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Molecular Complexes of CI Disperse Yellow 211 with Aromatic Compounds

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ABSTRACT

This paper describes some anomalous behaviour of the disperse monoazo dyestuff CI Disperse Yellow 211 which is able to form molecular complexes of the CT (Charge Transfer) type with various aromatic compounds. The complexes are formed in the solid phase. They are separated as crystalline substances of orange, red, ruby to blue-violet colour, whereas in organic solvents they are practically fully dissociated into the starting components. The complexes were isolated from an aqueous dyebath and recrystallized from organic solvents. Their composition, structure and properties were determined by elemental analysis, X-ray diffraction, spectrophotometry and liquid chromatography. From the crystal and molecular structure determinations, it was concluded that the crystals of the molecular complexes are stabilized by van der Waals forces and, partially, by the π–π interaction of the aromatic nuclei of the dye with those of the respective aromatic compound. The so far unpublished constitution of CI Disperse Yellow 211 has been determined and confirmed by independent synthesis.

1 INTRODUCTION

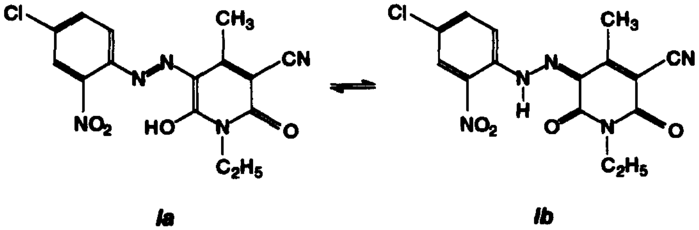
The yellow pyridine disperse monoazo dyestuff 5-(4'-chloro-2'-nitrophenyl)-azo-6-hydroxy-1-ethyl-3-cyano-4-methyl-1,2-dihydro-2-pyridone (formulae **Ia**, **Ib**), CI Disperse Yellow 211 exhibits unusual behaviour during bath dyeing with carriers. Addition of aromatic compounds, which are the effective components of carriers, into the dyebath results in very apparent precipitation of a fine suspension of dye with separation of coarse orange, red to ruby crystalline substances. This causes considerable problems with levelling during dyeing with carriers, whereas the levelling of dyeings without added carriers is very good.

A study of the causes of this phenomenon showed that CI Disperse Yellow 211 forms molecular complexes of the CT type with a variety of aromatic compounds.

Literature[1–7] data reports a number of pyridine derivatives which form molecular complexes of various types, the pyridine heterocycle usually playing the role of electron acceptor. However, no cases of analogous behaviour of azo compounds with pyridone azo components have so far been described.

2 RESULTS AND DISCUSSION

The constitution of CI Disperse Yellow 211 (**Ia**, **Ib** in Structure 1) is consistent with the results of elemental analysis (Table 1), ^{1}H-NMR and IR spectra (Table 2), TLC and X-ray diffractograms (Table 3). It was confirmed by independent synthesis (see Section 3). The ^{1}H-NMR and IR spectra (Table 2) as well as the results of X-ray determination of crystal and molecular structure, (Table 4, Figs 1 and 2)[8] confirm the structure of the hydrazone tautomer Ib, which agrees with the data on azo-hydrazone tautomerism of azo dyestuffs derived from pyridone coupling components.[9–11]



Structure 1. CI Disperse Yellow 211.

The molecular complexes of the dyes with aromatic compounds were first obtained by isolation from a real dyebath containing a dispersion of the dyestuff and a carrier emulsion. For more detailed investigations, the pure complexes were prepared by crystallization from solutions of the dyes and an aromatic compound from organic solvents such as acetone, dioxane, dimethyl phthalate, dimethyl sulphoxide, or N,N-dimethylformamide. Alcoholic solvents such as methanol, ethanol and higher aliphatic alcohols, prevent the formation of molecular complexes in

