Conformational analysis by magic-angle spinning NMR spectroscopy for a series of polymorphs of a disperse azobenzene dyestuff

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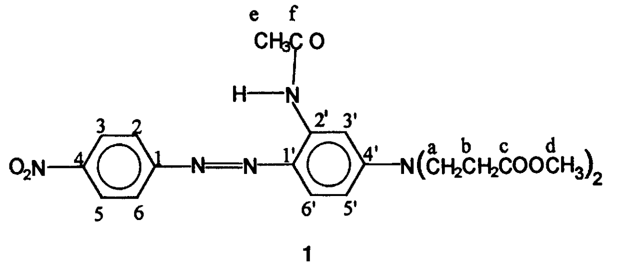
Polycrystalline powder samples of an azobenzene disperse dyestuff have been investigated using solid-state and solution-state ^{13}C and ^{15}N NMR spectroscopy in an attempt to understand the effect of polymorphism. Assignment of the ^{13}C spectra indicates that it is possible to form an intramolecular hydrogen bond resulting in two conformations co-existing in the crystal structure of two of the polymorphs, as well as in solution, and differing by internal rotation of a side-chain acetamido group. This is clearly evident in the solid-state spectra at ambient temperature and in solution at sufficiently reduced temperatures. Each polymorph contains varying amounts of each conformer as a result of different crystal interactions, and conformer interchange can be shown to occur even in the solid state. This remarkable finding is accounted for by the open nature of the crystal structures, resulting from the steric effects of substituents, as attested by packing coefficients and molecular modelling. The conformational variations are confirmed by ^{15}N spectra, and isotopic labelling by ^{15}N allows tensor analysis to be applied which shows that the azo nitrogen's principal shielding components are significantly influenced by the formation of the hydrogen bond in one of the conformations.

Introduction

Monoazo compounds have become the single most important class of dye, particularly as disperse dyes for the dyeing of polyester fibres. Subtle changes in substituents at various positions are known to significantly influence the colour and fastness properties.[1] Intramolecular hydrogen bonding can influence spectral parameters.[2] Properties relating to the dyeing process such as solubility and saturation value in the fibre are related to the free energy of the dye molecule in the crystal state.[3] Hence, the solid-state structure is becoming an increasingly important area for investigation.[4–9] Most of such studies utilise single-crystal XRD or molecular modelling. Classically the crystal state is thought to be composed of an array of molecules held together by strong intermolecular interactions creating a static lattice. Solid-state NMR has shown in the past that this representation is not perfectly valid for all cases. Molecular motion can occur in crystalline materials, just as in solution, of which intramolecular conformational exchange and molecular rotations are common examples.[10]

High-resolution NMR spectra of azo disperse dyestuffs have formed the subject of a number of investigations, with a comprehensive study having been reported by Federov and co-workers.[11] In solution, however, the structural information pertaining to crystal packing is lost and problems such as polymorphism cannot be tackled. Crystal polymorphism is a ubiquitous feature in chemistry, particularly in industrial applications.[12] In the dyeing process it is important that the lowest free-energy (*i.e.* the most stable) polymorph is used, such that recrystallisation to a more stable polymorph at the elevated temperatures used does not occur. Very little attention has been paid to high-resolution solid-state NMR techniques as applied to disperse dyes until recently, although the first example for an azo dye was reported by Chippendale *et al.*[13] in 1981. Substituted phenylazo–naphthols have received significant attention in both solution and solid-state NMR investigations, and many of the spectral features can be transferred to the present investigation.[14] One of the few exponents of solid-state NMR spectroscopy in the analysis of colorants, Antonin Lycka, has recently published a review article on the subject.[15] One of the main reasons why solid-state NMR spectroscopy has not received adequate attention in this field is the complexity of the spectra, with the consequent difficulty of their interpretation. Many common solution-state spectral assignment techniques are not feasible for solid-state ^{13}C analysis.

