Solution-state carbon-13 nuclear magnetic resonance studies of polyaniline

A. M. Kenwright* and W. J. Feast
IRC in Polymer Science and Technology, University of Durham, South Road, Durham DH1 3LE, UK

and P. Adams
University of Durham Industrial Research Laboratories, Mountjoy Research Centre, South Road, Durham DH1 3LE, UK

and A. J. Milton and A. P. Monkman
Department of Physics, University of Durham, South Road, Durham DH1 3LE, UK

and B. J. Say
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK

(Received 9 December 1991; accepted 18 February 1992)

Solution-state ^{13}C nuclear magnetic resonance spectra are presented for the emeraldine base and leucoemeraldine base forms of polyaniline. The bulk of the leucoemeraldine base sample gives a simple two-line spectrum, which is readily assignable. The emeraldine base samples give spectra of much greater complexity, showing many more lines than there are carbons in the postulated chain repeat unit. This is rationalized in terms of slow interchange of the many conformers available to the emeraldine base form. A quantitative 'region assignment' is made. Gel permeation chromatography measurements show that interconversion between the two forms is achieved without either significant crosslinking or chain scission. The minor peaks in the spectrum of the leucoemeraldine base form due to chain defects (including chain ends) are compared with chemical shift values calculated for postulated structures, and some structures can be rejected on the basis of this.

(Keywords: conducting polymers; polyaniline; ^{13}C nuclear magnetic resonance; conformations)

INTRODUCTION

Polyaniline is the generic term given to the products of the oxidative coupling of aniline. This reaction has been known for about 150 years[1,2], and it is recognized that the properties of the material produced can be changed by further oxidation or reduction, as well as by protonation by strong acids. Trivial names have been associated with several of the forms produced in this way and structures have been postulated for them[3,4], some of which are shown in *Figure 1*, but little hard evidence has been produced to support these postulated structures.

In the past decade there has been an explosion of interest in polyaniline because of its conductivity and processing properties, and many papers have appeared concerning the preparation and characterization of the various forms. The bulk of the characterizations have relied on some combination of elemental analysis, molecular-weight determination (by, for example, gel permeation chromatography (g.p.c.)), identification of functional groups present (by, for example, vibrational spectroscopy[5]), identification of chromophores by ultraviolet/visible (u.v./vis) spectroscopy and determination of oxidation state (by, for example, redox titrations). Others have concentrated on the characterization of low-molecular-weight 'model' compounds[6–8], or the synthesis of polymers under more controlled conditions[9] whose properties could be compared with the conventionally produced polyanilines. While these techniques go some way towards characterizing the material, they provide relatively little in the way of detailed information on the structure of the polymer chains. Solid-state ^{13}C and ^{15}N nuclear magnetic resonance (n.m.r.)[10–16] have been used in an effort to characterize the materials structurally and have yielded spectra that could be explained in terms of the postulated structures. Unfortunately, the available resolution, particularly in the case of the ^{13}C spectra, was insufficient to allow the positive identification of the postulated structures, or indeed of any other structures that might have been present. In this work we have used solution-state ^{13}C n.m.r. to examine polyaniline samples, and find the available resolution considerably increased, allowing a much greater insight into the possible structures present.

EXPERIMENTAL

The 'emeraldine base' form of polyaniline was prepared as follows. Aniline (0.1 mol) was added to hydrochloric

