High-resolution ^{13}C Nuclear Magnetic Resonance Spectra of Some Solid Anthraquinone Dyestuffs and Related Species

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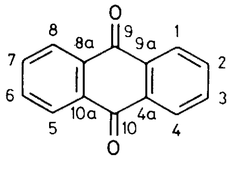
^{13}C N.m.r. spectra of the solid phase have been obtained for anthraquinone and a series of its substituted derivatives. Whilst some species show essentially similar spectra in the solid and solution phases, clear differences are apparent in other cases. The differences are attributed to the loss of molecular symmetry associated with the locking of particular conformations in the solid. In the case of 1,4-bis-(n-butylamino)-anthraquinone, the molecular asymmetry indicated by n.m.r. in the solid was confirmed subsequently by *X*-ray crystallographic examination.

High-resolution n.m.r. spectra obtained from materials in solution have been a major source of structural information for many years. However, the application of conventional n.m.r. methods to solid materials has failed to yield similarly useful information since, in general, solids show excessively broadened spectra owing to residual, non-averaged nuclear dipole–dipole interactions and shielding anisotropy. Recently, techniques have been developed [1,2] to overcome these difficulties. Most usually, a combination of three experiments is employed, and, using ^{13}C as an example, these are (a) high-power proton decoupling to remove (^1H, ^{13}C) dipolar broadening and (^1H, ^{13}C) scalar interactions,[3] (b) magic-angle rotation (MAR) to eliminate shielding anisotropy effects and broadening from other second-rank tensor interactions,[4] and (c) magnetisation transfer from ^1H to ^{13}C (cross-polarisation) to improve the sensitivity of observation of the ^{13}C signals.[3,5]

Much of the early work using these methods concentrated on polymeric species [1] or relatively simple monomers.[6] In a previous publication [7] we explored the potential of the methods to give useful information on moderately complex monomeric organic species by examining some dyestuff species based on *trans*-azobenzene. Differences were observed between the spectra obtained from these species in solution and in the solid state. One of these was a function of the n.m.r. experiment, *i.e.* the asymmetric doublet splitting observed for some carbon atoms bonded to nitrogen in spectra from solids, which arises when the nitrogen quadrupole moment prevents the MAR from completely averaging the carbon–nitrogen dipolar interactions.[8-11] Others were a function of the structure of the materials in the solid state. Thus, signals from some carbon atoms that are averaged by rotation in solution become separated when particular conformations of the azobenzene species are locked in the solid state. Also, chemical-shift differences were observed for particular carbonyl carbons in the solution and solid states that could be connected, possibly, with differences in hydrogen bonding in the freely rotating and locked species.

In the present paper, our investigations have been extended to species based upon a second major chromophore in dyestuff chemistry, namely the anthraquinone moiety:



Indeed, three of the species discussed below are listed dyestuffs of the Disperse Blue and/or Solvent Blue categories. These are 1,4,5,8-tetra-aminoanthraquinone (Colour Index No. 64500), 1,4-bis-(isopropylamino)anthraquinone (CI 61551), and 1,4-bis-(n-butylamino)anthraquinone (CI 61554).

Table 1. Proton relaxation characteristics of solid anthraquinones

Compound	$T_1(^1H)$/s	$T_{1\rho}(^1H)$/ms
Anthraquinone (AQ)	10—20	>600
1,4-$(OMe)_2$-AQ	2.2	41
1,4-$(OH)_2$-2,3-Me_2-AQ	4.1	0.71
1,4-$(Bu^nNH)_2$-AQ	0.81	~100
1,4-$(Pr^iNH)_2$-AQ	1.1	>300
1,4,5,8-$(NH_2)_4$-AQ	1.5	17.7
1-NMe_2-AQ	2.8	6.4