TABLE 1
Elemental Analysis Data

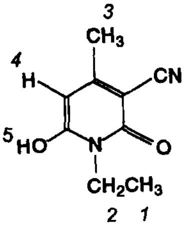
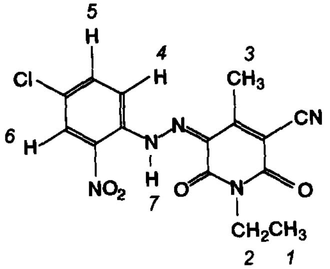
Substances	*Formula and M.W.*	*C%*	*H%*	*Cl%*	*N%*
		Calc. *Found*	*Calc.* *Found*	*Calc.* *Found*	*Calc.* *Found*
Dye D. Yellow 211	$C_{15}H_{12}N_5O_4Cl$	49·81	3·79	9·80	19·36
	361·74	49·73	3·58	9·63	19·19
CT-complex	$C_{40}H_{32}N_{10}O_8Cl_2$	56·41	3·79	8·33	16·45
Dye : naphthalene	851·66	55·92	4·03	8·08	16·21
(2 : 1) mol					
CT-complex	$C_{42}H_{34}N_{10}O_8Cl_2$	57·48	3·90	8·08	15·96
Dye : biphenyl	877·70	57·73	4·11	7·83	15·50
(2 : 1) mol					
CT-complex	$C_{42}H_{34}N_{10}O_{10}Cl_2$	55·45	3·77	7·79	15·40
Dye : 4,4'-dihydroxybiphenyl	909·70	55·25	3·54	8·03	15·61
(2 : 1) mol					
CT-complex	$C_{25}H_{20}N_5O_5Cl$	59·35	3·99	7·01	13·84
Dye : 1-naphthol	505·92	59·17	3·83	7·21	13·92
(1 : 1) mol					
CT-complex	$C_{40}H_{32}N_{10}O_9Cl_2$	55·37	3·72	8·17	16·14
Dye : 2-naphthol	867·66	55·47	3·92	8·33	16·31
(2 : 1) mol					
CT-complex	$C_{42}H_{34}N_{10}O_9Cl_2$	56·45	3·83	7·93	15·67
Dye : *o*-phenylphenol	893·70	56·61	3·66	7·74	15·86
(2 : 1) mol					
CT-complex	$C_{57}H_{44}N_{15}O_{12}Cl_7$	49·64	3·22	17·99	15·23
Dye : *p*-dichlorobenzene	1 379·23	49·76	3·26	17·78	15·44
(3 : 2) mol					
CT-complex	$C_{28}H_{23}N_6O_6Cl$	58·49	4·03	6·17	14·26
Dye : N-phenylanthranilic acid	508·75	58·21	4·20	6·01	14·40
(1 : 1) mol					

some cases. A detailed description of the preparation of the molecular complexes is presented in Section 3.

The molecular complexes cannot satisfactorily be characterized by their melting points; on heating they release vapours of the more volatile aromatic components, regenerating the parent dye CI Disperse Yellow 211. The complexes cannot therefore be dried at enhanced temperatures or in vacuum, and they were dried (after recrystallization from organic solvents) in air at room temperature. For this reason it was advantageous to use a volatile solvent such as acetone, for the preparation.

The molecular complexes precipitated very readily in well developed crystals whose colour was bathochromically shifted as compared with

TABLE 2
^{1}H-NMR and IR Data

Substance	*^{1}H-NMR* *$/(CD_3)_2SO/$*	*IR (cm^{-1})* *$/CHCl_3/$*
	1. δ = 1·15 ppm (3H) 2. δ = 3·97 ppm (2H) 3. δ = 2·25 ppm (1H) 4. δ = 5·68 ppm (1H) 5. δ = 8·46 ppm (1H) (broad band)	ν (C=O): 1648 ν (C≡N): 2216 ν (O—H): 3690 δ (O—H): 1431 γ (O—H): 826 ν (C—H): $/CH_3/$ 2990 $/C_2H_5/$ 2971 2880 2821
	1. δ = 1·20 ppm (3H) 2. δ = 3·94 ppm (1H) 3. δ = 2·59 ppm (3H) 4. δ = 7·95 ppm (1H) 5. δ = 8·18 ppm (1H) 6. δ = 8·32 ppm (1H) 7. δ = 15·49 ppm (1H) (broad band)	ν (C=O): 1645 1690 ν (NO_2): 1327 ν (C≡N): 2229 ν (N—H): 3100 ν (C—H): $/CH_3/$ 2975 $/C_2H_5/$ 2825 2930

the crystals of the parent dye. Whereas the latter are bright yellow, the molecular complexes exhibit (depending on the type of aromatic compound adopted) an orange, red, ruby, or even blue-violet colour. The colour of the crystalline complexes was characterized by spectrophotometric measurements and calculation of the respective CIELAB chromaticity coordinates (see Section 3 and Table 5).

