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Spectroscopic studies of Direct Blue 1 in solution and on cellulose surfaces: effects of environment on a bis-azo dye

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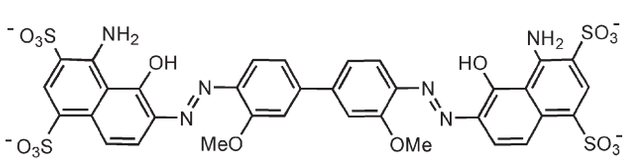
***Received* (in Durham, UK) 22nd January 2004, *Accepted* 6th April 2004**
***First published as an Advance Article on the web* 9th June 2004**

The bis-azo dye Direct Blue 1 (Chicago Sky Blue 6B) has been studied in solution and on cellophane and cotton surfaces using NMR, resonance Raman, infrared, and UV–visible spectroscopy. The data indicate that Direct Blue 1 is present as the hydrazone tautomer in all of these media, with distinct changes in the spectra with medium showing that the dye is affected by interactions with its environment. In DMF and DMSO solutions, the dye is present as a monomer that is internally hydrogen-bonded. It is also monomeric at low concentrations in aqueous solution, with subtle changes in the Raman spectra from those in DMF and DMSO being attributed to external hydrogen bonding with water. Direct Blue 1 is also present as a hydrazone monomer at low concentrations on cellophane and cotton: the Raman spectra indicate that there is hydrogen bonding with cellulose, and the UV–visible spectra indicate that it experiences an apolar environment which is attributed to its adsorption onto cellulose surfaces.

Introduction

Azo dyes are the dominant class of commercial dyes, with the larger molecules comprising two or more azo groups generally belonging to the class of direct dyes.[1,2] This classification arises historically from the ability to dye textile fibres directly, without the need for fixatives, due to the total strength of the intermolecular interactions of such dyes with cellulose.[3] Direct azo dyes continue to find new applications arising from developments in high-technology areas, such as ink-jet printing,[4] through to new biochemical assays and potential pharmaceutical treatments arising from their binding to proteins.[5–7] Although these dyes are well known, important questions remain about their intermolecular interactions with molecular surfaces, including those provided by proteins, cellulose fibres and other microporous media, because these interactions can have a significant effect on dye stability.

A typical example of a direct dye is the bis-azo dye, Direct Blue 1 (Chicago Sky Blue 6B), and here we report spectroscopic studies of it adsorbed onto cellophane and cotton, which are two microporous forms of cellulose. Cotton is used from the plant with limited processing whereas cellophane is created from the dissolution of wood fibres and is highly processed, and hence the two materials have different supramolecular structures although derived from the same polysaccharide building block.[8] Our earlier studies have shown that cellophane can act as a good mimic of cotton for studies of Direct Blue 1, with the practical advantage that its optical transparency enables UV–visible spectra to be taken *via* transmission rather than reflectance.[9]



Direct Blue 1

DOI: 10.1039/b401055h

The studies we report of cellophane and cotton samples are supplemented by those of Direct Blue 1 in DMF and DMSO, which are aprotic solvents of moderate polarity, and in water, which is a protic solvent of high polarity. The dye in solution can be studied more readily as a function of concentration, pH and solvent deuteration, and with a wider range of spectroscopic techniques than the cellulose samples. Together, these data from solution samples provide valuable spectroscopic fingerprints which greatly facilitate the interpretation of the spectra from cellophane and cotton samples.

We report NMR, resonance Raman, IR and UV–visible spectroscopic studies of Direct Blue 1. NMR spectra from solution samples provide information on tautomer form, hydrogen bonding, and deuterium exchange. Resonance Raman (RR) and IR spectra from solution samples, assigned with the aid of the NMR data, provide fingerprints for tautomer form and hydrogen bonding; by comparison, the RR spectra from cellophane and cotton samples then report on tautomer form and hydrogen bonding in cellulose. UV–visible spectra provide complementary information on aggregation and solvent polarity, with those from solutions aiding the interpretation of those from the dye in cellulose. This combination of spectroscopic data provides direct evidence of the effects of environment on Direct Blue 1, and on its interactions with cellulose.

Experimental

Materials

Direct Blue 1 (Aldrich) was purified first by repeated recrystallisation from water : ethanol (60 : 40), then by repeated salting-out with sodium acetate, and finally by washing with ethanol.[10] The UV–visible absorption spectrum of the purified dye in dilute aqueous solution gave a visible band at $\lambda_{max} = 621$ nm with an absorption coefficient of $\varepsilon_{max} = 8 \times 10^4$ dm^3 mol^{-1} cm^{-1}. The solvents DMF, DMSO (Aldrich, spectrophotometric grade), D_2O, DMF-d_7, and DMSO-d_6

