	—	556	47·0	536	—	—	548	—
II.5	NO_2	NO_2	Cl	171–172	559	44·6	—	—	568	45·8	544	—	—	563	—
II.6	Br	NO_2	Br	155–156	490	29·8	—	—	503	34·2	480	—	—	494	—
II.7 (**I.3**)	Br	NO_2	CN	186–187	592	49·8	589*	52·0	606	53·6	568*	600	—	582*	603

TABLE 3
Visible Absorption Spectral Data for Dyes I (λ in nm, ε in litres $mol^{-1} cm^{-1}$)

Ref.	*R*	*M.p.* (°C)	*Absolute ethanol* λ_{max}, $\varepsilon_{max} \times 10^{-3}$		*Dichloromethane* λ_{max}, $\varepsilon_{max} \times 10^{-3}$				*Cyclohexane* λ_{max}		*Benzene* λ_{max}	
I.1	H	239–241	574	31·1	—	—	598	45·6	—	—	—	—
I.2	CH_3	242–243	592	48·6	589*	49·2	607	52·8	564*	598	578*	603
I.3	CH_2CH_3	186–187	592	49·8	589*	52·0	606	53·6	568*	600	582*	603
I.4	$(CH_2)_2CH_3$	183–184	591	49·5	(589–608)**	—	600	53·9	—	—	—	—
I.5	$(CH_2)_3CH_3$	172–173	592	50·1	(590–608)**	—	599	54·3	—	—	—	—
I.6	$(CH_2)_4CH_3$	174–175	591	53·6	(586–606)**	—	600	54·4	564*	597	582*	604
I.7	$(CH_2)_8CH_3$	130–131	590	54·2	(586–606)**	—	599	54·6	—	—	—	—
I.8	$(CH_2)_{10}CH_3$	112–114	590	53·5	(586–606)**	—	598	54·7	566*	598	585*	605
I.9	$CH(CH_3)_2$	194–195	589	47·4	(584–610)**	—	598	51·3	—	—	—	—
I.10	$CH_2CH(CH_3)_2$	213–215	592	52·0	(587–610)**	—	599	48·6	566*	598	579*	604
I.11	$C(CH_3)_3$	173–174	564	42·6		—	572	43·8	560	—	565	—

I.12	$CH_2C(CH_3)_3$	253–254	593	47·4	(583–610)**	599	49·5	—	—	—	—	—
I.13	CH_2Cl	222–223	586	43·0	585*	44·2	602	48·8	557*	592	574*	597
I.14	CCl_3	161–162	555	42·0	—	—	557	43·9	532	—	545	—
I.15	CF_3	163–164	553	44·2	—	—	561	51·8	538	—	550	—
I.16	CH_2CH_2Cl	209–210	593	53·1	590*	51·5	606	53·8	563*	598	580*	602
I.17	$CHClCH_3$	195–196	585	46·1	586*	49·4	600	51·9	558*	593	575*	597
I.18	$CH_2C_6H_5$	253–254	593	52·6	586*	47·4	607	49·7	566*	600	580*	605
I.19	C_6H_{11}	272–273	588	47·5	(584–610)*	—	600	47·3	564*	600	580*	604
I.20	C_6H_5	215–216	562	43·4	—	—	572	48·4	551	—	562	—
I.21	$C_6H_4OCH_3$-*p*	206–207	564	41·4	—	—	573	49·7	—	—	—	—
I.22	$C_6H_4NO_2$-*p*	242–243	565	41·0	—	—	573	48·9	—	—	—	—
I.23	OC_2H_5	218–219	568	48·0	—	—	576	51·2	—	—	—	—
I.24	OC_6H_5	208–209	568	50·1	—	—	574	52·4	551	—	566	—
I.25	NHC_2H_5	191–192	613	52·9	591*	38·5	624	52·6	—	—	—	—
I.26	NHC_6H_5	262–263	610	44·7	592*	36·5	624	54·4	575*	612	584*	620
I.27	$SO_2C_6H_5$[c]	247–249	564	42·8	—	—	569	44·2	546	—	559	—

chromatography, 0·060–0·200 nm, pore diameter *c.* 4 nm, Janssen Chimica), applying from solution in toluene and eluting with toluene containing up to 2% ethyl acetate as appropriate.