The molecular complexes are readily formed in the solid phase. However, in dilute solutions in organic solvents, they are almost completely decomposed into the starting dyes and aromatic components. The electronic spectra of the solutions formed by dissolving the solid crystalline molecular complexes in organic solvents corresponded to a summation of

TABLE 3
X-Ray Diffractograms of CI Disperse Yellow 211 and Molecular Complexes

Dye		*CT-complex (DY 211: aromatic compounds)*															
CI Disp. Yellow 211		*Dye : naphthalene (2:1)*		*Dye : biphenyl (2:1)*		*Dye : 4,4′ dihydroxy-biphenyl (2:1)*		*Dye : 1-naphthol (1:1)*		*Dye : 2-naphthol (2:1)*		*Dye : o-phenyl-phenol (2:1)*		*Dye : p-dichloro-benzene (2:3)*		*Dye : N-phenyl-anthranilic acid (1:1)*	
d [pm]	*I_{rel} [%]*	*d [pm]*	*I_{rel} [%]*	*d [pm]*	*I_{rel} [%]*	*d [pm]*	*I_{rel} [%]*	*d [pm]*	*I_{rel} [%]*	*d [pm]*	*I_{rel} [%]*	*d [pm]*	*I_{rel} [%]*	*d [pm]*	*I_{rel} [%]*	*d [pm]*	*I_{rel} [%]*
1009·0	8	1060·0	9	1145·0	7	1154·0	13	735·1	100	1116·0	8	767·0	100	1107·0	6	1620·0	6
828·3	100	740·1	70	754·2	100	741·6	100	558·1	13	748·0	100	620·3	8	718·2	93	908·9	5
506·5	13	620·9	19	629·0	15	635·3	6	514·1	11	609·0	10	544·1	12	563·1	12	807·8	100
414·0	16	533·0	24	526·2	21	570·1	14	439·9	17	537·0	18	459·2	8	527·0	17	594·8	4
358·0	24	454·0	20	453·9	12	520·1	11	377·0	15	508·2	15	428·0	7	514·0	13	522·0	4
336·1	23	339·1	100	391·6	16	458·6	6	370·9	13	452·1	14	388·1	12	380·9	23	403·1	9
323·4	9	315·2	52	354·6	17	425·0	7	355·2	21	382·3	11	362·0	18	361·4	30	367·0	7
310·2	10	301·2	5	341·7	82	371·2	9	344·2	48	358·2	20	342·1	74	342·0	100	351·2	13
289·6	8	280·0	6	315·1	25	341·7	29	336·0	25	336·8	95	325·8	10	311·8	53	324·3	10
277·2	4	263·3	5	306·4	6	311·2	15	319·2	19	316·1	48	222·2	32	305·3	16	262·4	4

d, interplane distance; I_{rel}, relative diffraction intensity.

TABLE 4
CT-Complex CI Disperse Yellow 211 : Naphthalene (2 : 1). Basic Crystallographic Data, Measurement and Refinement Parameters