(Goss Scientific), and freshly deionised water were used without further purification. Small (*ca.* 1 × 2 cm) pieces of cellophane film (Sigma; measured thickness 45 μm) were dyed by soaking in a dye solution (typically 3×10^{-3} mol dm^{-3} for 30 min) at room temperature, and were then dried between lint-free tissues with a weight placed on top to prevent wrinkling of the film. The concentrations of the dye in cellophane were estimated by assuming that the maximum absorption coefficient of the visible band was the same in cellophane as that in aqueous solution. Dyed cotton samples were prepared by adding 15 × 15 cm pieces of desized, mercerised, non-fluorescent cotton to 1 dm^3 of water at 40 °C; solid dye was added, and the dye-bath heated to 95 °C; NaCl was then added at 10 g dm^{-3}, and the dye-bath was stirred at 95 °C for a further 1 h; the samples were then rinsed and air-dried. The dye loading on cotton was determined to be *ca.* 5×10^{-4} mol kg^{-1} by comparison with calibrated standards. The dyed fabric was cut into smaller pieces for spectroscopic study.

Methods

1D and 2D ^1H and ^{13}C NMR spectra were recorded using a Bruker AMX-500 spectrometer. A $^1J(^{15}N, ^1H)$ coupling constant was measured using a Bruker DRX-400 spectrometer. Spectra were calibrated against residual protiated solvent resonances, and were processed using XWIN-NMR (Bruker).

Resonance Raman (RR) scattering was excited using the 530.9 nm line from a Kr^+ laser (Coherent Innova-90). Scattered light was collected at 90° to the incident beam, dispersed using a Spex 1403 double monochromator, and detected using a liquid-nitrogen cooled CCD detector (Wright Instruments, Ltd.) at *ca.* 5 cm^{-1} resolution and an accuracy of *ca.* ±2 cm^{-1}. Solution samples were held in a spinning quartz cell. Cellophane and cotton samples were held in a spinner and excited with the spinning surface at *ca.* 60° to the collection optics. The laser power was typically 30 mW for solution samples, and <5 mW for cellophane and cotton samples to avoid any significant photofading of the solid samples. Total collection times were typically 15 min, comprising several readouts. The sample integrity following Raman data collection was confirmed by UV–visible spectroscopy for solution samples and visually, using a microscope, for cellophane and cotton samples; RR spectra recorded at the beginning and end of the total collection times were found to be similar in each case, providing additional confirmation of sample integrity. RR spectra were calibrated against solvent band positions and were baseline corrected using Grams/386 software (Galactic Industries Corp.). IR spectra were recorded using a Nicolet Impact 410 FTIR spectrometer, with a demountable cell (Harrick DLC-M25) with calcium fluoride windows and a measured pathlength of 56 μm.

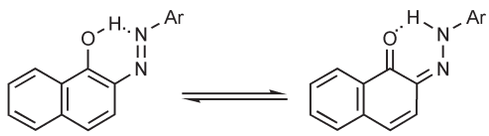
UV–visible absorption spectra were recorded using a Hitachi U-3000 spectrometer with either 10 cm, 1 cm, or 1 mm fixed pathlength quartz cells, or with the demountable cell with quartz windows and a measured pathlength of 16 μm for solution samples; or by transmittance directly through cellophane samples. UV–visible diffuse reflectance spectra were recorded using a Perkin-Elmer Lambda-15 spectrophotometer fitted with an integrating sphere, and were converted to Kubelka-Munk units. A UV–visible spectrophotometric titration of Direct Blue 1 in aqueous solution (1×10^{-5} mol dm^{-3}, 293 K, ionic strength 0.05) was recorded over a range of pH 7–13.

Results and discussion

NMR spectroscopy

^1H, ^{13}C, and COSY NMR spectra of Direct Blue 1 in DMF-d_7, DMSO-d_6, and D_2O were recorded at high concentration (3×10^{-2} mol dm^{-3}) because of the relatively low sensitivity of the technique. Short-range and long-range HMQC and NOESY spectra were recorded for the DMSO-d_6 and D_2O samples, and aided the full assignment of the ^1H and ^{13}C spectra in these solvents; partial ^{13}C assignments of the DMF-d_7 sample were made by comparison. Table 1 lists the ^1H and ^{13}C NMR chemical shifts, ^1H splittings, and assignments according to the atom numbering given in Fig. 1: there was no evidence of inequivalence between the two halves of the Direct Blue 1 molecule in any of the three solvents. In a separate experiment, the $^1J(^{15}N,^1H\alpha)$ coupling constant was found to be 95.9 Hz in DMSO-d_6.

Azo dyes in which the azo group is conjugated with a hydroxyl group can exhibit azo-hydrazone tautomerism, and NMR spectroscopy is established as an effective technique to study tautomer composition.[11–13]



Dyes that occur as the azo tautomer show a ^{13}C resonance at *ca.* 156 ppm from the carbon attached to the hydroxyl group, whereas those that occur as the hydrazone tautomer show a resonance at *ca.* 180 ppm for the same carbon atom within a carbonyl group. Dyes that occur as both tautomers show a single resonance between these limits, due to rapid tautomerisation, with the position determined by the relative concentrations of the two tautomers.[11] The ^{13}C NMR spectra from DMF, DMSO and D_2O samples of Direct Blue 1 all show a resonance at *ca.* 180 ppm assigned to C9 (Table 1) and, thus, Direct Blue 1 is present as the hydrazone tautomer (*ca.* 100%) in all three solvents, as illustrated in Fig. 1. The $^1J(^{15}N,^1H\alpha)$ coupling constant of 95.9 Hz for the DMSO sample of Direct Blue 1 is comparable to those of 91–96 Hz for model dyes that exist as the hydrazone tautomer,[12,13] providing further support for this interpretation. The positions of the other respective ^{13}C resonances are also similar between the three solvents, although there are some small differences (Table 1).