Principal zones were eluted, solvent removed *in vacuo*, and the products recrystallised from ethanol (Norit). All dyes showed only one component on TLC (Kodak Chromagram Sheets, Type 13181 Silica Gel with fluorescent indicator; toluene:ethyl acetate:glacial acetic acid, 8:2:1 as eluent). Mass spectra (EI) showed the parent ion varying in intensity from 25 to 90%, with a high intensity fragment at $(M—CH_3)^+$, and base peak for the majority of dyes due to fragmentation of the coupler–azo link, giving an ion corresponding to *m/z* (coupler-H)$^+$. Characterization data for the dyes are given in Tables 2 and 3.

Similarly prepared was the reference dye from 2-bromo-4-nitro-6-cyanoaniline and *N,N*-diethylaniline, m.p. 196–197°C (ethanol), λ_{max} (ε_{max}) 541 (35, 134) in ethanol; 551 (36, 408) in dichloromethane.

2.5 General

Electronic spectra were recorded on a Philips PU8730. ^{1}H-NMR data were obtained using a JEOL GX270 FT NMR Spectrometer; values reported are for spectra in d_6-DMSO, δ values being relative to TMS. IR spectra (KBr) were recorded on a Nicolet 205 FT-IR Spectrometer and mass spectra on an AEI MS 902, EI ionisation, 8 kV accelerator voltage, source plot temperature 230°C.

3 RESULTS AND DISCUSSION

3-Acylamino-*N,N*-dialkylanilines can be synthesised by a variety of methods, the simplest being the controlled mono-acylation of the readily available 1,3-phenylenediamine, followed by alkylation; a variant of this procedure involves acylation of 3-nitroaniline, with subsequent reduction and alkylation. The synthesis of a range of intermediates using this method is tedious, since the alkylation process needs to be effected for each acylamino substituted derivative (although, for industrial process for which a more limited range of intermediates is required, such techniques are obviously cost-saving).

For more facile small-scale evaluations, it is more convenient to generate the appropriate 3-nitro-*N,N*-dialkylaminoaniline, either by nitration of the pertinent amine or by alkylation of 3-nitroaniline. After reduction, the resultant 3-amino-*N,N*-dialkylaniline can then readily be converted into the desired 3-acylamino derivatives. In this investigation *N,N*-diethylaniline was nitrated in concentrated sulphuric acid and separation of the 3-nitro isomer

from the 4-nitro derivative was effected by differential solubility factors dependent on pH adjustment resultant from gradual addition of ammonia to the diluted nitration liquor. Whereas with *N,N*-dimethylaniline, both nitro isomers are solids,[12] *N,N*-diethylaniline affords, as initial precipitate, the 4-nitro isomer as a yellow solid, followed by, on further addition of ammonia, the predominantly formed 3-nitro isomer as an orange oil. The colour differences inherent in the separation of the isomers from *N,N*-dimethylaniline,[12] was also apparent with *N,N*-diethylaniline; but clean separation of the initially deposited 4-nitro isomer as homogeneous material was difficult. To ensure that the required 3-nitro isomer was isolated in an essentially homogeneous form, the initial precipitation of the 4-nitro isomer (not required) in conjunction with some 3-nitro isomer was preferred, the subsequently precipitated 3-nitro isomer being of sufficient purity for subsequent acylation. Overall recovery yield, after vacuum distillation, was 63%. Similar nitrations, with isomer separation using sodium hydroxide, have afforded 21% 4-nitro isomer and 74% 3-nitro isomer,[14] the latter being reduced and acylated *in situ* without isolation of the nitro precursor.

The 3-nitro derivative was clearly reduced using Pd/C and hydrazine hydrate in ethanol, and the resultant 3-amino derivative used, without further purification, for reaction with acid chlorides, chloroformates, isocyanates and sulphonyl chlorides using standard techniques.

The influence of polar, H-bonding and steric factors originating from a variety of 2-substituents in 4′-nitro-4-*N,N*-diethylaminoazobenzene has been discussed and the effects rationalised for such substituents.[11] The value of the 2-acylamino substituent in imparting bathochromic shifts, high tinctorial strength and brightness is apparent. In dyes **II**, colour differences resultant from increased substitution in the diazo component by electron acceptor groups follow an order similar to that observed in analogous dyes from other coupling components, e.g. *N*-β-hydroxyethyl-*N*-cyanoethylaniline.[15–17] $\Delta\lambda$, in ethanol, between the aniline and 2-bromo-6-cyano-4-nitroaniline derived dyes is 141 nm, compared to 112 nm for dyes from *N*-β-hydroxyethyl-*N*-β-cyanoethylaniline and 181 nm for dyes from 3-acetylamino-5-methoxy-*N*-β-hydroxyethyl-*N*-β-cyanoethylaniline.[18]