---

* To whom correspondence should be addressed

0032-3861/92/204292–07

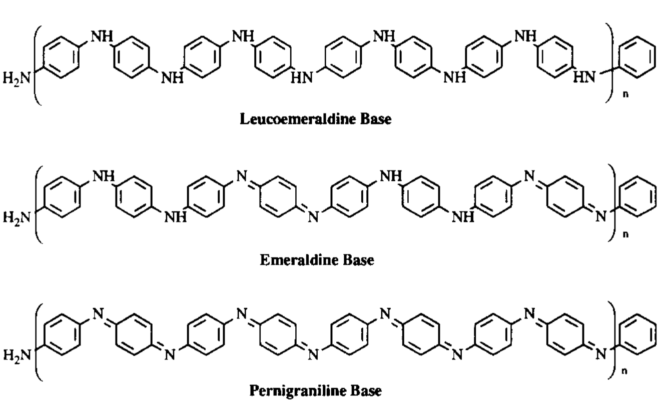


Figure 1 Postulated structures for various oxidation states of polyaniline

acid solution (100 ml, 3.5%, ca. 0.1 mol HCl) in a 250 ml beaker, and mixed using a magnetic stirrer to give a solution with a final pH between 1 and 2, as measured by indicator paper. Ammonium persulphate (0.1 mol) was dissolved in distilled water (60 ml), and this was added to the stirred reaction mixture. The mixture turned a dark blue/green colour and the reaction was observed to be slightly exothermic over a period of about 10 min. The mixture was left to stir for a total of about 6 days, after which it was filtered and washed with two lots of water, methanol (to remove any low-molecular-weight species) and finally with more water. The filter cake was added to an ammonia solution (100 ml, 35%) and stirred for 7 h before filtering and repeatedly washing with water, occasionally interspersed with washing with isopropanol. At this point the filtrate was colourless. The filter cake was then dried under vacuum at 323 K for 24 h to give a brown/purple product, which was crushed using a mortar and pestle. Elemental analysis showed that the material contained small residual amounts of chlorine (0.50 wt%) and sulphur (0.38 wt%). Some 4.69 wt% was not accounted for and is ascribed to oxygen, possibly associated with the chlorine or sulphur, or with trapped solvent species (water, methanol or isopropanol). Indeed, isopropanol was subsequently positively identified in the ^{13}C spectra. Chlorine and sulphur residues are normally found in the products of such preparations and they remain largely unchanged by attempts to wash them out, suggesting that they may be present as ring substituents.

The 'leucoemeraldine base' form of polyaniline was prepared from emeraldine base (2.0 g), which was placed in a 250 ml beaker with high-performance liquid chromatography (h.p.l.c.)-grade *N*-methyl-2-pyrrolidone (NMP) (20.0 g) and stirred. The beaker was then placed in an ultrasonic bath for about 15 min to disperse the emeraldine base before phenylhydrazine (2.50 g) was added and the mixture stirred for 24 h at room temperature, by which time the solution had turned dark brown. This was transferred to a nitrogen-atmosphere glove-box and toluene was added with vigorous stirring to precipitate the leucoemeraldine base, which was recovered by filtration, washed four times with toluene, and left to dry on the Buchner funnel before transferring to a vacuum desiccator. The desiccator was evacuated in the glove-box and then taken out of the box and subsequently kept under dynamic vacuum for 2 days in an effort to remove the toluene residues. (In spite of this, traces of toluene were still evident in the ^{13}C n.m.r. spectra—see below.) The desiccator was then returned to the glove-box and the leucoemeraldine base ground using a mortar and pestle to give a light-tan coloured powder.

A sample of the leucoemeraldine base was subsequently reoxidized as follows. Leucoemeraldine base (1.09 g) was added to a solution of $FeCl_3.6H_2O$ (0.812 g, 0.003 mol) in aqueous hydrochloric acid (50 ml, 2 M), and the mixture was stirred vigorously for 24 h under air in a fume hood. The product was recovered by filtration and washed several times with water before being added to ammonia solution (50 ml, 35%) and stirred for a further 6 h. It was filtered again and washed several times with water before being dried under vacuum at 323 K for 24 h.

Gel permeation chromatography (g.p.c.) measurements (Polymer Labs PL-gel mixed column, NMP+0.1% LiCl) carried out on all three samples gave identical responses, showing that the interconversion from one form to another did not result in significant amounts of either chain scission or crosslinking.

N.m.r. samples were prepared by adding powdered polyaniline (0.4 g) to an approximately 50/50 v/v mixture of NMP and perdeuterated dimethylsulphoxide (d_6-DMSO) (4 g) with stirring. The mixture was then placed in an ultrasonic bath for about 15 min to ensure dispersion of the polyaniline, after which it was transferred to a 10 mm diameter n.m.r. tube, which was capped and sealed with 'para-film'. The ^{13}C spectra of the polyaniline samples were obtained on a Bruker AMX-500 spectrometer at an operating frequency of 125.77 MHz, and a nominal probe temperature of 303 K. The ^{13}C spectra of model compounds were run in d_6-DMSO on a Varian VXR400-S spectrometer at an operating frequency of 100.577 MHz, and at ambient probe temperature (about 293 K). All chemical shift values are quoted relative to tetramethylsilane (TMS), although referencing was done via the d_6-DMSO peak, which was taken to be at +39.5 ppm.