Table 1 ^1H and ^{13}C NMR chemical shifts (ppm) and assignments, and ^1H splittings, of Direct Blue 1 in DMF-d_7, DMSO-d_6, and D_2O[a]

	DMF-d_7		DMSO-d_6		D_2O	
Atom no.	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1	6.95 d		7.02 d	127.9	7.06 d	131.5
2	8.26 d		7.99 d	121.9	7.5 d	117.2
3				135.7		137.8
4				121.8		124.5
5	8.71 s		8.37 s	132.8	8.01 s	131.5
6				127.1		120.5
7		151.4		150.3		150.9
8				113.7		115.6
9		182.4		181.3		179.4
10				133.6		132.9
11				130.4		128.8
12		149.1		148.6		148.5
13	7.6 s	110.4	7.51 s	110.1	6.84 s, br	107.8
14				137.4		136.2
15	7.56 d		7.52 d	120.4	6.98 d, br	118.6
16	7.9 d		7.89 d	115.3	7.09 d, br	114.9
17	4.18 s	56.6	4.14 s	56.8	3.99 s	55.9
α	15.81 s		15.77 s			
β_1	7.9 s, br		7.5 s, br			
β_2	9.8 s, br		9.7 s, br			

[a] Numbering given in Fig. 1.

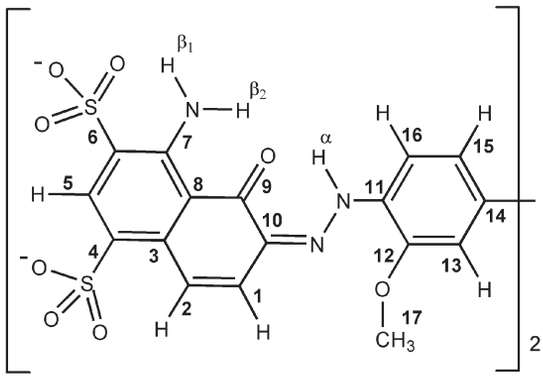


Fig. 1 Atom numbering for the assignment of ^{1}H and ^{13}C NMR spectra of Direct Blue 1.

The positions of the ^{1}H resonances assigned to the hydrazone proton and the amino protons report on the hydrogen bonding of Direct Blue 1 in DMF and DMSO. The downfield positions of the resonances from the hydrazone proton Hα[14] and one of the amino protons Hβ_2 are attributed to internal hydrogen bonding in which the carbonyl oxygen is hydrogen bonded to both of these protons (Fig. 1). The observation of two distinct resonances from the two amino protons indicates that this internal hydrogen bonding is locked on the NMR timescale, and the moderately downfield position of the resonance assigned to the other amino proton Hβ_1 suggests that it may be hydrogen bonded to a sulfonate oxygen (Fig. 1). The ^{1}H NMR spectrum of Direct Blue 1 in D_2O shows no resonances from Hα, Hβ_1, or Hβ_2, indicating that the hydrazone proton and the two amino protons exchange for deuterons.

The ^{1}H resonances of Direct Blue 1 are, in general, more sensitive to solvent than the ^{13}C resonances, and they report on changes within the dye between the three solvents. Fig. 2 shows the 6.75–8.80 ppm region of the ^{1}H NMR spectra of Direct Blue 1 in DMF-d_7, DMSO-d_6, and D_2O. The changes in most peak positions on going from DMF to DMSO are relatively small (<0.1 ppm), with the largest changes occurring within the naphthyl group as upfield shifts of the resonances from H2 (0.27 ppm) and H5 (0.34 ppm), and from the amino proton assigned as Hβ_1 (0.5 ppm). These shifts arise from changes in the shielding environment around the protons, and the larger changes observed for H2, H5, and Hβ_1 may be attributed to more specific interactions involving the solvent and the sulfonate groups adjacent to these protons (Fig. 1). All of the aryl ^{1}H resonances show relatively large upfield shifts on going from DMSO to D_2O: all of the shifts except one (H1) are larger than those between DMF and DMSO, with the resonances of the protons on the central biphenyl group, *i.e.* H13, H15, and H16, showing the largest upfield shifts (0.5–0.8 ppm) on going to D_2O. However, an interpretation of these shifts is not straightforward because UV–visible studies show that Direct Blue 1 aggregates in water but not in DMF or DMSO (*vide infra*); from detailed aggregation studies,[15] we estimate that the D_2O sample studied here by NMR comprised >95% dimer.

