High-resolution ^{13}C Nuclear Magnetic Resonance Spectra of Some Solid *trans*-Azobenzene and Dyestuff Species

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^{13}C N.m.r. spectra of *trans*-azobenzene and a series of its substituted derivatives have been obtained in the solid phase. Additional effects are observed, not present in the solution spectra of the species, and these are shown to be due to the locking of the molecules into particular conformations in the solid. The first ^{13}C n.m.r. spectrum of a reasonably complex solid dyestuff is shown and an assignment of this has been attempted, based upon the effects observed in the solid reference compounds.

METHODS for obtaining high-resolution n.m.r. spectra of materials in solution have been developed for many years. However, application of these conventional methods to solid materials is generally uninformative since in solids non-averaged nuclear dipole–dipole interactions cause excessive broadening, which usually results in only a single very broad line, tens of kHz in width, being observed. However, fairly recently, methods have been developed[1,2] which largely overcome these difficulties with solid materials, so that n.m.r. spectra of dilute spin species (usually ^{13}C) can now be obtained which approach the resolution of solution spectra.

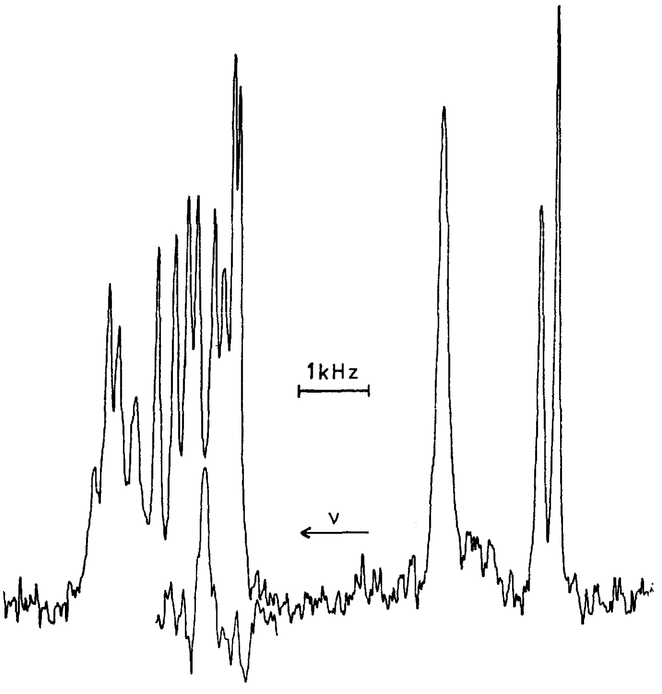
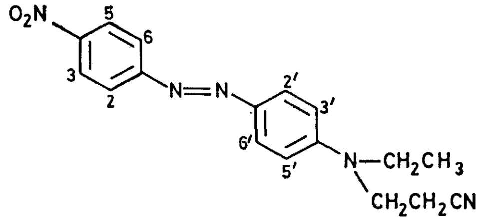


FIGURE 1 22.63-MHz ^{13}C N.m.r. spectrum of the solid dyestuff, Disperse Orange 25 (I). The following spectrometer conditions were used: contact time 5 ms; recycle time 750 ms; number of f.i.d.s acquired 80 000. The peak due to the cyanide carbon, obtained from a non-quaternary suppression experiment using f.i.d.s, is shown beneath the main spectrum; the experiment used a dipolar evolution period of 40 μs

The experiments use a combination of three principal techniques, these being: (a) high-power proton decoupling to eliminate $^{1}H,^{13}C$ dipolar broadening[3] (and to remove effects of $^{1}H,^{13}C$ scalar interactions), (b) magic angle rotation (m.a.r.) to eliminate shielding anisotropy effects[4] and broadening arising from other second-rank tensor interactions such as $^{13}C,^{13}C$ and $^{13}C,X$ dipolar coupling, and (c) magnetisation transfer from ^{1}H to ^{13}C (' cross-polarisation ') by double irradiation with radio-frequency fields fulfilling the Hartmann–Hahn condition,[5] to improve the sensitivity of observation of the ^{13}C signals.[3] This combination of techniques has been reviewed elsewhere.[6,7] While much of the earlier work in this area has been performed on polymeric solids,[1] particularly species that could be machined into rotors, more recently hollow rotors capable of spinning powdered samples routinely have been developed.[8-10] Nevertheless, relatively few high-resolution n.m.r. spectra of typical monomeric organic solids have yet been published, particularly of species of moderate complexity. To explore this area, we have examined some typical dyestuff molecules, and in Figure 1 report what we believe to be the first ^{13}C n.m.r. spectrum of a material of this type, Disperse Orange 25 (I), run as a microcrystalline solid.