Crystal packing:	
a = 7·953(1) Å	V = 982·8(3) A^3
b = 11·608(2) Å	Z = 2
c = 11·717(2) Å	D(calc) = 1·480 g/cm^2
α = 101·89(2)°	Triclinic, Space group $P\bar{1}$
β = 94·27(2)°	$\mu(M_0K_\alpha)$ = 2·31 cm^{-1}
γ = 109·91(2)°	F(000) = 452
Crystal dimensions	0·2 × 0·2 × 0·4 mm
Diffractometer and radiation used	Enraf-Nonius CAD4, $M_0K\alpha$, λ = 0·71073 Å
Scan technique and temperature	$\omega/2\Theta$; 296 K
No. and Θ range of reflections for lattice parameter refinement	18; 19 − 21°
Range of h, k and l	$-10 \rightarrow 10$, $-13 \rightarrow 13$, $-13 \rightarrow 13$
Standard reflections	−3 3 −9, 2 −1 3
Standard reflections monitored in interval; intensity fluctuation	60 min; −0·6%
Total number of reflections measured, 2Θ range	2 053; 0 − 42°
Value of R_{int}	0·020
Number of unique observed reflections	1 768
Criterion of observed reflections	$I \geq 1{\cdot}96\ \sigma(I)$
Function minimized	$\sum w(\lvert Fo\rvert - \lvert Fc\rvert)^2$
Weighting scheme	$w = [\sigma^2(F) + 0{\cdot}0009F^2]^{-1}$
Parameters refined	335
Value of R, wR and S	0·054; 0·048; 1·78
Ratio of max. least-squares shift to e.s.d. in the last cycle	0·001
Max. and min. heights in final $\Delta\rho$ map	0·34; −0·66 e$Å^{-3}$
Source of atomic scattering factors	SHELX 76[15]
Programs used	SHELX 86,[16] SDP[17] SHELX 76,[15] PARST[18] MOLDRAW[19]

the spectra of the pure dye and that of the respective aromatic component, without any CT-band of the corresponding molecular complex. This behaviour was utilised for the determination of the molar ratio of the dye and the aromatic component in the complex. The solutions prepared by dissolving the molecular complexes in solvents were then analysed as solutions of mixtures of the components (dye and aromatic component) spectrophotometrically and by liquid chromatography (see Section 3 and Table 6). The molar ratio of azo dye and aromatic component in the molecular complex was also confirmed by elemental analysis (Table 1).

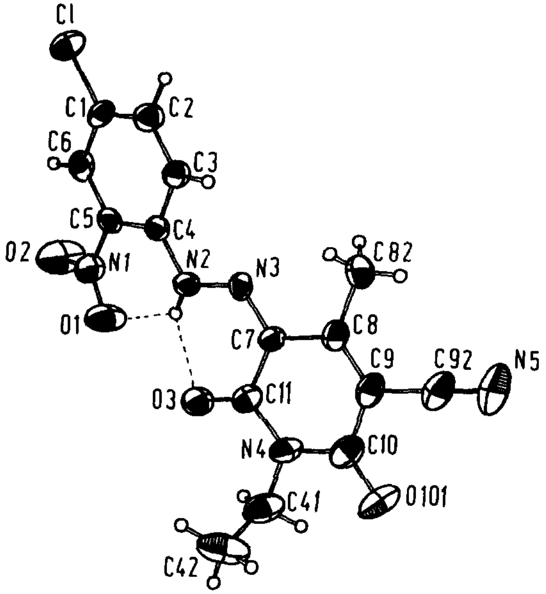


Fig. 1. View of the pyridone azo dye molecule. Thermal ellipsoids are drawn at the 50% probability.

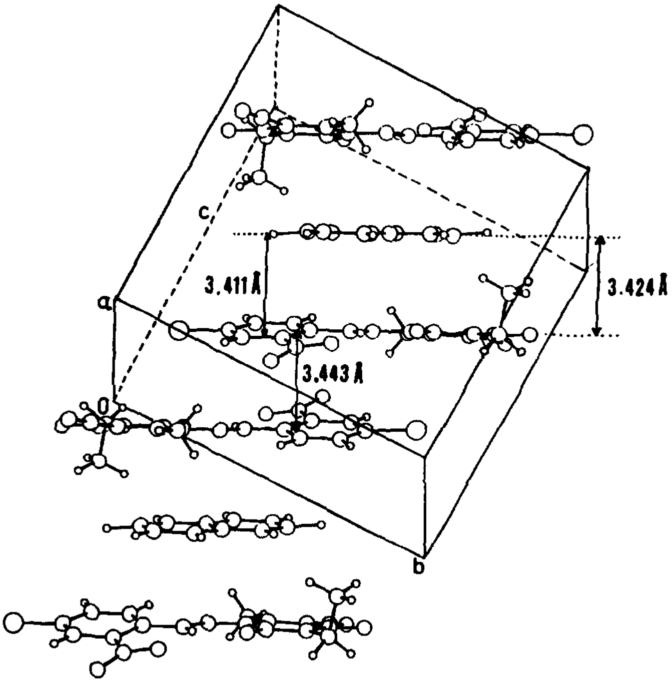


Fig. 2. Crystal packing.