In this work, ^{13}C and ^{15}N cross-polarisation magic-angle spinning (CPMAS) NMR techniques were applied to an azo disperse dyestuff 2′-acetamido-4′-[*N*,*N*-bis(2-methoxycarbonylethyl)amino]-4-nitroazobenzene, **1**, for three polymorphs A, B and C. The single-crystal structure of polymorph A has been obtained[16] and it shows that molecular packing is dominated by π–π stacking interactions between adjacent molecules. The molecular stacks themselves form a herring-bone arrangement. The structure also indicated that the molecule was present in the non-hydrogen bonded conformer, but the *R*-factor for this X-ray diffraction experiment was rather large, 20%, indicating a high degree of long-range disorder. The melting points of the polymorphs vary from about 110 to 130 °C as measured by differential scanning calorimetry (DSC). Industrial application of this dye has shown that polymorph C is the most stable of the known forms.



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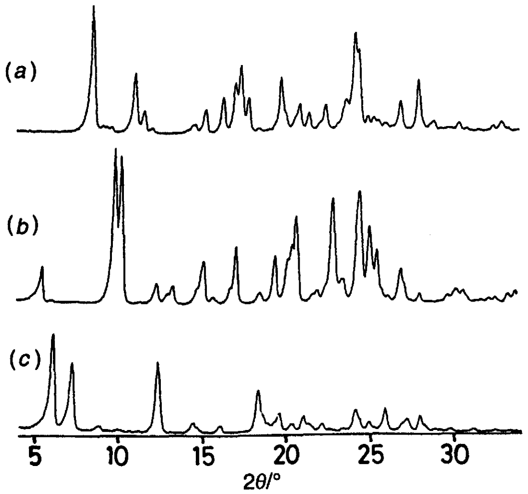


Fig. 1 X-Ray powder diffraction patterns for (*a*) polymorph A, (*b*) polymorph B and (*c*) polymorph C

Experimental

All the samples were supplied by Zeneca Specialties, with the polymorphic form verified by powder X-ray diffraction, see Fig. 1, and sample purity by solution-state ^{1}H NMR spectroscopy.

The high-resolution ^{13}C CPMAS NMR spectra were recorded at both 50.33 MHz and 75.43 MHz on Chemagnetics CMX200 and Varian VXR300 spectrometers, respectively. All spectra obtained utilised multinuclear, broad-band tunable, double-resonance, double-bearing probes. Dry air was used to spin the 7 mm o.d. Zirconia pencil rotors to typical rates of ~ 5 kHz. At higher spin rates the cross-polarisation efficiency for quaternary carbons was severely reduced due to the Hartmann–Hahn matching profile breaking up into sidebands. During variable temperature operation nitrogen gas was used for the heater gas, while ambient temperature air was used for the bearing and drive. A single-contact spin-lock sequence with spin-temperature alternation, high-power proton decoupling and flip-back was used. Around 300 mg of polycrystalline sample was packed into the rotor. Typical acquisition conditions were: spectral width, 20 kHz; ^{1}H 90° pulse duration, 4 μs; recycle delay, 10–30 s; number of transients, 1000–5000; contact time, 5 ms. In all cases ^{13}C chemical shifts were referenced by replacement against the high-frequency line of adamantane at 38.4 ppm relative to TMS. The Hartmann–Hahn matching condition was also set using adamantane, using relatively slow MAS rates. The dipolar dephasing sequence with a refocusing π pulse[17] was applied using a 40 μs dephasing window for the selective removal of signals from relatively rigid protonated carbons, *i.e.* CH and CH_2 signals, to aid the assignment procedure.

The ^{15}N CPMAS spectra were recorded at 20.2 MHz using the Chemagnetics spectrometer and at 30.4 MHz using the Varian system, with the proton 90° pulse duration being 7.5 μs, corresponding to a field strength of ~ 33 kHz, whilst a high-power proton decoupling field corresponding to 63 kHz was utilised. Spectral conditions used were: spectral width, 45 kHz; contact time, 10 ms; recycle delay, 30 s. The Hartmann–Hahn matching conditions, referencing and angle-setting were carried out using 20% ^{15}N doubly-enriched NH_4NO_3, the NO_3 signal (high-frequency) being externally referenced to −5.1 ppm relative to that for CH_3NO_2. Spinning speeds ranged from 1–6 kHz.