Experimental

The solid-state spectra of the anthraquinone species were obtained in the main using a purpose-built double-resonance spectrometer capable of performing dipolar decoupling, cross-polarisation, and magic-angle rotation. Details of the system, which operates at 22.63 MHz for carbon, have been given elsewhere.[11] The n.m.r. device, which uses cylindrical glass rotors 5 mm in diameter, has also been described previously.[12] The samples were examined as powders or microcrystalline solids, with the rotor taking about 100 mg of highly packed material, and being spun at 2—2.5 kHz. Other experimental details, *e.g.* the availability of flip-back and non-quaternary suppression (NQS) pulse sequences as well as the standard cross-polarisation routine, the measurement of proton T_1 and $T_{1\rho}$ values so that the operational parameters for ^{13}C can be optimised, and the calibration procedures remain as indicated in our previous paper.[7] The measured values of $T_1(^1H)$ and $T_{1\rho}(^1H)$ are listed in Table 1. Optimum contact times are related to $T_{1\rho}(^1H)$ and were usually set at between 5 and 10 ms, but a low value (1 ms) was necessary for 1,4-dihydroxy-2,3-dimethylanthraquinone. Recycle times were generally held to *ca.* $T_1(^1H)$ following flip-back. Anthraquinone itself relaxes very slowly (T_1 *ca.* 10—20 s) and a recycle time of 10—15 s was used with flip-back *and* multiple contacts (8 per cycle). Typically, between 5 000 and 20 000 transients were acquired for each spectrum. The decoupling field was set to 60 kHz. Windows for coupled decay in NQS experiments were set to *ca.* 40 μs.

Some solid-state ^{13}C spectra were also recorded at 75.46

Table 2. ^{13}C N.m.r. shifts [a] of anthraquinone and several derivatives

		Chemical shifts (p.p.m. from Me_4Si)						
Compound	MHz	C(1),(4)	C(2),(3)	C(5),(8)	C(6),(7)	C(9),(10)	C(4a),(9a)	C(8a),(10a)
Anthraquinone (AQ)	22.63	126.6	133.5	126.6	133.5	181.2	131.5	131.5
		(126.2)	(133.9)	(126.2)	(133.9)	(182.0)	(132.8)	(132.8)
1,4-$(OMe)_2$-AQ	22.63	152.3	119.6	128.4	134.0	185.5	123.0	137.8
		(153.6)	(121.6)	(125.4)	(132.9)	(181.6)	(122.2)	(133.5)
1,4-$(OH)_2$-2,3-Me_2-AQ	22.63	157.2	139.2	130.0	133.8	185.7	109.7	133.8
		(156.0)	(137.4)	(126.0)	(134.1)	(185.4)	(109.1)	(132.6)
1,4-$(Bu^nNH)_2$-AQ	75.46	145.2	121.9	128.1 125.8	132.0 131.1	181.2 179.4	108.4	135.2
	22.63	145.4 [b]	122.7	128.8 126.6	133.0 131.8	181.3 179.8	109.1 [b]	136.0
		(146.2)	(123.5)	(126.0)	(131.8)	(182.1)	(109.6)	(134.6)
1,4-$(Pr^iNH)_2$-AQ	22.63	141.6 [b]	121.2	126.4 [c] 123.5 [c]	133.0 [c] 129.8 [c]	181.3	109.7 [b]	133.0
		(145.3)	(123.8)	(125.8)	(131.7)	(181.8)	(109.5)	(134.6)
1,4,5,8-$(NH_2)_4$-AQ	75.46	144.0 [b]	124.4 [d]	144.0	127.4 [d] 125.6 [d]	187.5	113.6	113.6
		(143.8)	(125.9)	(143.8)	(125.9)	(185.8)	(111.1)	(111.1)

[a] Values are given for the solid state, with those for the solution state in parentheses. [b] Corrected for the effect of splitting by (C,N) dipolar interaction. [c] There is some uncertainty over these assignments, since components may be obscured by the bands assigned to C(2),(3) and C(8a),(10a). [d] Assignments interchangeable.

MHz on a Bruker CXP 300 spectrometer at Bruker-Physik, Karlsruhe.

All compounds were obtained from the ICI Reference Collection of Fine Chemicals, with their structures and purities being confirmed by their ^{1}H and/or ^{13}C n.m.r. spectra in solution. These, and the solution chemical-shift values quoted in this paper, were obtained using Bruker WH90 and WM250 spectrometers with either $CDCl_3$ or D_6-DMSO as solvent. Chemical-shift assignments for the spectra of the solid materials were made largely by comparison with the solution spectra supplemented by information from the NQS spectra.