The ^{13}C n.m.r. spectra of (I) obtained as a solid and in solution show clear differences, particularly in the aromatic carbon region. To explain these differences and to help understand the effects likely to be observed in general for the *trans*-azobenzene unit, which is one of the main entities in dyestuff chemistry, a series of solid disubstituted *trans*-azobenzene reference compounds has been examined.



(I)

EXPERIMENTAL

The solid-state spectra of the azobenzenes were obtained using a purpose-built double-resonance spectrometer capable of performing dipolar decoupling, cross-polarisation, and m.a.r. Details of the spectrometer system, which operates at 22.63 MHz for ^{13}C resonance, have been given elsewhere.[11] The m.a.r. device, which uses cylindrical glass rotors 5 mm in diameter, has also been described elsewhere.[9] The samples consisted of powders or microcrystalline solids, and were packed into the rotors with light tamping so as to use *ca.* 100 mg of material. Spinning rates were generally in the region 2—2.5 kHz, and spinning sidebands were rarely seen. A Nicolet 1180 computer (with a Nicolet 293A pulse programmer) was used to control the spectrometer, and software has been written to perform a number of pulse sequences, in addition to the standard cross-polarization routine. Thus the flip-back [12] and non-quaternary suppression [11,13] sequences have been used as appropriate. Proton T_1 and $T_{1\rho}$ values were measured using a low-resolution pulse spectrometer prior to obtaining the ^{13}C spectra, so that the operational parameters can be optimised. Values of $T_1(^1H)$ ranged from *ca.* 500 ms [for (I)] to >30 s [for (III)], and those of $T_{1\rho}(^1H)$ were generally $\geqslant 30$ ms. Carbon spectra were obtained under conditions of external proton field/frequency locking. Chemical shifts were measured using the tube replacement method.

TABLE 1

^{13}C Chemical shifts (p.p.m. from tetramethylsilane) for 4,4′-*trans*-azobenzene species $RC_6H_4N{=}NC_6H_4R$ in the solid phase, together with solution chemical shift values in parentheses

Substituent R	MHz	C-1	C-2	C-3	C-4	C-5	C-6	Mean of C-2 and -6	C=O	CH_3
H	22.63	152.5	130.7	130.7	130.7	130.7	117.9	124.3		
		(152.7)	(122.9)	(129.1)	(130.9)	(129.1)	(122.9)	(122.9)		
OH	22.63	148.0	132.6	115.1	162.7	115.1	115.1	123.9		
		(145.2)	(123.9)	(115.7)	(159.8)	(115.7)	(123.9)	(123.9)		
COCl	22.63	154.3	130.2 *	130.2 *	132.4 *	130.2 *	114.4	122.3	173.3	
		(154.3)	(122.5)	(130.3)	(133.3)	(130.3)	(122.5)	(122.5)	(166.3)	
CO_2H	50.30	153.5	130.0 *	132.6 *	132.6 *	130.0 *	114.0	122.0	172.9	
		(154.2)	(122.1)	(130.1)	(133.3)	(130.1)	(122.1)	(122.1)	(166.1)	
$NHCOCH_3$	50.30	147.0	132.3	119.5 *	140.8 [a]	118.2 *	115.6	124.0	169.5 [a]	23.6
		(147.7)	(122.9)	(119.2)	(141.6)	(119.2)	(122.9)	(122.9)	(168.4)	(23.7)
CH_3	50.30	149.8	*b*	131.0 *	139.8	128.9 *	*b*			(19.8)
		(150.1)	(121.9)	(129.4)	(140.7)	(129.4)	(121.9)	(121.9)		(20.4)

* These assignments are interchangeable.