Table 1 Solution-state assignments for ^{13}C spectra of **1** in solution, given in ppm relative to the signal for TMS

	δ(solution)			
	CD_2Cl_2			
		−80 °C		
Carbon	20 °C	**2**[a]	**3**	[$^2H_6$]DMSO 20 °C
1	156.64	154.78	155.71	156.15
2, 6	122.29	121.01	122.00	122.80
3, 5	125.10	124.50		124.83
4	147.48	145.85	146.09	146.68
1′	131.61	129.58	130.48	132.12
2′	138.20	134.58	140.63	139.68
3′	101.35	99.57		101.98
4′	152.27	150.87	151.62	151.79
5′	107.76	106.55	107.04	108.12
6′	129.35 (broad)	138.32	116.93	121.81
a	47.42	46.30		46.43
b	32.44	31.07		31.55
c	172.11	171.86		171.64
d	52.12	52.02		51.58
e	25.76	25.80	25.40	24.83
f	169.65	170.25	168.58	169.32

[a] The more intense peaks are assigned to this conformer.

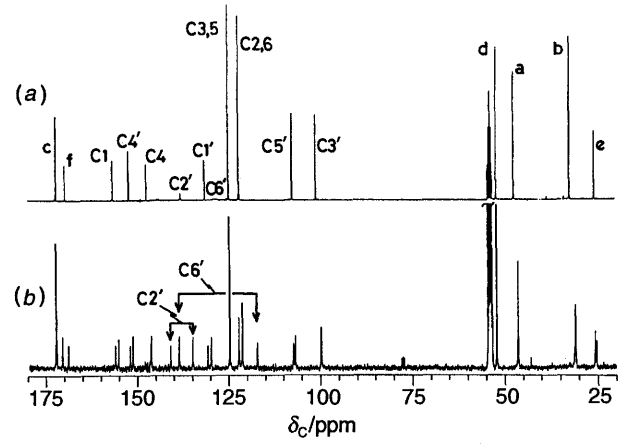
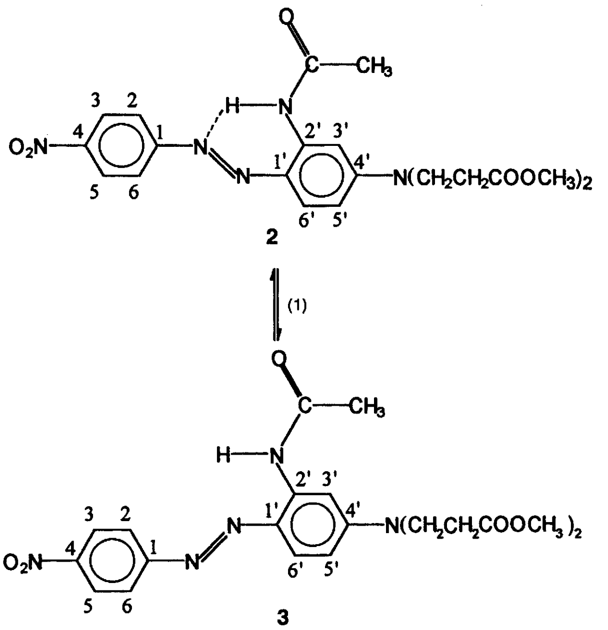


Fig. 2 Solution-state ^{13}C spectra recorded at 100.58 MHz in CD_2Cl_2 (*a*) at room temperature, with the assignments shown, and (*b*) at −80 °C. The presence of two conformers in solution is realised at −80 °C.