In summary, the NMR data show that Direct Blue 1 occurs as the hydrazone tautomer in DMF, DMSO and D_2O, and that there is internal hydrogen bonding at the amino and hydrazone groups in DMF and DMSO; these protons exchange in D_2O.

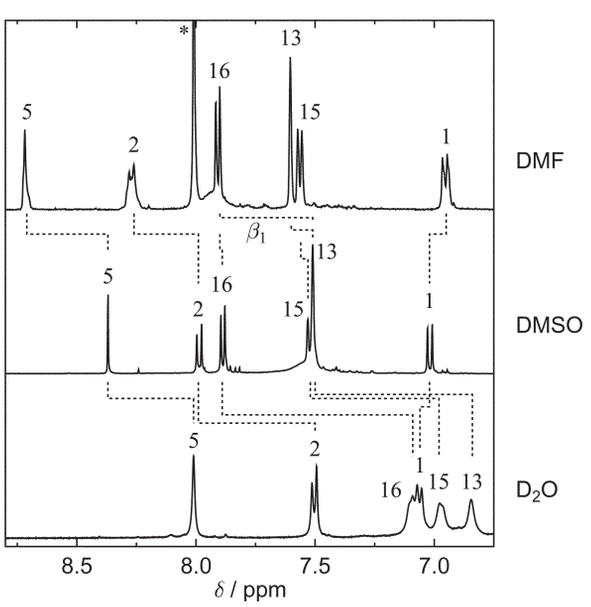


Fig. 2 ^{1}H NMR spectra of Direct Blue 1 in DMF-d_7, DMSO-d_6, and D_2O (3×10^{-2} mol dm^{-3}). * indicates residual protiated DMF.

Resonance Raman spectroscopy

Fig. 3 shows the RR spectra of Direct Blue 1 in DMF, DMSO, and aqueous solutions, and on cellophane and cotton. Here, we shall use the vibrational spectra only for fingerprint identification because assignments are not well established for azo dyes,[16–18] and our own DFT calculations show that most vibrational modes in large dyes such as Direct Blue 1 involve the motion of many atoms and cannot generally be described in terms of localised oscillations.[15] The RR spectra of all of the Direct Blue 1 samples are notably similar, with a number of strong bands, such as those at *ca.* 1620, 1599, 1565, and 1328 cm^{-1}, occurring for all of the samples. This consistent RR fingerprint indicates that there are no major changes in the structure of Direct Blue 1 between the different media and, from the interpretation of the NMR data above, all of these spectra may be assigned to the hydrazone tautomer. Importantly, the RR spectra indicate clearly that the dye

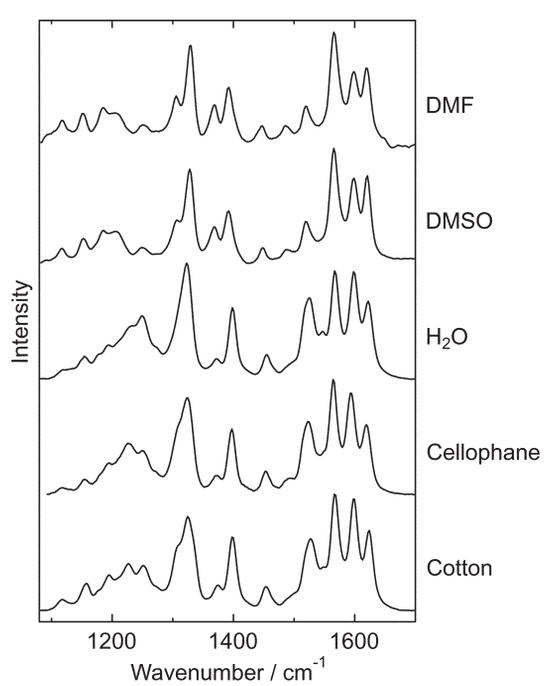


Fig. 3 RR spectra of Direct Blue 1 in DMF, DMSO, and H_2O solutions (all 2×10^{-4} mol dm^{-3}), in cellophane (*ca.* 2×10^{-3} mol dm^{-3}), and on cotton (5×10^{-4} mol kg^{-1}), recorded with 530.9 nm excitation. Solvent bands have been subtracted from DMF and DMSO spectra.

remains as the hydrazone tautomer on adsorption onto cellophane or cotton.

Subtle changes in the RR spectra of Direct Blue 1 do occur between the different media, and they report on how the different environments affect the internal structure and bonding of the dye. The data may be separated into two sets that are distinguished most readily by their two different profiles at *ca.* 1170–1380 and 1470–1555 cm^{-1}. First, the DMF and DMSO samples give almost identical spectra, with very similar band positions and relative intensities: from the NMR results, these spectra can be assigned to a hydrazone tautomer in an aprotic environment, with internal hydrogen bonding. Second, the aqueous, cellophane, and cotton samples give a different set of similar spectra: the spectra can be assigned to a hydrazone tautomer in which the internal hydrogen bonding is modified by competitive intermolecular interactions with the surrounding protic medium. The similarity of the RR spectra within this second set indicates that the dye structure is essentially retained on going from water to cellulose, while small variations in band positions and relative intensities at *ca.* 1170–1320 cm^{-1} indicate that the intermolecular interactions with water are slightly different from those with cellulose. The close similarity of the RR spectra from cellophane and cotton samples indicates that there is similar hydrogen bonding with cellulose in these two materials, although some of the bands are sharper from the cotton sample.