RESULTS AND DISCUSSION

Our initial objective was to see whether or not it was possible to obtain reasonable-quality solution-state ^{13}C spectra of polyaniline samples, since we could find no record of other workers having done this. We looked first at the 'as-made' emeraldine base sample, and found that we could observe relatively high-quality spectra without undue difficulty. The region of interest from the normal proton-decoupled ^{13}C spectrum and d.e.p.t.-90[17] spectrum (distortionless enhancement by polarization transfer) are shown in *Figure 2*. The effect of the d.e.p.t.-90 sequence is to select only those carbons having one directly bonded proton, and it is therefore a very valuable assignment tool in this case. From these spectra we can readily identify the quaternary (in the sense of non-proton-bearing) carbons, and observe that there are peaks in all the spectral regions we would expect for the postulated structure. However, it is also immediately evident that the spectrum is considerably more complicated than might be expected from naive consideration of the postulated structure as drawn in *Figure 1*. It is therefore not possible to make an immediate assignment on the basis of these spectra alone.

We next looked at the sample of leucoemeraldine base prepared by reduction of the emeraldine base using phenylhydrazine. A normal proton-decoupled ^{13}C spectrum of this material is shown in *Figure 3*, together with a vertical expansion showing the minor peaks in the

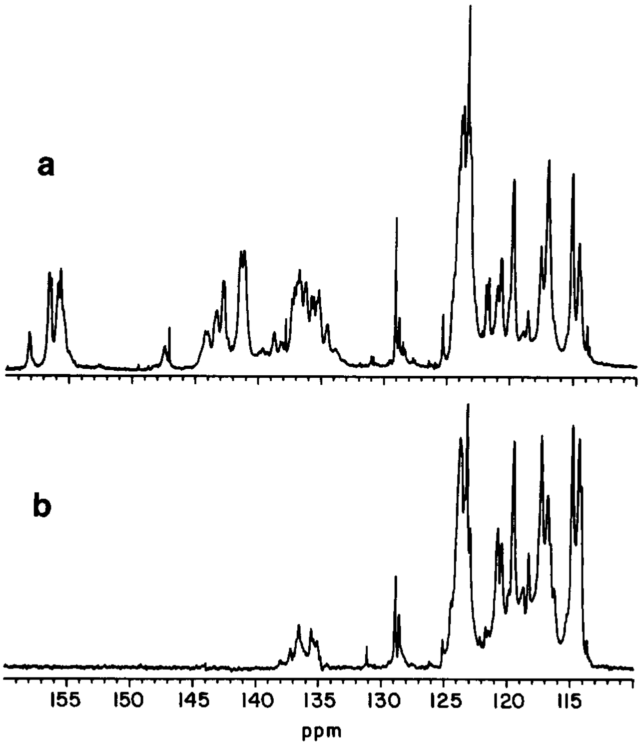


Figure 2 Emeraldine base as made. (a) $^{13}C\{^1H\}$: 5 s recycle, 90° pulse, 0.47 s acquisition, 40000 transients, continuous decoupling. (b) D.e.p.t-90: 1 s recycle, 0.47 s acquisition, 38000 transients