The solution-state ^{13}C spectra were obtained at 100.6 MHz on a Varian VXR 400 spectrometer using [$^2H_6$]DMSO, CD_2Cl_2 and $CDCl_3$ as solvents, the recycle delay being 2 s, with a 1 s acquisition time. The ^{15}N solution-state spectra were recorded on a Bruker AMX400 spectrometer at 40.56 MHz. The solvents used were $CDCl_3$ and [$^2H_6$]DMSO, with $Cr(acac)_3$ added as a relaxation agent.

Results and discussion

The assignments of the solution-state spectra, Fig. 2, were obtained by comparison with those for related structures,[11,18] as shown in Table 1. Substituent chemical shift calculations are of some use in substituted azobenzenes, but are limited because of the modification of the electron density distribution in one ring by substituents on the other ring. These effects are maximum at the *ipso* and *para* positions relative to the azo linkage. The assignment is based on the assumption that the azo linkage is present in the *trans* orientation, which indicates that each pair of *ortho* and *meta* resonances are inequivalent. However, if rapid (on the NMR timescale) phenyl ring rotation occurs around the Cl–N and/or Cl′–N bond(s) then motional averaging will simplify the spectrum significantly. This is indeed the case, C2 and C6 giving one resonance at 122.3 ppm, while C3 and C5 signals similarly average to 124.5 ppm. Although the equivalence is lost in the other ring due to the presence of the acetamido group it is possible to verify that rapid ring rotation also occurs by analysis of the actual chemical shift values. The presence of an acidic proton on the *ortho* substituted acetamido group provides the opportunity for the formation of a six-membered ring *via* an N • • • H-N hydrogen bond.[2] Sterically the non-hydrogen bonded conformer (**3**) is favoured, with the *ortho* substituent pointing towards the neighbouring nitrogen lone pair. To overcome the steric hindrance the N • • • H-N hydrogen bond must be sufficiently strong to compensate for this, and it becomes possible to have a dynamic equilibrium between the two conformers [equilibrium (1)]. Gas-phase molecular mechanics calculations[19] show that the energy barriers for phenyl ring rotations within this compound are ~7 kJ mol^{-1} and that conformer **2** is favoured by 2.5 kJ mol^{-1}. Such relatively small values indicate that dynamic interconversion between the two conformers should proceed quite readily. The sole existence of the hydrogen-bonded conformer (**2**) would result in a C6′ resonance at ~132 ppm, but if conformer **3** is present then the C6′ resonance would be moved to low frequency by ~15 ppm to 117 ppm.[18] The origins of the observed splittings will be discussed later. Similarly, it is predicted that C2′ should give rise to signals at *ca.* 135 and 141 ppm for conformers **2** and **3**, respectively. The C6′ resonance frequencies show a rather large solvent dependency, which can be explained by solvation of the acetamido group in the DMSO solution, forcing the equilibrium to that of conformer **3**. CD_2Cl_2 and $CDCl_3$ are relatively inert solvents, so the structures obtained for such solutions should correlate more closely to that of the isolated molecule. The resonances of C2′ and C6′ are broadened significantly at room temperature (~20 °C) for solutions in CD_2Cl_2 and $CDCl_3$ due to molecular motion, for a 400 MHz spectrometer, presumably because this is slightly above the coalescence point. Upon reduction of the temperature more peaks broaden and only those which are expected to have nearly identical shifts in both conformations are left as sharp lines at the reduced temperatures. Such lines all arise from the long aliphatic chain at C4′, together with those from the C3, C5 pair. Fig. 2(*b*) gives the spectrum obtained at −80 °C in CD_2Cl_2, which clearly shows the presence of two conformers, with approximately equal populations, in the solution-state. The assignments are given in Table 1. It is not possible in all cases to identify which signals belong to **2** and which to **3** by chemical shift values alone; the small differences in intensity were used to produce unambiguous assignments. From the assignments it is possible to verify that the phenyl flips are still fast for the unsubstituted ring, but are frozen for the other at the reduced temperature. As mentioned before, the C6′ splitting was found to be 21.4 ppm which is larger than expected.