The sensitivity of the RR spectrum to changes in structure and bonding was explored by recording spectra of Direct Blue 1 in aqueous solution at different pH values, and in D_2O, as shown in Fig. 4. The RR spectrum of Direct Blue 1 at pH 13.0 is quite distinct from that obtained at lower pH, and is consistent with the known deprotonation of azo dyes in alkaline conditions to give a "common anion" which, in general, can form from either the azo or hydrazone tautomers (Fig. 5).[19] The total loss of the characteristic four-band pattern in the 1500–1650 cm^{-1} region at high pH (Fig. 4) indicates that the change from the hydrazone form is total rather than partial: thus, the spectrum of Direct Blue 1 at pH 13 may be assigned to a "common anion" in which both halves of the molecule are deprotonated, as shown in Fig. 5. By contrast, a change from neutral to acidic pH results in essentially no change in the RR spectrum of Direct Blue 1, indicating that the same hydrazone species is present at pH 1.3 and 7.1.

The overall RR fingerprint of Direct Blue 1 is retained on changing from H_2O to D_2O (Fig. 4), consistent with the presence of the hydrazone tautomer in both solvents. However, there are significant changes which, from the NMR results, can be attributed specifically to band-shifts arising from exchange of the hydrazone (Hα) and amino (Hβ_1 and Hβ_2) protons for deuterons. The largest changes between the RR spectra of the H_2O and D_2O samples occur in the regions at *ca.* 1160–1280 and 1470–1555 cm^{-1}, indicating that bands in these regions report on the structure and bonding at the hydrazone and amino groups. Large changes between the RR spectra of the H_2O and DMF or DMSO samples also occurred in these regions (Fig. 3), and were assigned above to changes in hydrogen bonding at the hydrazone and amino groups: the changes observed on deuteration support this assignment.

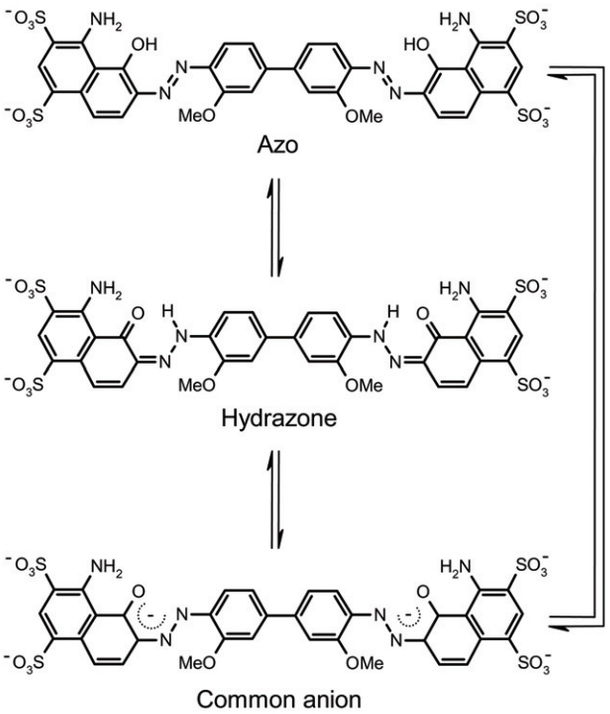


Fig. 5 Possible equilibria involving the azo, hydrazone, and common anion forms of Direct Blue 1; only the symmetric forms are shown, in which the structures of both halves of the molecule are equivalent.

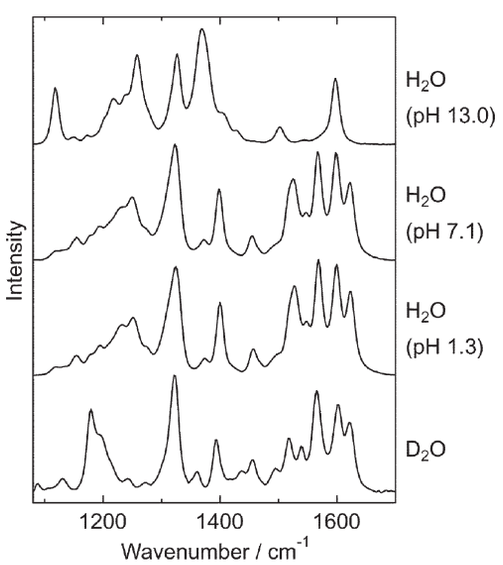


Fig. 4 RR spectra of Direct Blue 1 in water (2×10^{-4} mol dm^{-3}) at pH 1.3, 7.1, and 13.0, and in D_2O. All spectra recorded with 530.9 nm excitation.