[a] Average of splittings due to incompletely averaged $^{13}C,^{14}N$ dipolar interactions (see the text). [b] Broad unresolved band, 115—130 p.p.m. (see the text).

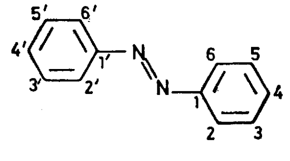
Solid-state ^{13}C spectra were also obtained at 50.30 MHz from the dyestuff (I) and three of the reference compounds. These were recorded on a Bruker CXP 200 spectrometer at Bruker-Physik, Karlsruhe.

All compounds were obtained from the I.C.I. Reference Collection of Fine Chemicals. Their structures and purities were confirmed by their ^1H and/or ^{13}C n.m.r. spectra in solution. The ^{13}C n.m.r. chemical shift values in solution quoted in this paper were obtained at 22.62 MHz on a Bruker WH90 spectrometer, using either [$^2H_6$]DMSO or $CDCl_3$ as solvent.

RESULTS AND DISCUSSION

The aliphatic carbon chemical shifts for (I) are very similar in the solid state (22.63 and 50.30 MHz) and solution spectra. Thus we find the following values: CH_3 12.3 (12.6), CH_2CN 17.2 (16.4), and CH_2N 46.8 and 48.0 p.p.m. (46.0 and 46.7 p.p.m.), where all shifts are referenced to tetramethylsilane and the values in parentheses refer to $CDCl_3$ solution. The shifts quoted for the solid state were obtained at 50.30 MHz. However, the aromatic carbon region is considerably more complicated in the spectrum from the solid, indicating that nuclei which are equivalent for the solution spectrum become non-equivalent for the solid. To gain a better understanding of the reasons for this, *trans*-azobenzene itself and a series of symmetrically *para*-disubstituted derivatives were examined.

The results obtained from azobenzene and the 4,4′-disubstituted derivatives examined as solids are shown in Table 1. For convenience, the chemical shift values obtained from the species in solution are shown in parentheses. The numbering in (II) is used for the *trans*-azobenzene species.



(II)

In solution, rapid rotation about the C–N bonds causes C-2 and -6 to become equivalent and to have the same chemical shift. The same is true for C-3 and -5. From Table 1, it can be seen for azobenzene itself that the chemical shift values for C-1, -3, -4, and -5 are essentially identical in the solid and solution phases. However, no peak is observed in the solid at the position of C-2 and -6 in solution (122.9 p.p.m.). Instead a new peak is seen at 117.9 p.p.m.

The simplest explanation of this observation is to assume that in the solid azobenzene, rotation of the rings cannot occur, and the molecule becomes locked in the planar *trans*-configuration (II). Here C-2 and -6 are no longer equivalent, and if one of these has the 'new' chemical shift of 117.9 p.p.m. the other would be expected to occur at *ca.* 127.9 p.p.m., based upon the average shift of 122.9 p.p.m. observed for the pair in solution.