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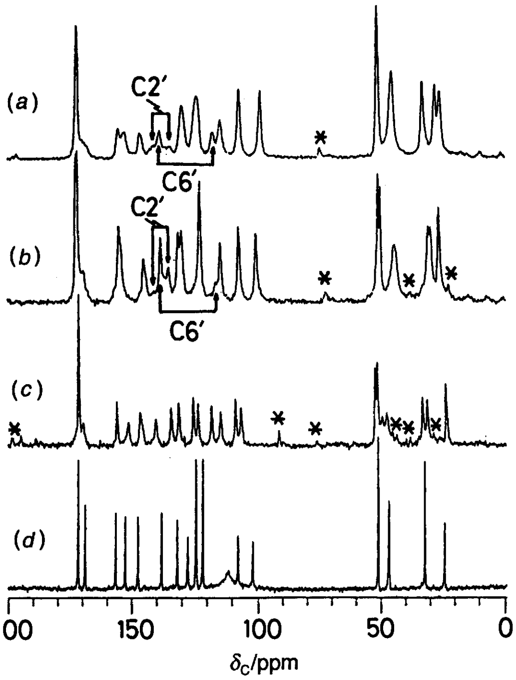

Fig. 3 Solid-state 50.33 MHz ^{13}C CPMAS spectra of (*a*) polymorph A, (*b*) polymorph B and (*c*) polymorph C. Spinning sidebands are indicated by asterisks. Fig. 3(*d*) shows the spectrum of the melt of polymorph B obtained at 150 °C, with the broad peak centred at 112 ppm being attributed to a background signal.

At first inspection it would appear that, although some spectral features are similar, there are some significant differences between the solid-state and room temperature solution-state spectra. Also, when comparing the three polymorphs the spectra again vary quite dramatically (Fig. 3). It is clear from the complexity of the spectra and from comparison with the low temperature solution-state spectrum that two of the polymorphs contain conformationally different molecules in the crystals, with non-integral intensity ratios, thus acounting for difficulties in obtaining detailed structures from single-crystal X-ray diffraction. This is a most unusual situation even for a single crystalline form of a compound, let alone for two distinct polymorphs. Moreover, conformational interchange occurs in the solid state on the NMR timescale at elevated temperatures; a detailed experimental study is in progress. Even at ambient probe temperature not only are the resonance frequencies different between the polymorphs, but also the linewidths. Thus polymorph A has much broader lines within the aromatic region, possibly accounted for by exchange broadening. To verify this, variable temperature ^{13}C analysis was carried out on both forms A and B, with form B being heated above the melting point (130 °C) and studied at 150 °C. As expected, the temperature-dependent line-broadening for the solid state shows that the phenyl ring rotations (both rings) are significantly slower than in solution at ambient temperature. The complexity of the ^{13}C spectra, however, prevents bandshape analysis to determine the actual rates with any degree of confidence.

With the assumption that the polymorphs contain differing proportions of each of the conformers **2** and **3**, accounting for exchange broadening, it is then possible to assign the spectra of all three polymorphs (Table 2) using the same scheme as for the solution spectra, but only after consideration of the spectra

Table 2 Solid-state ^{13}C assignment of the polymorphs, expressed in ppm relative to the signal for TMS

	δ(solid)		
Carbon	Polymorph A	Polymorph B	Polymorph C
1	155.7	155.3	156.0
2	130.5	130.3	131.4
6	114.9	115.0	114.9
3, 5	124.2	123.0	123.8
			125.7
4	147.0	145.3	146.7
1′	130.0	131.7	134.4
2′	141.4	141.5	140.5
	135.2	135.9	
3′	99.0	100.8	106.7
4′	153.7	155.3	151.4
5′	107.5	107.6	109.0
6′	138.8	138.7	118.4
	117.9	116.7	
a	46.0	45.2	49.9
			48.2
b	33.8	31.3	33.7
	28.6	30.5	31.8
c	172.6	172.6	171.4
		172.1	
d	51.9	51.6	52.6
		50.7	51.9
e	26.6	27.0	24.3
f	170.0	169.7	169.8