Chemical shifts for the solids are reported with respect to the resonance frequency of Me_4Si in solution, but were measured by the sample-replacement technique with respect to solid adamantane (assumed chemical shift $\delta_C = 37.7$ p.p.m.) for the 22.63 MHz work or to the carbonyl resonance of glycine (assumed shift $\delta_C = 176.06$ p.p.m.) for the studies at 75.46 MHz. It may be noted [13] that corrections for differences in bulk isotropic magnetic susceptibilities are unnecessary in MAR spectra. Internal chemical-shift differences are considered to be accurate to *ca.* 0.2 p.p.m. but absolute shifts may be in error by up to 2 p.p.m. Linewidths at 22.63 MHz are typically 1.0—1.5 p.p.m. The origin of the linewidths is not clear, but different procedures of sample manipulation (*e.g.* use of crystallites or ground samples) do not seem to make any marked improvements in resolution. The various factors responsible for ^{13}C linewidths for solids have been discussed by Garroway *et al.*[14] Some of these (*e.g.* dispersions of chemical shifts) are proportional to the static magnetic field. In practice, for the cases studied here, we find that on the whole the useful resolution of the spectra obtained at 75.46 MHz was only *ca.* 50% better than that for 22.63 MHz spectra. In general, problems from spinning sidebands are more severe at the higher field.

Results and Discussion

The majority of carbon atoms in the compounds concerned are aromatic, and the aromatic-carbon chemical shifts for the species, run as solids and in solution, are collected in Table 2. The carbon-atom numbering for anthraquinone (AQ) and the substituted anthraquinones is given above. The results for the compounds fall into two roughly equal categories, *i.e.* those for which little, if any, difference is observed between the solid- and the solution-state spectra and those where marked differences are apparent.

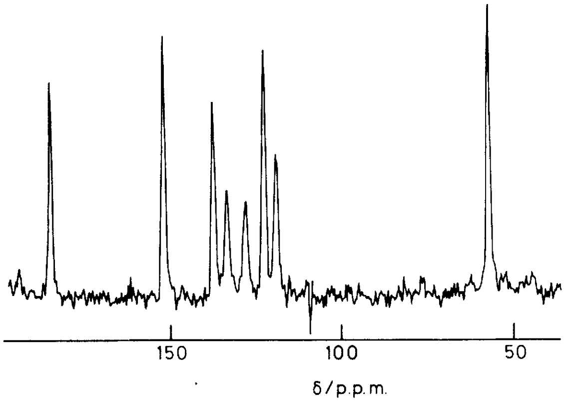


Figure 1. 22.63 MHz ^{13}C n.m.r. CP/MAR spectrum of solid 1,4-dimethoxyanthraquinone obtained using 5 ms contact time, 2.0 s recycle time, and 9 500 transients

Anthraquinone.—All the carbon-atom chemical shifts derived from the solid at 22.63 MHz are identical, within experimental error, to the solution values, and there were no suggestions of additional splittings in the solid state. A detailed crystallographic study of anthraquinone has been reported,[15] and, indeed, much crystallographic and other data for anthraquinones in general have been reviewed.[16] Anthraquinone itself has space group $P2_1/a$, with two symmetry-related molecules per unit cell. The molecular dimensions show that the planar molecule is not completely symmetrical although a centre of symmetry exists, *i.e.* the asymmetric unit is half the molecule. Thus the bond lengths C(1)–C(2) and C(5)–C(6) are equal (1.390 Å), but slightly different from C(3)–C(4) and C(7)–C(8) (1.381 Å). The lack of full molecular symmetry in the crystal environment appears to be insufficient to affect the ^{13}C spectra, at least at the resolution of the present work, so