TABLE 5
Objective Measurement of Colour of Crystalline Molecular Complexes of CI Disperse Yellow 211 with Aromatic Compounds

Crystalline substance	*Colour*	*Trichromatic coordinates*			*CIELAB*		
		X	*Y*	*Z*	*L**	*a**	*b**
Dye DY 211	Yellow	52·364	47·801	15·018	74·70	19·30	52·54
CT-complex Dye-X X = naphthalene	Orange	29·334	21·788	10·724	53·79	37·37	27·52
CT-complex Dye-X X = biphenyl	Orange	40·384	28·832	12·177	60·63	45·90	35·30
CT-complex Dye-X X = 4,4'-dihydroxybiphenyl	Blue-black	9·291	9·771	9·850	37·32	0·70	1·71
CT-complex Dye-X X = 1-naphthol	Red	21·336	17·912	14·954	49·39	22·29	9·05
CT-complex Dye-X X = 2-naphthol	Ruby	21·057	15·537	10·143	46·36	34·01	16·42
CT-complex Dye-X X = *o*-phenylphenol	Red	17·077	13·768	9·914	43·90	24·20	12·86
CT-complex Dye-X X = *p*-dichlorobenzene	Yellow orange	34·995	26·905	11·270	68·89	35·89	34·77
CT-complex Dye-X X = N-phenylanthranilic acid	Violet	22·090	18·776	13·994	50·42	21·37	13·10

The stoichiometric ratios of the dye to aromatic component in individual molecular complexes were approximately 2:1, 1:1 and 2:3 (see Tables 1 and 6). The molecular ratio 2:1 was also confirmed by X-ray determination of the complete crystal structure and the molecular structure of the molecular complex of the dye and naphthalene (see Section 3, Table 4, Figs 1 and 2).

Figure 1 shows a perspective view of the pyridone azo dye molecule; the crystal packing is depicted in Fig. 2. The atomic numbering system used is arbitrary and does not correspond to conventional chemical nomenclature.

The largest displacement from the plane of the substituted phenyl ring (C1, C2, C3, C4, C5, C6; $\chi^2 = 2{\cdot}759$) is at C5 (0·004(3) Å). The pyridine moiety (C7, C8, C9, C10, N4, C11) is also planar with deviations varying from −0·023(4) Å (for C10) to 0·020(4) Å (for C9). Multiple bond character was found for C8–C9 (the bond order is 1·82). The phenyl and pyridine

TABLE 6
Spectrophotometric and HPLC Determinations of the Molar Ratio of CI Disperse Yellow 211 and Aromatic Component in the Molecular Complex
λ_{max}[nm]—Wavelength of Maximum Spectral Absorption
ε_{max}[l g^{-1} cm^{-1}]—Mass Extinction Coefficient

Substance	*Spectrophotometric data*			*HPLC data*	*Results*
	λ_{max} *[nm]*	ε_{max} *[l/g cm]*	*Stoichiom. X : dye [mol : mol]*	*Stoichiom. X : dye [mol : mol]*	*Complex dye : X [mol : mol]*
Dye D.Y. 211	436	104·744	—	—	—
CT-complex Dye-X X = naphthalene	436	88·21	0·529 : 1	0·496 : 1	2 : 1
CT-complex Dye-X X = biphenyl	436	86·15	0·506 : 1	0·503 : 1	2 : 1
CT-complex Dye-X X = 4,4'-dihydroxybiphenyl	436	82·77	0·516 : 1	0·511 : 1	2 : 1
CT-complex Dye-X X = 1-naphthol	436	75·97	0·950 : 1	1·041 : 1	1 : 1
CT-complex Dye-X X = 2-naphthol	436	86·19	0·540 : 1	0·506 : 1	2 : 1
CT-complex Dye-X X = *o*-phenylphenol	436	84·41	0·512 : 1	0·502 : 1	2 : 1
CT-complex Dye-X X = *p*-dichlorobenzene	436	81·81	0·689 : 1	0·668 : 1	2 : 3
CT-complex Dye-X X = N-phenylanthranilic acid	436	63·31	1·110 : 1	1·050 : 1	1 : 1