obtained at both field strengths. This is in part due to the enhanced resolution and reduced exchange broadening at the higher static field. Chippendale *et al.*[13] observed splittings of 13–18 ppm between C2 and C6 and 0–3 ppm between C3 and C5 in related dyestuffs. These splittings are mainly due to the shielding effects of the nitrogen lone pairs. In this case we observe a splitting of 15 ppm for the C2, C6 pair, but none for the C3, C5 pair for forms A and B. Form C, however, shows a 2 ppm splitting for the C3 and C5 resonances. The chemical shifts for form C suggest that the orientation of the acetamido group may be locked out of the plane of the molecule. Out-of-plane rotation would affect the resonances corresponding to C1′ and C3′ primarily, and it is noteworthy that the shift for the latter, for form C, is more than 5 ppm higher than for forms A and B or for the solution-state. Two peaks for each of the C2′ (141.4 and 135.2 ppm) and C6′ (138.8 and 117.8 ppm) carbons for polymorphs A and B are observed, the splittings being similar to those for the solution state. This indicates that two conformations are present for each form in the solid state. Other conformational splittings observed in the solution state are not resolved for the solids. Molecular rotation is actually present for the acetamido-substituted ring, though, as shown by the variable temperature solid-state spectra. Typically, compounds with large *ortho* substituents are present in locked conformations, and intuitively one would expect large amplitude molecular rotations to be hindered by the presence of adjacent molecules in the crystal structure. However, the packing coefficient (defined as the van der Waals volume of all the molecules in the unit cell divided by the unit cell volume)[20] is about 0.6, a relatively low value for small organic molecules. Thus, in the present case, we believe intermolecular packing, strongly influenced by the bulky amino side-chains *trans* to the azo group, creates effective voids, allowing the conformational variation and the exchange.

The relative populations of each conformer can be obtained by measuring the intensities of the pairs of signals from C2′ and C6′. Polymorph A was found to contain ~50% of each conformation at room temperature, in contrast to the X-ray result,[16] while polymorph B was predominantly hydrogen bonded in nature and polymorph C appeared to be wholly non-hydrogen bonded. Only rough estimates of relative intensities, considering only the peaks at the isotropic shifts, are feasible. In principle, the sideband intensities should also be involved in the analysis because of the large anisotropy of aromatic carbon signals, although the relative intensities are unlikely to be affected by the cross-polarisation dynamics in this instance.

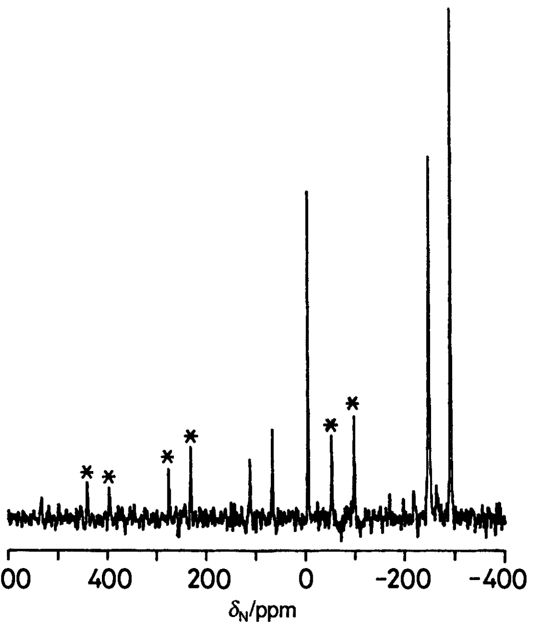

Fig. 4 Natural-abundance ^{15}N CPMAS spectrum of polymorph C at 30.4 MHz. 36 000 transients were acquired using a contact time of 10 ms and a recycle delay of 2 s. Spinning sidebands are indicated by asterisks. Note the referencing is relative to the NO_3 line in NH_4NO_3, in contrast to the data in Table 3.