In dichloromethane, substituent effects in the diazo component are essentially the same as in ethanol, all λ_{max} being displaced to longer wavelength; $\Delta\lambda$ values between the two solvents are lowest (8 nm) for the aniline based dye **II.1**, tending to increase with increasing electron acceptor substitution in the diazo component, to 14 nm for the bromo-cyano-nitroaniline based dye **II.7**, although increases are not regular. Whilst both solvents can be regarded as being polar, in ethanol there is the additional possibility of H-bonding between the solvent and the nitrogen atoms of the amino substituents in the coupler, particularly the 2-acylamino group.

For comparative purposes, spectra of the dyes were run in benzene and in cyclohexane as typical more weakly polar non-H-bonding media (qualitatively: whilst most dyes had good solubility in benzene, that in cyclohexane was very limited for several days, cf. Ref. 11). The parent dye from 2-bromo-4-nitro-6-cyanoaniline and *N,N*-diethylaniline showed λ_{max} 534 nm (benzene), 511 nm (cyclohexane), 551 nm (dichloromethane) and 541 nm (ethanol); dye **II.7**, containing the 2-acylamino substituent, showed λ_{max} 572 sh and 603 nm (benzene), 568 sh and 600 nm (cyclohexane), 589 sh and 606 nm (dichloromethane) and 592 nm (ethanol), i.e. $\Delta\lambda$ values between the 2-unsubstituted and 2-acylamino derivatives were 51 nm (ethanol), 55 nm (dichloromethane), 69 nm (benzene) and 89 nm (cyclohexane), reflecting combinations of solvent polarity and H-bonding capacity.

In dichloromethane, the increased solvent polarity results in a large bathochromic shift in the 2-unsubstituted dye, relative to both benzene (17 nm) and cyclohexane (40 nm), but in the 2-acylamino derivative **II.7**, spectra in all three solvents are similar, except for the marked hypsochromic shift in the lower wavelength inflexion in cyclohexane. Solvent polarity factors are, therefore, more limited in **II.7** and intramolecular H-bonding in this dye appears to be the more dominant influence. In ethanol, the increased solvent polarity results in the anticipated bathochromic shifts in the 2-unsubstituted dye, viz. 7 nm with respect to benzene and 30 nm with respect to cyclohexane, but these differences are not apparent in **II.7**, in which negative solvatochromic effects are shown for the resolved longer wavelength absorption. This may be resultant from ground-state stabilisation by intermolecular H-bonding, thus diminishing the colour imparting electronic and/or intramolecular H-bonding between the 2-acylamino and azo nitrogen atoms.

It has been previously noted[11] in a series of dyes from 4-nitroaniline and various 3-substituted *N,N*-diethylanilines that, with many 3-donor substituents, the extent of the bathochromic shift in λ_{max} resultant from them is in accord with their electron-donating character. Dyes from the 3-amino derivative and 3-acetylamino derivative, despite the presence of the electron acceptor residue in the latter, have similar λ_{max} (in 95% ethanol), indicating the compensatory effect of intramolecular H-bonding. Where steric hindrance factors originating from the substituent, as in *N*-ethyl-*N*-acetylamino, are such as to inhibit any mesomeric influence, only inductive (—I) effects of the nitrogen atom are involved and the dye has λ_{max} displaced to slightly lower wavelength than the parent 3-unsubstituted dye. In dyes derived from 2-bromo-6-cyano-4-nitroaniline, it is of interest to note that when coupled to 2-*N*-methylamino-4-*N,N*-diethylaniline, the resultant dye[19] is hypsochromic in all solvents relative to the 2-acetylamino analogue **I.2**, despite the presence of the stronger electron donor 2-amino moiety, viz.

571 nm (dichloromethane), 535 sh and 564 nm (benzene), 525 sh and 551 nm (cyclohexane), 562 nm (ethanol (cf. **I.2**, Table 3). These data clearly indicate the influence of factors additional to those of electronic origin.

Solvent effects in other **II** are less well defined. Whilst all dyes showed λ_{max} in benzene at 3–6 nm longer wavelength than in ethanol, in cyclohexane the negative solvatochromism is only apparent in **II.7**, other **II** showing the longer wavelength absorption in ethanol.