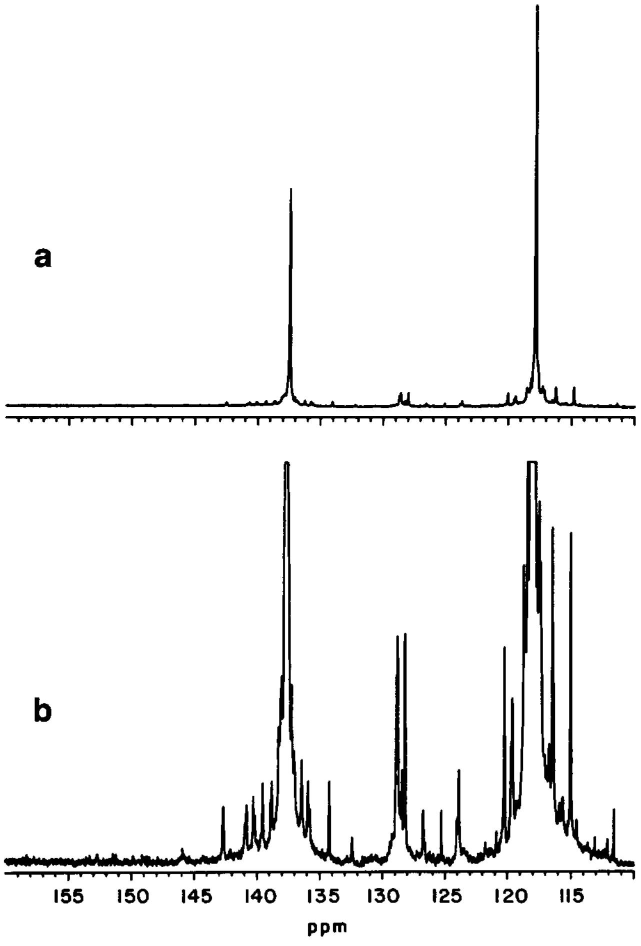


Figure 3 Leucoemeraldine base. (a) $^{13}C\{^1H\}$: 5 s recycle, 90° pulse, 0.47 s acquisition, 10000 transients, continuous decoupling. (b) Vertical expansion

baseline. It is immediately obvious that the major features in the region of interest are just two lines at 117.84 and 137.44 ppm. When a spectrum of this sample is recorded under quantitative conditions (decoupler gated off during 30 s recycle), the two peaks have an intensity ratio of 2:1 within experimental error, and the two peaks account for more than 95% of the intensity in the 110 to 160 ppm region of the quantitative spectrum when the peaks due to residual toluene (125.3, 128.2 and 128.8 ppm—quarternary at ~137.5 ppm presumed under the major peak) have been eliminated. In a d.e.p.t.-90 spectrum only the peak at 117.84 ppm is seen, while a ^1H spectrum recorded on the decoupler coil of the 10 mm probe, while not of optimal resolution, clearly showed two broad peaks centred at 6.98 and 7.51 ppm having an intensity ratio of 4:1 within experimental error. All of the above is completely consistent with the postulated structure and, when taken in conjunction with the other available data on the sample, is proof that the vast majority of the sample has the structure postulated for leucoemeraldine base. We will return to the question of the minor peaks later.

We then looked at the sample prepared by reoxidation of the leucoemeraldine base. The proton-decoupled ^{13}C spectrum of this material is shown in *Figure 4*, together with a spectrum of the original emeraldine base run under similar conditions for comparison. It can be seen that the two spectra are practically identical, except that the linewidth is possibly slightly greater in the reoxidized material. This may be due to the presence of paramagnetic residues following the treatment with $FeCl_3$. The fact that these two spectra are so similar, together with the evidence from g.p.c. showing that neither chain scission nor crosslinking occurred during these reactions,