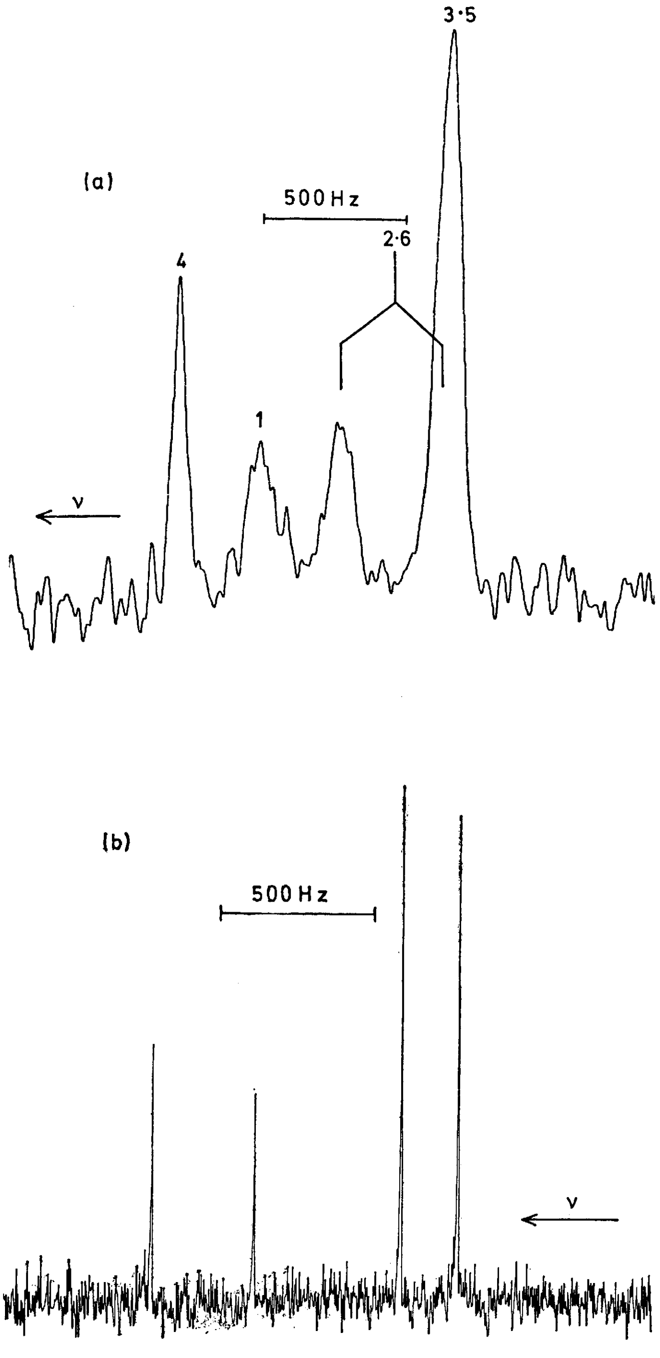


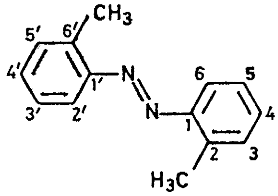
FIGURE 2 ^{13}C N.m.r. spectra of 4,4′-dihydroxyazobenzene (a) in the solid phase using 10 ms contact time, 1.5 s recycle time, and 5 000 f.i.d.s, and (b) as a solution in [$^2H_6$]DMSO

On the basis of structure (II), C-3 and -5 are also non-equivalent, but any difference in chemical shift will be appreciably smaller than for the C-2 and -6 pair. In fact, only one large peak is observed experimentally at 130.7 p.p.m. This is believed to be due to four overlapping signals, *i.e.* from C-3, -4, and -5 and the higher-frequency component of the C-2 and -6 pair.

Table 1 also shows that the chemical shift values for 4,4′-dihydroxy-, -diacetamido-, -dicarboxy-, and -bischlorocarbonyl-azobenzene follow the same trends as those for azobenzene. Thus, the shift values for C-1 and -4 are the same in the solid and solution phases and C-2 and -6 are split giving a pair of signals, the average of which corresponds well with the solution value for this pair.

These points are illustrated in Figure 2 which shows the ^{13}C n.m.r. spectra of 4,4′-dihydroxyazobenzene in the solid and solution phases. In the 50.30 MHz solid state spectrum of the diacetamido-derivative C-3 and -5 are also split.

To test the supposition that, in the solid state, azobenzene and the 4,4′-disubstituted derivatives are locked in conformation (II), and if so, to assign the separate ^{13}C signals seen for C-2 and -6, 2,2′-dimethylazobenzene was examined. For steric reasons, the preferred conformation for this compound is likely to be (III) in both solution and solid phases.[14]



(III)