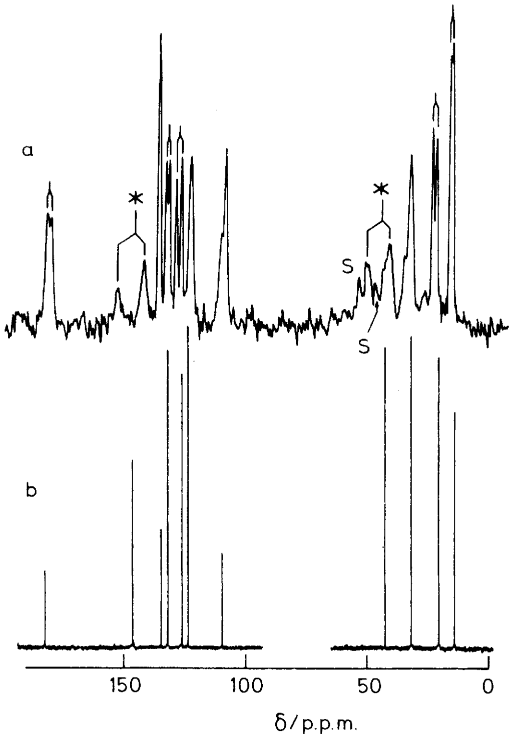


Figure 2. ^{13}C N.m.r. spectra of 1,4-bis-(n-butylamino)anthraquinone. a, In the solid phase: CP/MAR spectrum at 22.63 MHz, using 5 ms contact time, 1.0 s recycle time, and 15 000 transients. Sideband peaks are labelled 'S.' Unsymmetrical doublet splittings arising from residual (C,N) dipolar interactions are indicated by asterisks for C(1),(4) and the α-carbons of the Bu^n chain. The shoulder for the C(4a),(9a) signal, tentatively also assigned to such interactions, is clearly visible. Doublet splittings arising from the lifting of molecular symmetry in the crystal are marked on the Figure. b, As a solution in CDCl$_3$ (at 62.9 MHz)

Table 3. Residual dipolar (^{13}C,^{14}N) splittings

Compound	C,N dipolar splitting (Hz) [a] Aromatic C	Aliphatic C
1,4-(Bu^{n}NH)$_2$-AQ	240	199
1,4-(Pr^{i}NH)$_2$-AQ	260	204
1,4,5,8-(NH$_2$)$_4$-AQ	250	—
1-Me$_2$NH-AQ	256	181 [b]

[a] At 22.63 MHz. [b] Approximately equal for the two methyl groups.

that the chemical-shift values for carbon-atom pairs, such as C(1) and C(4), C(2) and C(3), are not separated in the solid state.

1,4-*Dimethoxyanthraquinone*.—The ^{13}C n.m.r. spectrum of the solid at 22.63 MHz is shown in Figure 1. No additional splittings are observed compared with the solution spectrum, and the majority of peaks are at closely similar positions. However, three related carbon-atom pairs show small differences in chemical shift between the solid- and solution-state spectra, namely C(9),(10) (3.9 p.p.m.), C(8a),(10a) (4.3 p.p.m.), and C(5),(8) (3.0 p.p.m.). The cause of these variations is not known but could be connected with small differences in the orientation of the methoxy groups and/or differences in intermolecular interactions between the solid and solution states of the molecule. The difference does not extend to the methoxy groups, which give a single peak in the solid (57.4 p.p.m.), at a similar position to that of the solution spectrum (56.7 p.p.m.).

Table 4. Aliphatic chemical shift assignments for 1,4-(Bu^{n}NH)$_2$-AQ

	α	β	γ	δ
Solution	42.6	31.7	20.4	13.9
Solid, 22.63 MHz	44.1	32.3	23.4 21.7	16.2 15.3
Solid, 75.46 MHz	44.5	32.2 31.1	22.1 20.7	15.3 14.4