Infrared spectroscopy

In common with many dyes, Direct Blue 1 has high absorption coefficients in the UV–visible but lower absorption coefficients in the IR which, in combination with strong solvent absorption, makes IR studies of dye solutions difficult. IR spectra of Direct Blue 1 at 10^{-2} mol dm^{-3} in DMF, DMSO, and H_2O solution are shown in Fig. 6, with regions of high solvent absorption omitted. IR spectra of the dye in cellophane or cotton could not be obtained, even at the highest concentrations used on these surfaces, due to dominant bands of the cellulose.

Although the IR data are limited, they are consistent with the interpretation that Direct Blue 1 is present as a hydrazone tautomer, with DMF and DMSO solvents interacting differently with the dye from H_2O. The IR spectra of DMF and DMSO samples cannot be compared across the whole region, but both show similar strong bands at *ca.* 1205 cm^{-1} which are absent from the spectrum of the aqueous sample. The IR spectra of DMSO and aqueous samples can be compared across a wider region: they show some common features, such as the pair of bands at *ca.* 1484 and 1498 cm^{-1}, but there are also clear differences. A number of IR bands shift on changing the solvent from H_2O to D_2O and, as for the RR band-shifts,

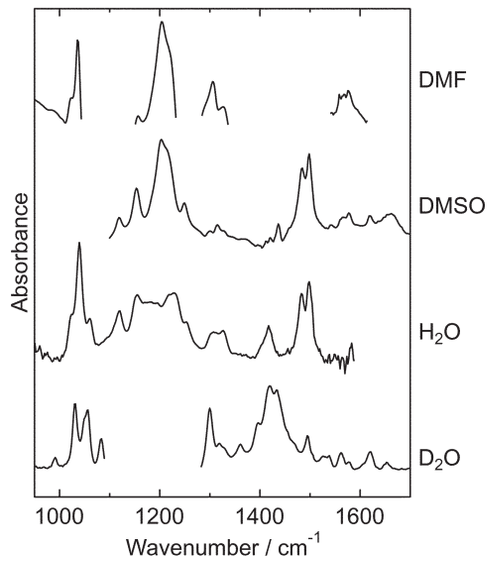


Fig. 6 IR spectra of Direct Blue 1 in DMF, DMSO, H_2O, and D_2O solutions (all 1×10^{-2} mol dm^{-3}). Regions of high solvent absorption are omitted.

they are attributable to exchange of the hydrazone and amino protons for deuterons.

UV–visible spectroscopy

UV–visible absorption spectra of Direct Blue 1 in DMF, DMSO, and aqueous solutions, and on cellophane and cotton are shown in Fig. 7, with band positions listed in Table 2. The spectrum in each medium shows a strong visible band, which gives the intense blue colour of the dye, and a weaker UV band at *ca.* 320 nm. The profile of the visible band is sensitive to environment: in DMF and DMSO solutions, the main peak is at *ca.* 645 nm with a shoulder at *ca.* 610 nm; in water, it is shifted to 621 nm; and in cellophane and cotton, the peak occurs at 656 nm with a shoulder at *ca.* 618 nm.

The UV–visible spectrum of Direct Blue 1 in DMF or DMSO showed no changes with concentration over the range 1×10^{-5} to 3×10^{-2} mol dm^{-3}, indicating that the dye is present as a monomer at all concentrations studied for these solvents. By contrast, the UV–visible spectrum of Direct Blue 1 in water showed a clear dependence on concentration (Fig. 8), indicating that aggregation occurs[20] and that the monomer is observed only at the lowest concentration studied here (10^{-6} mol dm^{-3}): its spectrum comprises a main visible peak at 621 nm with a partially resolved shoulder at *ca.* 590 nm, and a main UV peak at 319 nm.

The UV–visible spectrum of Direct Blue 1 in water varied with pH and with deuteration (Fig. 8 and Table 2). Lowering

Table 2 UV–visible absorption band positions of Direct Blue 1 in different media (from Fig. 7) and at different pH values and in D_2O (from Fig. 8)

Medium	λ_{max}/nm				
DMF	641	608 sh	467	411 sh	323
DMSO	645	611 sh	469	418 sh	324
H_2O[a]		621		403	319
Cellophane	656	618		418	330
Cotton	656	617		420	331
H_2O (pH 1.4)		617		404	325
H_2O (pH 13.0)		587		360	319
D_2O		612		408	324

[a] At pH 7.1.