To analyse the position of equilibrium more accurately, it was thought that natural abundance ^{15}N spectroscopy would be a useful probe. Although ^{15}N has a low natural abundance it possesses a large chemical shift range resulting in good dispersion of signals, which simplifies spectral assignment significantly. However, as a result of the long recycle delays required, only spectra with rather poor signal-to-noise ratios were obtained. The only solid-state spectrum of good quality was that obtained for polymorph C (Fig. 4), due to the short proton spin-lattice relaxation time (T_1) and absence of any exchange broadening. Here the spinning sideband manifold for both azo nitrogens can be clearly identified. A full assignment of both the solid-state (polymorphs B and C) and solution-state ^{15}N NMR spectra is given in Table 3. In the solid-state spectra of polymorph B the azo signals are not evident, probably a result of the large shielding anisotropy of azo nitrogens spreading the intensity over many sidebands. Wasylishen *et al.*[21] determined shielding anisotropies of *ca.* −500 ppm for simple *trans*-azobenzenes (the definition of shielding anisotropy being given in the heading for Table 4). To solve this problem, isotopic labelling of one of the required azo nitrogens with ^{15}N was carried out. Labelling of the β-nitrogen (adjacent to the ring with the *ortho* substituent) resulted in a single broad ^{15}N peak being observed at room temperature, for a solution of $CDCl_3$, at a chemical shift of $\delta_N = 112.9$ (again indicating conformational averaging). In the solid state a ^{15}N NMR spectrum with two isotropic shifts ($\delta_N = 120.4$ and 88.8) was observed for polymorph A, and the corresponding spinning sidebands (Fig. 5) cover about 1300 ppm. The two signals arise from the presence of the two conformations. However at the moment no distinction can be made as to which signal arises from which conformer. Analysis of the sideband intensities using an iterative computer program[22] based on the Maricq and Waugh[23] method gives the principal shielding tensor values (Table 4). These relate to the shielding in the molecular

Table 3 ^{15}N Chemical shift assignment for polymorphs B and C (natural abundance samples). Chemical shifts are in ppm relative to the signal for nitromethane

	δ(solid)		δ(solution)	
Nitrogen	Polymorph B	Polymorph C	[$^2H_6$]DMSO	$CDCl_3$
N_α		59.3	62.3	
N_β		104.7	111.3	
NO_2	−14.3	−12.4	−11.9	−13.2
$NHCOCH_3$	−249.5	−254.8	−254.7	−253.9
$N(CH_2\cdots)_2$	−291	−298.0	−294.4	−294.7

Table 4 ^{15}N Shielding tensor information for the isotopically labelled dye (polymorph A). The tensor components were obtained by taking the average for two spinning speeds (1.0 and 4.2 kHz), resulting in an estimated error of ± 5 ppm. The ordering of the shielding components is according to $|\sigma_{33} - \sigma_{iso}| \geqslant |\sigma_{11} - \sigma_{iso}| \geqslant |\sigma_{22} - \sigma_{iso}|$. ζ is the shielding anisotropy defined as $\sigma_{33} - \sigma_{iso}$. η is the shielding asymmetry, defined as $(\sigma_{22} - \sigma_{11})/\zeta$

	δ_N(iso) = 89	δ_N(iso) = 120
$\sigma_{33} - \sigma_{ref}$	−576	−609
$\sigma_{22} - \sigma_{ref}$	−11	−25
$\sigma_{11} - \sigma_{ref}$	317	271
η	0.67 ±0.02	0.61 ±0.02
ζ	−487	−488