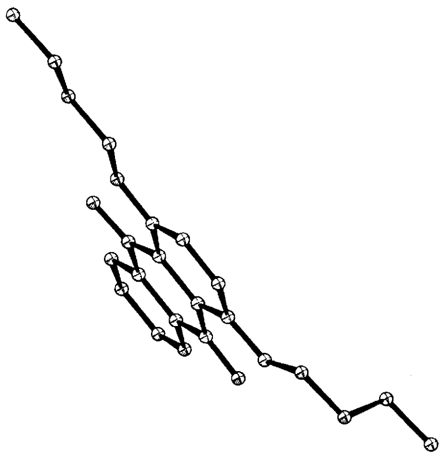


Figure 3. Conformation of 1,4-bis-(n-butylamino)anthraquinone in the crystalline state, as determined from an *X*-ray diffraction study

1,4-*Dihydroxy*-2,3-*dimethylanthraquinone*.—Again the ^{13}C spectra of the solid and solution are very similar. Only one carbon-atom pair shows any significant difference in chemical shift in the two states, namely C(5),(8) (4.0 p.p.m.). The methyl-carbon shift is essentially the same at 12.6 p.p.m. in the solid and 11.4 p.p.m. in solution.

1,4-*Bis*-(*n-butylamino*)*anthraquinone*.—The ^{13}C n.m.r. spectra of the solid at 22.63 MHz and the solution are shown in Figure 2. It is clear that the spectrum of the solid contains many more peaks than that of the solution. Some of these arise from residual (C,N) dipolar couplings. Thus an asymmetric doublet is observed from C(1),(4) and from the α carbon atoms of the butyl groups, owing to the neighbouring nitrogen atoms (see Table 3). There also appears to be a small asymmetric splitting of the C(4a),(9a) resonance, which may be a residual two-bond (C,N) dipolar coupling.

In addition, two peaks are detected (approximately equally separated in p.p.m. at 22.63 and 75.4 MHz) from several of the other pairs of carbon atoms that in solution give a single resonance. The aromatic chemical shift assignments for the solid at both frequencies are given in Table 2 and the aliphatic assignments are in Table 4. There are two possible explanations for these additional peaks. One is that the crystal structure contains two inequivalent molecules per unit cell. The detection of such effects in the ^{13}C n.m.r. spectra of solids has been reported.[11] An alternative explanation is that 1,4-bis-(n-butylamino)anthraquinone molecules have a lowered symmetry in the solid, such that all the carbon atoms are inequivalent. To distinguish between these possibilities an *X*-ray crystal structure was obtained. This showed conclusively

Table 5. ^{13}C N.m.r. shifts of *N,N*-dimethyl-1-aminoanthraquinone

	Chemical shifts (p.p.m. from Me_4Si)							
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
Solid (75.46 MHz)	151.9 [g]	120.9	133.0	116.7	126.7 [e]	133.0 [f]	134.8 [f]	127.4 [e]
Solution	152.7	122.6	133.2	117.0	125.9 [a]	132.8 [b]	134.4 [b]	126.6 [a]

	Chemical shifts (p.p.m. from Me_4Si)						
	C(9)	C(10)	C(4a)	C(8a)	C(9a)	C(10a)	$-N(CH_3)_2$
Solid (75.46 MHz)	181.8	185.0	136.3 [d]	134.8 [d]	118.5	131.9 [d]	50.0 [g] 41.0 [g]
Solution	180.6	183.5	135.8 [c]	135.8 [c]	119.2	132.3 [c]	43.6

Assignments for the *a*, *b*, *c*, *d*, *e*, and *f* sets of peaks are tentative and possibly interchangeable. [g] Corrected for the effect of splitting by (C,N) dipolar interaction.

that the second explanation is the correct one. The compound crystallises in the space group $P2_1/c$, with four molecules per unit cell, and the asymmetric unit is a complete molecule. Figure 3 shows the conformation that the molecules adopt. It is clear that whilst the carbon atoms of one of the butyl-groups for a given molecule lie approximately in the same plane as the anthraquinone ring system, the γ carbon of the other one skews sharply out of this plane. The bond lengths and bond angles of the aromatic system also confirm this lack of symmetry. A difference of 0.029 Å was observed between the C(5)–C(6) and C(7)–C(8) bond lengths. The pairs of carbon atoms for which the largest splittings were observed in the carbon n.m.r. spectra correspond well with those for which the largest differences were detected in the crystal structure, *i.e.* the butyl groups and the C(5),(8) and C(6),(7) pairs. The differences in the environments of some of the other pairs of carbon atoms are presumably too small to detect in the n.m.r. spectra. Full *X*-ray crystallographic parameters can be supplied on request.