ring planes are mutually tilted by 13·8(1)°. The planar arrangement of the naphthalene ring system was confirmed by the χ^2-test value of 2·639. Possible intramolecular hydrogen bonds were found between the N2 . . . O1 and N2 . . . O3 atoms with N2 acting as a double proton donor. The donor–acceptor distances and the donor–hydrogen-acceptor angles are as follows: 2·634(4) Å and 126(3)° for N2–HN2 . . . O1 and 2·601(4) Å and 136(4)° for N2–HN2 . . . O3. No intermolecular hydrogen bond contacts appear to be present, the crystal structure being stabilized by van der Waals forces, and partly by π–π stacking interactions among the naphthalene, phenyl and pyridine rings. As may be seen from Fig. 2, the packing arrangement consists of . . . dye–dye–naphthalene–dye–dye–naphthalene . . . layer sequence. Two stacked phenyl rings (C1, C2, C3, C4, C5, C6 and C1i, C2i, C3i, C4i, C5i, C6i) are related to each other by the translation symmetry operation (i: 1-x, 1-y, 1-z). The corresponding mean interplanar spacing is 3·443(4) Å. As follows from the dihedral angle 4·3(2)° between the pyridine (C7, C8, C9, C10, N4, C11) and naphthalene rings, they are nearly coplanar with a mean interplanar distance of 3·424(4) Å. Finally, the stacking interaction between the phenyl (C1, C2, C3, C4, C5, C6) and the second naphthalene rings is 3·411(4) Å and their dihedral angle equals 9·4(2)°.

More details of this analysis are given elsewhere.[8] For other molecular complexes investigated, we only determined the classic X-ray diffractograms (see Table 3). The diffractions of individual molecular complexes are mutually different and also differ from that of pure CI Disperse Yellow 211.

The existence of the complexes only in the solid phase restricts the range of methods applicable for investigation of their structure. IR spectra measured in the solid phase in Nujol gave only incomplete information. For instance, the molecular complex of CI Disperse Yellow 211 with biphenyl showed small changes of bands in other regions, beside new weak bands due to complex formation at wavelengths 762, 777 and 828 cm^{-1}. With the other complexes, the findings were similar. Facilities for the determination of NMR spectra in the solid phase were not available to the authors.

A simple qualitative analytical test (described in Section 3) allowed an investigation of a wider range of organic solvents and constitutionally similar azo dyes from the standpoint of the ability to form molecular complexes.

The range of aromatic compounds forming molecular complexes with CI Disperse Yellow 211 involves aromatic compounds with electron donating substituents such as OH and SH (e.g. 1- and 2-naphthol, 2-phenylphenol, 4,4'-dihydroxybiphenyl, 1,5-dihydroxynaphthalene, thionaphthols). With regard to the dye structure (pyridine derivative), it is likely that the dyes of formula **Ib** represent the electron acceptor part of the complex, as is usual for molecular complexes involving pyridine derivatives.[1-7] However, molecular complexes with CI Disperse Yellow 211 are also formed by unsubstituted aromatic hydrocarbons (naphthalene, biphenyl, anthracene). Their nature is described in detail on the basis of the crystal structure and molecular structure determined by means of X-ray diffraction (Table 4 and Figs 1 and 2). The ability to form molecular complexes is also exhibited by some aromatic compounds containing only weakly electron acceptor substituents (4-dichlorobenzene, N-phenylanthranilic acid). The formation of these complexes is probably supported also by the lower energy of the crystal lattice of the mixed complex, as compared with the pure dye and pure aromatic compound, the so-called packing factor, e.g. as in the case of the 3 : 1 complex of 4,4'-dinitrobiphenyl/biphenyl, which is stable only in the crystalline state.[12]