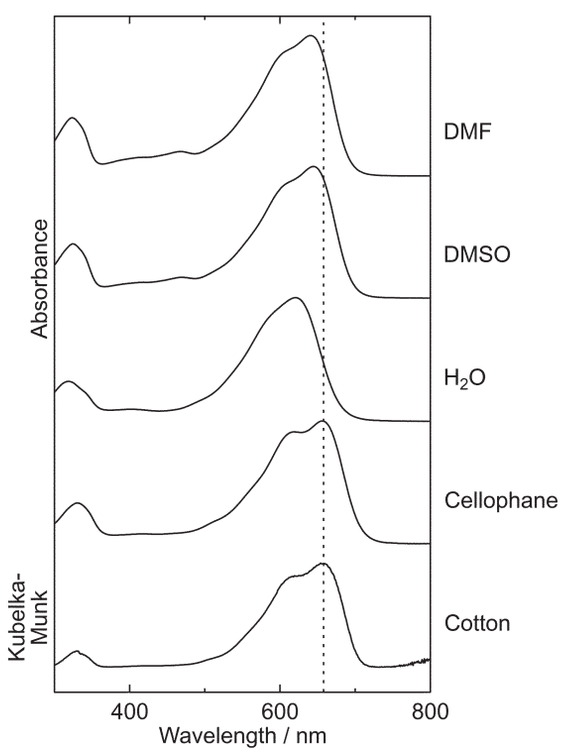


Fig. 7 UV–visible spectra of Direct Blue 1 in DMF, DMSO (both 1×10^{-4} mol dm^{-3}), and H_2O solutions (1×10^{-6} mol dm^{-3}), in cellophane (*ca.* 2×10^{-3} mol dm^{-3}), and on cotton (5×10^{-4} mol kg^{-1}). The dashed line at 656 nm indicates the absorption maximum of the cotton sample.

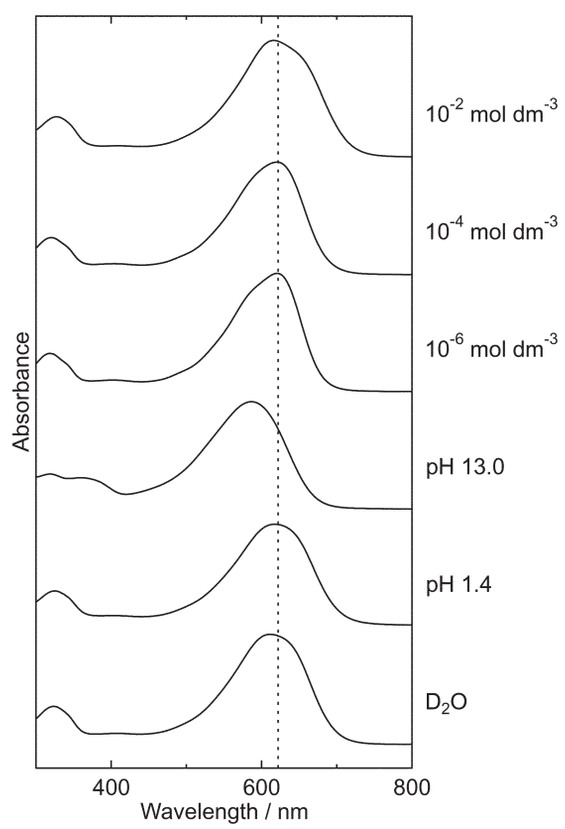


Fig. 8 UV–visible spectrum of Direct Blue 1 in water and its variation with concentration at pH 7.1 (10^{-2}, 10^{-4}, 10^{-6} mol dm^{-3}), with pH at 10^{-5} mol dm^{-3} (pH 1.4, 13.0), and with solvent deuteration (D_2O, 10^{-5} mol dm^{-3}). The dashed line at 621 nm indicates the absorption maximum of the sample at 10^{-6} mol dm^{-3} and pH 7.1.

the pH from 7.1 to 1.4 has a small effect whereas increasing the pH to 13.0 gives much larger changes, shifting the main band to 587 nm and altering the profile in the UV region: these changes are consistent with the formation of a "common anion" at high pH (Fig. 5). A spectrophotometric titration gave a single acidity constant of $pK_a = 10.5$. The observation of a single pK_a value indicates that the two acidic groups are too remote to influence one another, and supports the RR evidence that both halves of the molecule are deprotonated at pH 13. Importantly, the high pK_a value indicates that the hydrazone protons are internally hydrogen bonded in water.[21] On changing the solvent from H_2O to D_2O, the main band blue-shifts by *ca.* 10 nm.

Together with the NMR, RR, and IR results, the UV–visible data indicate that Direct Blue 1 in DMF and DMSO solutions is present as a hydrazone monomer with internal hydrogen bonding at the hydrazone and amino protons. In aqueous solution, the data indicate that it is present as a hydrazone, that it is a monomer only at low concentrations, that the hydrazone proton is internally hydrogen bonded, and that the hydrogen bonding is subtly different from the internal network present in DMF and DMSO due to competitive external hydrogen-bonding interactions with water.