1,4-*Bis-(isopropylamino)anthraquinone*.—The ^{13}C n.m.r. spectrum of the solid is similar in many respects to that of the analogous n-butylamino-derivative. Asymmetric doublets are observed at 22.63 MHz for C(1),(4) and the methine carbon atoms of the isopropyl groups (Table 3). Once again, there appears to be a small asymmetric splitting of the C(4a),(9a) resonance. To within experimental error the splittings for the two compounds are very similar. This is not unexpected because the immediate environment of each nitrogen atom will be similar, owing to the presence of strong H-bonding of the NH protons to the carbonyl oxygen atoms, which will determine the conformation in this part of the molecule.

In the solid the methine and methyl resonances were at 42.6 and 22.7 p.p.m. To within experimental error these values are similar to the solution ones of 43.6 and 23.4 p.p.m. The methyl peak is not observably split for the solid, so that if the substituent conformation is locked (as must be expected), any difference in the electronic environment of the methyl groups is small. However, in the aromatic part of the spectrum of the solid at least one pair of carbon atoms, probably C(5),(8), gives two peaks. Since this effect is detected from the same part of the anthraquinone moiety as for the n-butylamino-compound, it is thought that its origin may once again be a loss of molecular symmetry in the solid.

1,4,5,8-*Tetra-aminoanthraquinone*.—Three single peaks observed in the solution ^{13}C n.m.r. spectrum of this material remain unchanged in the solid state, *i.e.* from C(1),(4),(5),(8), C(4a),(8a),(9a),(10a), and C(9),(10). However, the remaining peak from C(2),(3),(6),(7) (at 125.9 p.p.m. in solution) is split into three peaks in the spectrum from solid material (124.4, 125.6, and 127.4 p.p.m.) at 75.46 MHz. It is not possible to state at present whether this results from inequivalent molecular conformations in the solid or from a single conformation that is not fully symmetric. At 22.63 MHz the resonance at 144.0 p.p.m., assigned to C(1),(4),(5), and (8), shows a typical splitting owing to residual (C,N) dipolar interactions.

N,N-*Dimethyl-*1-*aminoanthraquinone*.—The carbon-atom chemical shift assignments for both the solution- and 75.46 MHz solid-state spectra are given in Table 5. All the aromatic carbon atom shifts from the solid are very similar, to within experimental error, to the solution values. In solution, because of rotation about the C(1)–N bond, an average chemical shift is observed for the two methyl-carbon atoms of the dimethylamino group. However, for the solid, as in our previously reported work [7] on *trans*-azobenzene derivatives, a locked conformation is obtained, so that separate peaks are observed for these methyl-carbons, their mean position being similar to the solution value. This observation indicates that the two methyl groups occupy inequivalent positions in the molecule. The most likely conformation that fulfils this requirement has the two methyl groups on one side of the ring system and the lone pair of electrons on the other. A comparison of the chemical shifts for C-(2) and -(9a) with those for solid anthraquinone shows that the dimethylamino group induces shifts at these positions of 12.6 and 13.0 p.p.m., respectively. The fact that these substituent shifts are identical, within experimental error, also suggests that the dimethylamino group is symmetrically located with respect to C(2) and C(9a). The nonequivalence of the two carbonyl groups (3.2 p.p.m.) owing to the effect of the NMe_2 substituent is, as might be expected, larger than that caused by crystallographic effects for 1,4-$(Bu^nNH)_2$-AQ.

Residual dipolar (C,N) couplings are detected at 22.63 MHz for C(1) and both the methyl-carbon atoms in the solid (see Table 3).