The influence of the nature of the 2-acylamino (and related) substituent in dyes **I** derived from 2-bromo-6-cyano-4-nitroaniline is shown in Table 3. Several dyes showed, in dichloromethane, a plateau extending over *c.* 20 nm, with no defined maxima; λ_{max} values in the table are from extrapolation of the plateau into a smoothed curve; 'plateau' ranges are also given and ε_{max} values pertain to the plateau and not to the smoothed absorption maxima. The parent dye from *N,N*-diethylaniline has λ_{max} 541 nm (in ethanol, in which solvent all the following data pertain to, unless stated otherwise). Introduction of a —CHO group into the 2-position (**I.1**) results in a bathochromic shift to 574 nm, and replacement of the aldehyde proton by the methyl group (**II.2**) gives further shifts to 592 nm, compatible with the increased electron donating nature of the substituent. The substituent R in dyes **I** will influence the electron availability on the amino nitrogen atom, and hence its electron donor and H-bonding capacities, depending on electronic and steric effects. Increasing the chain length of the alkyl group, in both straight and branched chain homologues (dyes **I.3**–**I.10**, **I.12**) has negligible effect on λ_{max} relative to the acetylamino derivative **I.2**. The presence of a chlorine atom in the side chain, by virtue of its —I effect and consequent decrease in electron availability at the amino nitrogen atom, would be expected to result in hypsochromic shifts. Such shifts are apparent in the α-chloro derivatives **I.13** and **I.14**, but in the β-chloro derivative **I.16**, damping of the inductive effect restores λ_{max} to that of the unsubstituted alkyl analogue **I.3**. In the trichloromethyl derivative **I.14**, λ_{max} is shifted significantly to lower wavelength (555 nm) relative to the methyl analogue **I.2** (592 nm), reflecting inductive and/or steric influences of the three α-chloro substituents. Industrive effects in the trifluoromethyl derivative **I.15** will be higher than those in **I.14**, but steric factors less; the relative influences result in a similar absorption maxima (553 nm) to that of the trichloromethyl derivative. Steric factors are evident also in the trimethylacetyl derivative (**I.11**) which, despite the presence of three donor methyl groups, absorbs (564 nm) at 28 nm lower wavelength than the acetyl precursor **I.2**. Where the three methyl groups are present on the β-carbon atom, however, as in the *tert*-butylacetyl chloride derivative **I.12**, only polar effects typical of an alkyl substituent occur, λ_{max} (593 nm) being similar to that of the straight chain homologues. A small hypsochromic shift occurs in the cyclohexyl derivative

I.9, and whilst the presence of a phenyl moiety in the alkyl chain (**I.18**) has little effect, the benzoylamino derivative (**I.20**) shows significant colour shifts, absorbing at lower wavelength than the sterically crowded trimethylacetyl derivative **I.11** and shifted hypsochromically by 30 nm relative to the acetylamino dye **I.2**. Replacement of an acetylamino substituent by benzoylamino usually results in small bathochromic shifts, e.g. 1-acetylamino- and 1-benzoylaminoanthraquinone, λ_{max} 400 and 405 nm respectively, in methanol.[20] The relative insensitivity in dyes **I** to substitution into the phenyl ring by electron donor and acceptor substituents (dyes **I.21**, **I.22**) indicates a lack of any significant electronic effect from the aroylamino residue and presumably the hypsochromic shifts are relatable to steric factors. The phenylsulphonamido derivative **I.27** absorbs in a similar region to the benzoylamino derivative **I.20**, despite the presence of the more strongly electron acceptor sulphone group, and similar λ_{max} is shown by the phenyl chloroformate derived dye **I.24**. Whilst replacement in the acyl type side chain of the phenyl moiety by a phenoxy substituent thus produces little colour change, similar comparison of the ethyl (**I.3**) and ethoxy (**I.23**) derivatives shows the latter to be hypsochromic by 24 nm, although it contains the more strongly electron donating substituent. The influence of increased donor-character in the side chain is, however, realised in the isocyanate derived dyes **I.25** and **I.25**, in which appreciable bathochromic shifts are apparent.

In dichloromethane, shifts in λ_{max} to longer wavelength are observed in all dyes **I** relative to ethanol, values being in the general area of 10 nm, with extremes of 16 nm for the chloromethyl derivatives **I.13** and 2 nm for the trichloromethyl derivative **I.14**.