The UV–visible spectrum of Direct Blue 1 in cellophane and cotton showed a dependence on concentration which was similar to that in water but in which significant aggregation occurred only at higher concentrations than those studied here; we estimate that the spectra in Fig. 7 arise from a sample comprising mainly ($>90\%$) monomer.[15] The main visible band of Direct Blue 1 in cellophane and cotton is red-shifted by *ca.* 35 nm (*ca.* 900 cm^{-1}) from that in water, and the vibronic structure is more resolved; the UV band is also red-shifted by *ca.* 11 nm (*ca.* 1000 cm^{-1}). These significant differences between the UV–visible spectra of Direct Blue 1 in aqueous and cellulose samples contrast the similarity of the RR spectra from these media described above, and they reflect the complementary nature of the two techniques. The RR spectra report on internal structure and bonding and, in these experiments, on the specific effects that competitive external hydrogen bonding in protic media have on the internal hydrogen bonding within the dye. By contrast, the UV–visible spectra report in part on the polarity of the surrounding medium,[22] which stabilises the electronic states through less specific interactions. The general shift in the UV–visible band positions with medium can be interpreted in terms of increasing polarity from cellophane and cotton ($\varepsilon \approx 5$),[23] to DMF and DMSO ($\varepsilon = 37$ and 47, respectively), to water ($\varepsilon = 80$), with the progressive blue-shift indicating that Direct Blue 1 is more polar in the ground state than in the excited state. Although the major effect can be attributed to medium polarity, it is likely that other effects will also influence the UV–visible spectrum of Direct Blue 1. One set of effects may arise from specific intermolecular interactions with the medium, including hydrogen-bonding, as evidenced by the *ca.* 10 nm blue-shift that results from the change from H_2O to D_2O solvent. Other effects may include structural changes within the dye that arise from surface adsorption. For example, biphenyl gives a characteristic red-shift on going from a twisted conformation in solution to a more planar form in the solid,[24–29] and the central biphenyl group within Direct Blue 1 may similarly be twisted around the central C–C bond in solution[30] and more planar on adsorption onto a surface.

Dye-cellulose interactions

The spectroscopic data provide direct evidence on the environment experienced by Direct Blue 1 in the two cellulose materials.

The polysaccharide chains in cellophane and cotton are arranged into amorphous regions, which are polar due to the presence of considerable amounts of water, and crystallites whose surfaces are strongly apolar.[3,8,23] In general, a guest molecule entering these nanoporous materials may move freely in the liquid-like amorphous regions or it may adsorb onto amorphous or crystallite cellulose surfaces.[31–34] The changes in the UV–visible spectrum on going from water to the cellulose samples indicate that Direct Blue 1 locates to an apolar environment, from which it may be deduced that it binds to cellulose; the changes in the spectra may also indicate that the dye adopts a more planar conformation on the cellulose surfaces.

In general, the polysaccharide chains comprising cellulose may interact with a guest molecule in several ways,[35] including specific dipole–dipole and hydrogen bonding interactions as well as non-specific induction and dispersion interactions; hydrophobic interactions may also be important. For direct dyes, it is recognised that their stabilisation on cellulose surfaces generally arises from the total effect of multiple intermolecular interactions.[1,2] The RR spectra from cellophane and cotton samples of Direct Blue 1 indicate that external hydrogen bonding interactions do occur between the dye and cellulose and, thus, that they contribute to its stabilisation on the surface. Direct Blue 1 is a tetrasulfonate, which confers water solubility, but the central biphenyl group is relatively nonpolar: the UV–visible spectra indicate that Direct Blue 1 locates to an apolar region of cellulose, suggesting that hydrophobic interactions may also contribute.

Conclusions

A combination of NMR, vibrational, and electronic spectroscopy has been used to deduce the molecular interactions of Direct Blue 1 in different solvents and in cellophane and cotton. NMR spectroscopy has reported effectively on azo-hydrazone tautomerisation in solutions at high concentration, on intramolecular hydrogen-bonding, and on proton exchange in aqueous media. The high sensitivity of resonance Raman and UV–visible techniques has enabled the dye to be studied down to low concentrations, and their applicability to surfaces has enabled the dye to be studied readily in cellophane and cotton environments. The RR fingerprint spectra have reported on tautomer composition, and on internal and external hydrogen-bonding interactions in aprotic and protic media, whereas the UV–visible spectra have reported on aggregation, and on the polarity of the surrounding environment.

The results indicate that Direct Blue 1 exists as a monomer hydrazone in DMF and DMSO solutions, in a conformation that is locked by an internal hydrogen-bonding network. It is also present as a hydrazone in aqueous solution, with the internal hydrogen bonding affected by external hydrogen bonding to the solvent. In cellophane and cotton, Direct Blue 1 exists as a hydrazone that undergoes hydrogen bonding to cellulose, and it experiences an apolar environment that is attributed to its adsorption onto cellulose surfaces. This information on dye–surface interactions is an essential requirement for understanding their effect on dye stability; our studies of Direct Blue 1 reactivity on cellulose surfaces will be reported elsewhere.

The changes experienced by Direct Blue 1 with environment are likely to be relevant to other azo dyes, and they may also be relevant to other guest molecules within cellulose or other media. This study demonstrates the value of a strategy that uses several media and several complementary techniques to report on different aspects of molecular structure for guest molecules within complex porous materials.

Acknowledgements

We thank Dr S B Duckett and Ms H Fish for helpful discussions and measurement of NMR spectra. We acknowledge the support of Unilever Research.

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