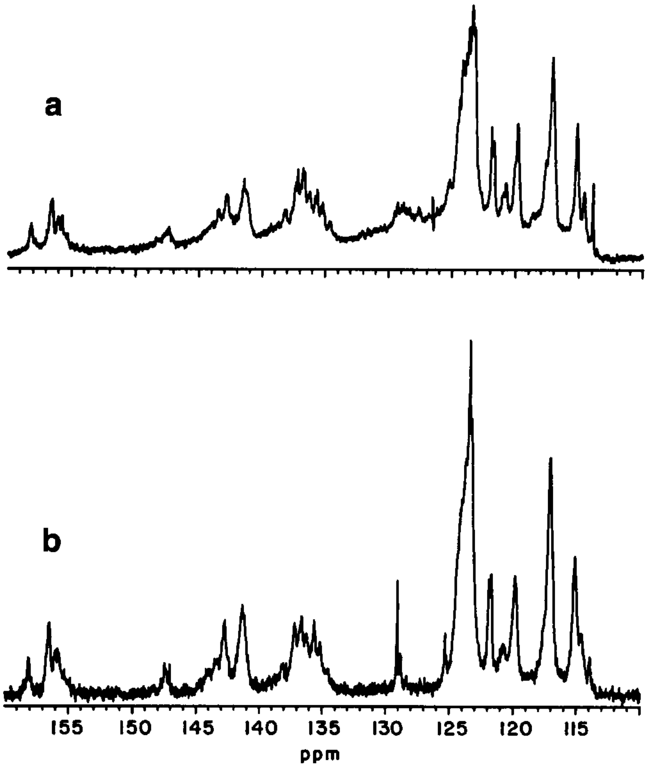


Figure 4 Emeraldine base $^{13}C\{^1H\}$. (a) Reoxidized from leucoemeraldine using $FeCl_3$: 1 s recycle, 90° pulse, 0.47 s acquisition, 11000 transients, continuous decoupling. (b) As made: 1 s recycle, 30° pulse, 0.47 s acquisition, 1000 transients, continuous decoupling

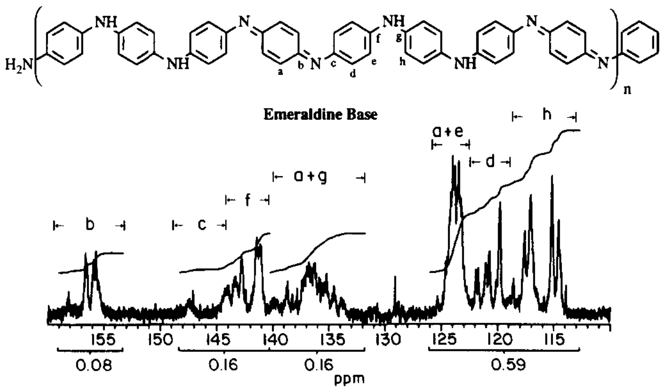
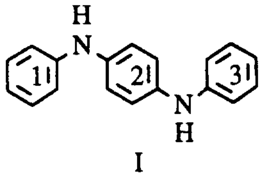


Figure 5 Emeraldine base as made, $^{13}C\{^1H\}$ under quantitative conditions: 30 s recycle, 90° pulse, 0.47 s acquisition, 4750 transients, decoupler gated off during recycle

is of key importance, since it clearly shows that the changes involved in going from emeraldine base to leucoemeraldine base are fully reversible, and almost certainly do not involve any major structural changes. It therefore follows that, since we have already shown the leucoemeraldine base sample to be almost entirely composed of phenylene rings connected by *para*-substituted nitrogens, the emeraldine base sample must have the same skeletal structure. This is entirely consistent with the postulated structure for emeraldine base, and would seem to be the first unequivocal confirmation of the structure.

With this in mind, we can turn to consider in more detail the spectrum of emeraldine base. We have previously identified the quaternary carbons in this spectrum from the d.e.p.t.-90 experiment. On the basis of this, studies of model compounds[2,13] (see also below) and the integrations from a spectrum obtained under quantitative conditions, the region assignments shown in *Figure 5* could be made. These assignments are in quantitative agreement with the postulated structure, confirming the assignments previously made by Kaplan *et al.*[14] on the basis of solid-state ^{13}C n.m.r., and correcting our earlier assignments of solid-state spectra[15]. It should be noted that it is possible to make much more definite assignments based on the solution-state data because the linewidths are reduced by more than an order of magnitude, and also because it is possible to obtain solution-state spectra under quantitative conditions.

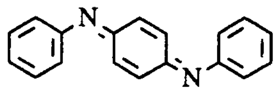
We are still left, however, with many more peaks than assignable carbons in the spectra of emeraldine base, suggesting a wealth of conformational effects, or a reduction in ring symmetry, or both. This is in marked contrast to the extreme simplicity of the leucoemeraldine base spectra. We must try to explain why this might be the case, even if we cannot as yet make a detailed assignment of each peak. X-ray crystallographic data on model compounds of polyaniline[7], as well as on other systems where two *para*-substituted phenylene rings are linked via one (essentially tetrahedral) atom, such as bisphenol derivatives and aromatic polyethers, show that on average the torsion angle between the phenylene rings is non-zero, the angle between the bridging bonds and the ring axes being fixed. This means that the two rings are effectively skewed with respect to each other. In principle, this renders the two sides of the rings inequivalent although this inequivalence is generally not seen in solution-state n.m.r. spectra because of the rapid ring-flipping motion (180° jumps) characteristic of *para*-substituted phenylene rings in polymer chains[18,19], which has the effect of averaging the inequivalence on the n.m.r. timescale. It is important to note that, in solution, a number of conformational possibilities exist resultant on the fact that the two bonds to the bridging atom allow rotational isomerism. For any given relative orientation of the two rings (angle of skew) there are four possible orientations of the bond from the bridge to ring 2 for any given orientation of the bond from ring 1 to the bridge. In the case of two phenylene rings these positions would be equivalent by virtue of being symmetry-related, but in the case of three phenylene rings, such as in the model compound *N*,*N*′-diphenyl-*p*-phenylenediamine (I):