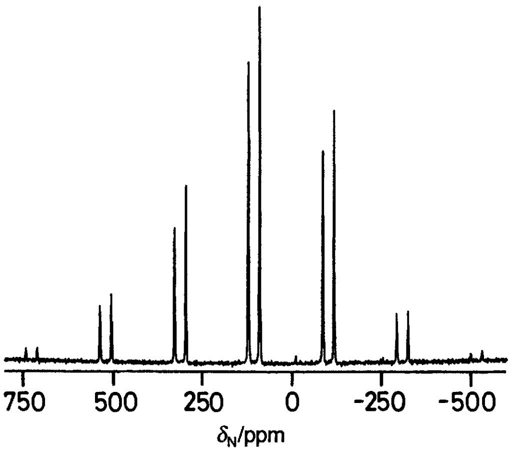

Fig. 5 ^{15}N CPMAS spectrum of an isotopically enriched sample of polymorph A. The spinning speed used was 4.2 kHz. 7600 transients were acquired using a contact time of 7 ms and a recycle delay of 20 s. This spectrum was further analysed using the spinning sideband fitting program developed by Ascenso *et al.*[22]

frame. Without carrying out further experiments it is impossible to orient the shielding tensors relative to the molecular frame in our case. Wasylishen and co-workers have analysed the shielding tensor for a series of diazines.[24] Essentially there should be very little difference between his results and those for the present investigation. Hence, it is possible to position σ_{33} perpendicular to the N–N bond and σ_{22} as roughly co-linear with the nitrogen lone pair. From the results it can be seen that the hydrogen bond formation primarily affects the asymmetry parameter, with very little change being observed for the anisotropy. However, it appears less obvious how the individual tensor components are affected.

One interesting feature of the two peaks is that there is no indication of any residual dipolar coupling (RDC) to the directly-bonded ^{14}N at room temperature. Generally, when the observed spin-$\frac{1}{2}$ nucleus is adjacent to a quadrupolar spin equal to one then an asymmetric doublet of intensity 2:1 is obtained.[25] Quite often in ^{13}C–^{14}N spin pairs this only manifests itself as a broadening of the line. Self-decoupling[26] is the phenomenon where this broadening (or doublet formation) is not observed. Self-decoupling can arise as a result of a very short spin–lattice relaxation time of the ^{14}N induced by fast molecular motion such as proton tunnelling or one of an orientational nature. However in the present case the absence of splitting is probably due to the fact that the RDC is proportional to the direct dipolar coupling constant *D* which has an r^{-3} dependence on the internuclear separation and also is proportional to the product of the relevant gyromagnetic ratios. Hence, for a ^{14}N–^{15}N pair very little, if any, RDC will be observed except for lines which are extremely narrow. The linewidths of the nitrogen signals in the present investigation are around 60 Hz, which would swamp any RDC effects. If quadrupolar relaxation of the ^{14}N nucleus was the origin of self-decoupling then reduction of the temperature would cause splitting or broadening of the lines. On reducing the temperature to −120 °C the linewidths were observed to have increased by a factor of two, with the only observable asymmetry being visible on the first sideband at high frequency. Analysis of the ^{13}C spectra of form A at similarly low temperatures showed that there appears to be very little second-order coupling to the carbons attached to the azo nitrogens, but the amide nitrogen produced significant broadening of the C2′ signal, resulting in a splitting of 100 ± 10 Hz at 4.7 Tesla.

Conclusions

All three polymorphs of the disperse dyestuff investigated have been characterised in terms of local conformations. Single-crystal X-ray analysis does not show the conformational exchange by phenyl ring rotations that is present at ambient temperature. Surprisingly, motion of the ring with the acetamido group attached also takes place even though steric hindrance *via* crystal-packing interactions would intuitively prevent the motion. Polymorphs A and B seem to adopt near-planar structures while in polymorph C the acetamido group is probably out of the molecular plane. It would require further experimental work and computer modelling of the solid structure to verify that polymorph C is thermodynamically the most stable.

It would prove to be useful to compare the solution-state and solid-state activation parameters *via* dynamic NMR techniques to show the relative barriers to phenyl ring rotations and the contribution of crystal packing interactions to those barriers.

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