The ^{13}C chemical shift values for (III) in solution and solid phases are given in Table 2. The shifts are identical within experimental error, fully supporting the view that the conformation is the same in both phases. An assessment of the effect that the azo-link, *in the solid phase*, has upon the aromatic carbon chemical shifts can be made by subtracting the chemical shift values in liquid toluene from the corresponding carbon chemical shifts in solid 2,2′-dimethylazobenzene, to give a set of aromatic substituent shifts Δ_1. These can then be compared with a similar set derived from the difference in shifts observed for corresponding carbons in solid azobenzene and liquid benzene, Δ_2:

TABLE 2

^{13}C Chemical shifts (p.p.m. from tetramethylsilane) for 2,2′-dimethylazobenzene as a solid and in solution in [$^2H_6$]DMSO

	C-1	C-2	C-3	C-4	C-5	C-6	CH_3
Solid	153.0	139.8	131.9	131.9	127.7	117.2	16.5
Solution	150.5	136.9	130.7	130.1	125.7	115.4	16.7

	C-1	C-2	C-3	C-4	C-5	C-6
Δ_1 (p.p.m.)	+23.7	+2.0	+2.6	+3.4	+2.1	−11.3
Δ_2 (p.p.m.)	+25.2	+1.4	+1.4	+1.4	+1.4	−10.0

The similarity of these two sets of parameters confirms the suggestion that the azobenzenes become locked in the *trans*-configuration in the solid phase and also enables the assignments of C-2 and -6 [as shown in (II)] to be made with certainty. Thus, when these become non-equivalent in the solid, C-2 will be to high frequency and C-6 to low frequency of the average solution value. This is shown in Table 1 for all the compounds concerned.

The results given in Table 1 show that the C-3 and -5 resonances are split in at least two spectra recorded at 50.3 MHz. Splittings of 1.3 and 2.1 p.p.m., respectively, are observed for the acetamido and methyl derivatives. As already discussed C-3 and -5 are non-equivalent in structure (II) and a small splitting might be expected. When substituents are introduced in the 4- and 4′-positions their interaction with C-3 and -5 may be different, unless the substituent is a single atom or a group located symmetrically with respect to C-3 and -5. A spectrum of solid acetanilide [15] obtained at 50.30 MHz shows a splitting of *ca.* 1.3 p.p.m. between the peaks from the two carbon atoms *ortho* to the substituent. In 4,4′-dimethylazobenzene, the splitting is probably due to the locked conformation about the azo-bond. In the acetamido-derivative it will arise from the combined effect of this and that due to the substituent.

The spectra of 4,4′-dimethylazobenzene at both 22.63 and 50.30 MHz, show an interesting effect. In this case, the resonance(s) from C-2 and -6 is extremely broad and ill defined relative to the rest of the spectrum. It is tempting to think that this might be due to some dynamic process, possibly limited ring mobility. If this were so it might be possible to freeze out the motion by examining at lower temperatures.

Splitting of the resonance of some carbon atoms when bonded to nitrogen in solid materials has been reported by ourselves [16] and other groups of workers.[17,18] This effect, which can cause an asymmetric doublet to be observed, has been described as resulting from the ^{14}N nuclear quadrupole moment preventing m.a.r. from completely averaging out the carbon–nitrogen dipolar interactions.[19] The theory predicts that any splitting should decrease at higher values of the magnetic field. In the azobenzene derivatives, there is no evidence in any of the spectra for splitting of the C-1 peak by the nitrogen atoms of the azo-group. However, in the 22.63 and 50.30 MHz spectra of 4,4′-diacetamidoazobenzene, both the carbonyl and C-4 resonances were split. There was considerable overlap of peaks in the 22.63 MHz spectrum and both the splittings were estimated to be *ca.* 200 Hz. However at 50.30 MHz the peaks were well resolved and the carbonyl and C-4 resonances were split by 73 and 88 Hz, respectively. In both cases the weaker peak of the doublet is clearly the one at higher frequency.

Three of the compounds examined contained carbonyl groups. Significant high-frequency shifts of 7.0 and 6.8 p.p.m. respectively were observed for the chlorocarbonyl and carboxy-derivatives on going from solution to the solid. However, to within experimental error, the shifts were the same for the acetamido-derivative. In the case of the carboxy-derivative, the difference could be explained in terms of increased intermolecular hydrogen bonding in the solid; for the chlorocarbonyl derivative it is more difficult to understand.