(C,N) *Dipolar Splittings*.—Mention has already been made of the splittings observed for resonances assigned to ^{13}C atoms directly bonded to ^{14}N. These arise from the competing influences of Zeeman and quadrupolar energies.[17] When these are of the same order of magnitude, there is no ' magic angle ' that will average (^{13}C, ^{14}N) dipolar interactions to zero. Rapid sample rotation at 54.7° to the static magnetic field frequently results [17] in doublets of intensity ratio 2 : 1. A number of examples has been presented in the literature,[9–11] including cases involving amino nitrogens. The theory of the phenomenon is well understood.[17–20] The magnitude of the splitting is a function of (a) the ratio of quadrupolar and Zeeman energies, (b) the inverse cube of the (C,N) distance, and (c) the angles between the (C,N) vector and the principal axes of the electric field gradient (e.f.g.) tensor at the nitrogen atom. It is also expected that if ^{14}N spin-lattice relaxation is rapid the splitting will disappear. In the ' high-field ' situation, where the quadrupolar energy is much less than the Zeeman energy, the splittings will also not be visible—this may result if high-field spectrometers are used or if local symmetry at ^{14}N yields a low e.f.g. The sense of the splitting in the spectrum (*i.e.* whether the more intense component is at higher or lower frequency than its weaker counterpart) depends on both the sign of the e.f.g. and on factor (c). In practice, both senses have been observed.[11,20] The true chemical shift is at the weighted average of the two peaks, and proper allowance for this has been made in the results reported here.

In the azobenzene series, no splittings were seen[7] for carbons bonded to the diazo-nitrogen atoms, though it is not clear whether this reflects a low e.f.g., a high $T_1^{-1}(^{14}N)$, or unfavourable geometry. Substantial splittings have been, however, observed for carbons bonded to nitro substituents.[11,20] For the aminoanthraquinones the splittings are also large, with the opposite sense to those for $C-NO_2$ carbons, *i.e.* with the stronger peak at low frequency. For three of the compounds, two types of carbon (aromatic and aliphatic) are involved for a given nitrogen. The data are summarised in Table 3. It may be seen that the splitting for the aromatic carbon is significantly greater than that for the aliphatic carbon in each case. Since the carbons in question are bonded to the same nitrogen, the e.f.g. components involved are the same, so that the ratio of splittings must involve the inverse cubes of the (C,N) distances and the angles between the (C,N) vectors and the e.f.g. principal axes. The observed splitting ratio is essentially as expected from the effect of distance-dependence alone. Thus, for 1,4-bis-(butylamino)anthraquinone the ratio of r_{CN}^{-3} for the two types of carbon is *ca.* 1.25, and the splittings are in the ratio 1.21. A negative quadrupole coupling constant has been shown[20,21] to be required to account for the sense of the doublet splitting in aromatic amines, and the same is likely to be true for the compounds studied here.

The origin of the splittings discussed above is confirmed by the fact that they diminish when spectra are taken at a higher magnetic field (75.46 MHz for ^{13}C resonance). In fact, in three of the cases no splittings can be resolved at the higher field, but for *N*,*N*-dimethyl-1-aminoanthraquinone splittings of 68 and 83 Hz are found for the aliphatic and aromatic carbons, respectively.

For both the n-butylamino and the isopropylamino derivatives the resonance assigned to C(4a) and C(9a) appears to have a poorly resolved splitting into peaks of unequal intensity in the spectra at 22.63 MHz. These splittings are of magnitude 38 and 48 Hz, respectively, in the two cases. No such splittings can be resolved in the 75.46 MHz spectra. It is therefore possible that a residual two-bond (C,N) dipolar interaction is responsible for the observations. Such a long-range effect has not been reported previously. Similar splittings were not seen for other carbons removed by two bonds from nitrogen, for the compounds considered here. It should be noted, however, that such splittings arise from direct (through-space) interactions and that the effect could in principle be *inter*molecular in origin.

Conclusion

The work presented in this and our previous publication[7] shows that it is now possible to obtain ^{13}C n.m.r. spectra in the solid state from relatively complex monomeric organic molecules with resolution approaching that of solution spectra. The spectra in the solid can differ from solution spectra in several ways and the differences provide information on solid-state structure, which can by-pass or supplement that obtained from established methods.

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