Whereas the range of aromatic compounds forming molecular complexes is relatively wide, from the point of view of dye structure it is rather restricted: it was found that only the azo compounds **Ia** and **Ib** were able to form molecular complexes. A number of structural analogues of CI Disperse Yellow 211 have been investigated, involving analogous dyes with different substituents at the N atom of the pyridone component (H, methyl, propyl, isopropyl, butyl, 2-hydroxyethyl, 2-acetoxyethyl, benzyl). Also investigated were a series of dyes having the same pyridone coupling component as in CI Disperse Yellow 211, but different diazo components (aniline, 2-nitroaniline, 4-chloroaniline, 4-nitroaniline, 2-chloro-4-nitroaniline, 3,4-dichloroaniline, 2,5-dichloroaniline, 4-methyl-2-nitroaniline, methyl and ethyl 4-aminobenzoates, 4-aminoacetanilide, 4-aminoazobenzene). In none of these cases, however, was any formation of molecular complexes observed.

3 EXPERIMENTAL

3.1 Chemicals

CI Disperse Yellow 211 was a commercial sample, Spolapren X^R (Spolchemie, Ústí nad Labem, Czech), a commercial carrier containing a mixture of naphthalene, biphenyl, xylene and an emulsifier based on calcium dodecylbenzenesulphonate and oxyethylated lauryl alcohol. Other chemicals used were commercial samples (Lachema Brno, Aldrich Chem., Janssen Chimica, Fluka A. G., Hoechst A. G.).

3.2 Analytical techniques

The IR spectra were measured with a Perkin-Elmer 621 in $CHCl_3$ solution or in Nujol suspension. The ^{1}H-NMR spectra were measured with an AMX-360 (Bruker) at 360·139 MHz at 296 K in hexadeuteriodimethyl sulphoxide; chemical shifts are referred to the solvent signal, ^{1}H(DMSO) $\delta = 2{\cdot}55$ ppm.

The UV-VIS spectra of solutions of CI Disperse Yellow 211 and its molecular complexes were measured with a Specord UV-VIS (Zeiss Jena) in acetone solutions at concentrations of 5–10 mg/litre. The X-ray diffractograms were obtained using a Diffractometer HZG 4B (VEB Freiberger Präzisionsmechanik, FRG), Radiation Cu Kα, for crystal

Structure Determination (see Table 4). HPLC was carried out on an HPLC chromatograph Model 5020 (Varian, USA) column: glass-Separon SGX C18, 150 × 3 mm ID (Tessek Prague); mobile phases: methanol/water.

The colour of the crystalline molecular complexes was characterized by means of objective measurements using a reflectance colorimeter, Datacolour type 3890, geometry of measurement dif./8 and calculation of coordinates of colour space CIELAB.

3.3 Preparation procedures

3.3.1 Isolation of CI Disperse Yellow 211 from commercial sample

The commercial dyestuff (20 g) was extracted with acetone (700 ml) in a Soxhlet extractor. After distilling off acetone the crude product (5·7 g) was purified by recrystallizations from ethanol. The yield of pure dye was 3·3 g, m.p. 224–225°C (Koffler). TLC: SiO_2–cyclohexane/ethyl acetate (1 : 1 by vol.), $R_F = 0{\cdot}64$; elemental analyses are given in Table 1, IR and ^1H–NMR data in Table 2, X-ray diffraction data in Table 3 and spectrophotometry data in Tables 5 and 6.

3.3.2 Synthesis of CI Disperse Yellow 211

3.3.2.1 Preparation of 1-ethyl-3-cyano-4-methyl-6-hydroxy-1,2-dihydro-2-pyridone. The coupling component was prepared by the Guareschi reaction according to the modified procedure described in Ref. 13. The 200 ml pressure vessel of a Linitest apparatus (Original Hanau) was charged with 33·9 g (0·3 mol) ethyl cyanoacetate and 90 ml (0·78 mol) *c.* 30% aqueous ethylamine. The vessel was hermetically closed and left to stand at room temperature with intermittent shaking for 1 h. It was then cooled by immersing in an ice bath and, after opening, a further 39 g (0·3 mol) ethyl cyanoacetate was added. The vessel was again sealed and stirred in the Linitest apparatus at 90°C for 6 h. The vessel was cooled in ice water, opened, and the reaction mixture diluted with distilled water up to a final volume of 900 ml; 190 ml (1·2 mol) 20% hydrochloric acid was then added with stirring. The white solid which separated was filtered, washed with 600 ml 0·01 M HCl, and dried at 60°C until constant weight. The yield was 57·6 g product (87%), m.p. 251–252°C (Koffler); ^1H-NMR and IR data are given in Table 2.