In the light of the results obtained from the simpler azobenzene derivatives, an attempt can be made to interpret the aromatic region of the solid-state spectra of the dyestuff (I). Comparison with the solution-state spectrum makes it clear that the four highest frequency peaks are due to aromatic C–N atoms. It was expected that some of these resonances might be split by incompletely averaged dipolar interactions (see above). However, the fact that the four bands have approximately the same shifts at both 22.63 and 50.30 MHz and in the solution-state spectrum suggests that this is not the case.

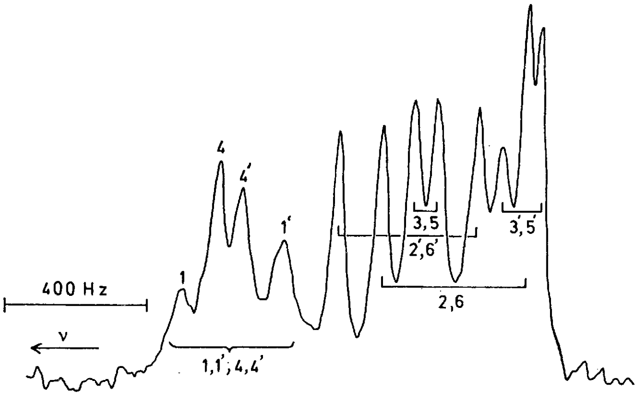


FIGURE 3 Expansion of the aromatic region of the 22.63 MHz ^{13}C n.m.r. spectrum (see Figure 1) of the solid dyestuff, Disperse Orange 25 (I) with proposed peak assignments

The linewidths for the remaining peaks in (I) are markedly smaller than those found in the reference compounds. The reason for this is not clear and is being investigated. However, it has enabled peaks due to all eight aromatic CH carbon nuclei to be resolved both at 22.63 and 50.30 MHz. The cyano-group carbon was identified by a non-quaternary suppression experiment [13] to be at δ_C 120 p.p.m. (see Figure 1). It is of low intensity and is not resolved in Figure 3.

TABLE 3

Chemical shifts for the aromatic carbons of dyestuff (I)

Carbon	Solid shift (22.63 MHz)	Mean shift	Solution shift
2, 6	129.2,[a] 113.7	121.5	122.9
2′, 6′	134.2,[a] 116.4	125.3	126.4
3, 5	125.2, 122.3	123.8	124.7
3′, 5′	110.2, 108.5	109.4	111.9
1	154.0		156.8
4	149.7		150.2
1′	141.1		144.8
4′	147.1		148.8

[a] The discussion concerning compounds (II) and (III) enables these resonances to be assigned to C-2 and -2′, respectively.

The aromatic peak assignments are given in Table 3 and on the spectral expansion shown in Figure 3. A slightly different assignment for the C-3′, -5′ pair and C-6 was made previously [11] based only upon the lower frequency spectrum. The present assignments fit better with the values of splittings now seen for the reference compounds and also with the solution chemical shifts for the dyestuff.

The magnitudes of the C-2, -6 and C-2′, -6′ splittings suggested in Table 3 are in line with those proposed in Table 1. The range observed, 13—18 p.p.m., can be taken as characteristic of the effects of a diazo-bond on *ortho*-carbons, and can presumably be explained in terms of anisotropy in the bond magnetic susceptibility or of electric field effects. The splittings C-3′, -5′ (1.7 p.p.m.) and C-3, -5 (2.9 p.p.m.) are also comparable to those detected for the reference compounds examined at 50.30 MHz. (Table 1). Their possible origins have already been discussed. It is clear that detailed information on chemical shifts for fixed conformations in solids will be of greater value for the evaluation and discussion of long-range shielding influences than the average results obtained for solutions.

Conclusions.—The work discussed above indicates that it is now possible to obtain ^{13}C n.m.r. spectra from quite complex organic molecules in the solid state with resolution comparable to solution-state spectra. Additional specific effects of several types are observed in the spectra of solids. These can be used to provide information on the solid-state structure of the species concerned.

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