Spectra of representative dyes were run in cyclohexane and in benzene (Table 3); several dyes had limited solubility in cyclohexane, and no comparisons with respect to ε_{max} were attempted (λ_{max} data only are also reported for benzene, although solubility in this solvent was good). Dyes in which the acylamino group contained an unsubstituted straight or branched alkyl group showed similar solvent effects to those who noted previously for **II.7** (i.e. **I.3**), e.g. **I.2**, **I.6**, **I.8**, **I.10**, **I.16**, **I.18** and **I.19**. Thus, for dyes which have similar λ_{max} in ethanol, and in which no major electronic or steric inhibition of the intramolecular H-bonding occurs, negative solvatochromic effects occur with respect to comparative spectra in benzene and ethanol, and between cyclohexane and ethanol. The ethanolic media disrupts the H-bonding and λ_{max} are displaced to lower wavelength. Additionally, solvent polarity factors are relatively small, principal resolved absorption maxima being in a similar area in benzene, cyclohexane and dichloromethane. Dyes showing a relatively small hypsochromic shift in ethanol compared to the above, viz. the α-chloroalkyl derivatives **I.13** and **I.17**, also show similar behaviour.

However, in the acylamino derivatives where the intramolecular H-bonding is disrupted by steric or electronic effects, with significant overall displacement of λ_{max} to lower wavelength than **I.3**, these solvent effects can be reversed to different extents. For dyes showing relatively large overall hypsochromic shifts, λ_{max} in ethanol is at similar wavelength to that in benzene, but at longer wavelength than that in cyclohexane, e.g. **I.11**, **I.20** and **I.24**. Where polar or steric effects have maximal interference with the H-bonding, positive solvatochromism is apparent in ethanol with respect to both benzene and cyclohexane, e.g. **I.14**, **I.15** and **I.27**.

In the phenylisocyanate derivative **I.26**, solvent polarity effects are apparent comparing λ_{max} in dichloromethane, benzene and cyclohexane; in ethanol, intermolecular H-bonding can occur at either of the side chain —NH sites. Whilst the increase in the electron donor nature of the 2-substituent in this dye is reflected in the longest wavelength absorption within the dyes investigated, solvent interaction at either NH group would diminish either electronic or intramolecular H-bonding. Either effect would tend to be hypsochromic and dye **I.26** also shows a negative solvatochromic effect in ethanol relative to both benzene and cyclohexane.

The negative or positive solvatochromism in ethanol with respect to less polar solvents thus appears to be dependent on the extent of intramolecular H-bonding in the dyes. Where such bonding is typified by an acylamino substituent carrying a simple alkyl group, intermolecular H-bonding in ethanol results in hypsochromic shifts; as the relative degree of intramolecular H-bonding is decreased by substituent effects, the effect of ethanol decreases, eventually giving a positive solvatochromism. The effect is additionally shown by comparison of λ_{max} in the more polar dichloromethane and weakly polar cyclohexane neither of which solvents would be expected to significantly stabilise the ground state of the dye by intermolecular H-bonding. Where the intramolecular H-bonding is strongest, solvent polarity effects are limited, e.g. **I.3**, $\Delta\lambda$ 6 nm; **I.6**, $\Delta\lambda$ 3 nm; **I.8**, $\Delta\lambda$ 0 nm; **I.10**, $\Delta\lambda$ 1 nm; **I.19**, $\Delta\lambda$ 0 nm; in cases where H-bonding is disrupted by electronic or steric factors in the 2-substituent, solvent effects are more evident, e.g. **I.11**, $\Delta\lambda$ 23 nm; **I.20**, $\Delta\lambda$ 21 nm; **I.24**, $\Delta\lambda$ 23 nm; **I.27**, $\Delta\lambda$ 23 nm.

It is well established than minor changes in the nature of the alkyl group in the 2-acylamino substituent in dyes of type **I** can have a significant effect on the colour yield of the dyes on polyester. X-ray diffractometer (XRD) data have not revealed differential configurations pertaining to build-up differences between acetylamino and propionylamino analogues,[21,22] but similar studies have indicated reasons for the lower light fastness of 2-acyl derivatives, in which H-bonding with the azo group cannot occur.[23] XRD investigations of selected dyes and an evaluation of the relative coloration properties of dyes **I** on polyester will be reported at a later stage.

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