3.3.2.2 Preparation of CI Disperse Yellow 211. The dye was prepared by established methods,[14] viz. 34·52 g (0·2 mol) 4-chloro-2-nitroaniline (Hoechst) was diazotized in 110 ml 36% HCl, 60 ml water and 140 g ice by adding 84 ml 2·5 N $NaNO_2$ (0·105 mol) at 10–18°C during 40 min.

The solution obtained was filtered (with 6 g charcoal) and its volume was adjusted to 1400 ml by the addition of distilled water; excess nitrous acid was removed by adding 6 ml 10% amidosulphuric acid. The diazonium solution was treated with 500 ml of an ice cold solution of 39·4 g (0·21 mol) 1-ethyl-3-cyano-4-methyl-6-hydroxy-1,2-dihydro-2-pyridone and 20g (0·5 mol) sodium hydroxide added over 30 min. The suspension was maintained at 10–18°C by adding ice. The mixture was then stirred for 1 h, heated to 95°C and stirred at this temperature for 1 h. It was left to cool to 50°C and the precipitated dye was filtered, washed with 1600 ml distilled water, and dried at 80°C to constant weight. The yield was 69·4 g (96%). The crude dye was purified by repeated (3×) recrystallizations from ethanol, which gave a product identical with that isolated from the commercial sample of CI Disperse Yellow 211.

3.3.3 Preparation of molecular complexes of CI Diperse Yellow 211 with aromatic compounds

3.3.3.1 The molecular complexes obtained at conditions of bath dyeing with disperse dyes. A commercial sample of 4 g CI Disperse Yellow 211 was dispersed in 300 ml distilled water. An emulsion of 4 g carrier Spolapren X^R (a mixture of naphthalene, biphenyl, xylene and emulsifier of the type calcium dodecylbenzenesulphonate and oxyethylated lauryl alcohol) in 200 ml water was added to the dyestuff. The mixture was stirred for 30 min with simultaneous heating to 95°C and then stirred at the same temperature for 10 min. It was then cooled to 60°C and the separated portion of the crystalline molecular complex was filtered, washed with water, and dried in air at room temperature until constant weight. The yield was 1·85 g of crystalline molecular complex containing the dye, naphthalene and biphenyl. A uniform molecular complex of the dye with naphthalene was obtained in an analogous way using, instead of Spolapren X^R, a mixture of 2 g naphthalene, 2 g xylene and 1 g emulsifier formed from equal amounts of 2-hydroxyethylammonium dodecylbenzene-sulphonate and oxyethylated lauryl alcohol (1 mol lauryl alcohol + 20 mol EO). The yield was 1·28 g orange crystalline molecular complex. A similar procedure using the same amount of biphenyl instead of naphthalene gave 1·32 g of an orange-red crystalline molecular complex.

3.3.3.2 Preparation of molecular complexes by crystallization from acetone. A mixture of 5 g dye and 1·7 g naphthalene was dissolved by refluxing in the minimum quantity of acetone (*c.* 140 ml) and the resulting solution was slowly cooled to room temperature. The red-orange crystals of the CT complex were filtered and dried in air at room temperature to constant weight; the yield was 4·42 g. In an analogous way, molecular complexes with other aromatic compounds were prepared.

3.3.4 Qualitative test for determining range of compounds forming molecular complexes

About 30 mg dye and the same amount of crystalline aromatic components were charged into a test tube, and about 10 drops of acetone were added along the wall of the test tube. Coloured crystals of the molecular complex were formed in the contact area between the two solid substances during several seconds to several minutes.

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