I

this means that there are four possible orientations of the 1,4-axis in ring 3 for any given orientation of the 1,4-axis in ring 1. Interchange between these orientations is, of course, possible by rotation about the carbon–nitrogen bonds. If we therefore consider the chain in leucoemeraldine base to be composed of short stiff segments (the phenylene rings) coupled by rotational junction points (the nitrogens), we can easily envisage that relatively rapid conformational interchange could occur in solution via the normal types of chain motional behaviour. Taking this in conjunction with the averaging due to phenylene ring flipping, the simple two-line spectrum obtained for leucoemeraldine base becomes fully understandable. Rapid conformational interchange would not be expected in solid samples below T_g, however, and this doubtless goes a long way towards explaining the very much broader lines observed for leucoemeraldine base in solid-state ^{13}C spectra[14].

Turning to emeraldine base, the obvious chemical difference is the inclusion of quinoid–imine rings. This not only gives rise to more lines by reducing the structural symmetry of the chain, but also has several other effects by virtue of its bonding. First, because the carbon–nitrogen bonds in the quinoid–imine system are double bonds, there is no possibility of ring flipping and therefore differences may be observed between the two sides of the ring. This is clearly demonstrated in studies[6] on the model compound *N*,*N*′-diphenyl-2,5-cyclohexadiene-1,4-diimine (II):



II

and these effects are reproduced in the observed spectra of emeraldine base, with peaks corresponding to the proton-bearing carbons of the quinoid–imine ring being observed in both the 134 to 137 ppm and 122 to 125 ppm ranges. Since the carbon–nitrogen bonds are constrained to be coplanar with the quinoid–imine ring and the double bonds are effectively rotationally locked, the whole quinoid–imine system shows *cis*–*trans* isomerism, which presumably affects the shifts not only of the

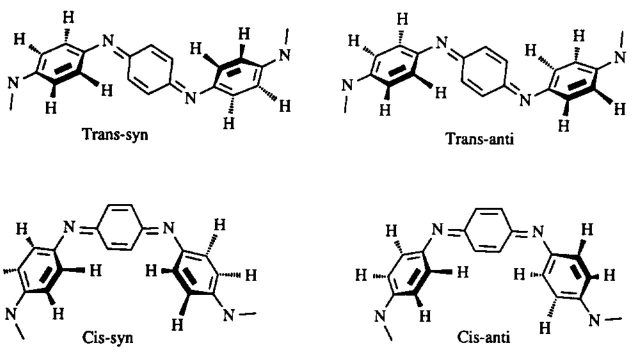


Figure 6 Possible chain conformations about the quinoid–imine ring

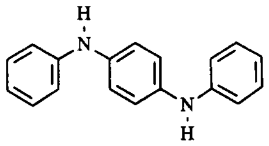
quinoid–imine ring but also of the two phenylene rings attached to it, and indeed the amine-bonded ring beyond that (which would be subject to two such sets of effects, one from either direction down the chain), since it has been shown in the case of other poly(*para*-linked phenylenes) that substituent and other effects at a given site can be detected up to three rings away[20]. It is also the case that, since phenylene ring flips are believed to be at least partially cooperative in the cases where more than one ring is involved, another effect of having the quinoid–imine locked with respect to its substituents would be to block, or at least considerably slow, the ring flipping of the phenylene groups attached to it. If this were the case then differences across the phenylene rings might be apparent in the spectra, and added conformational complexity would be expected because of the relative orientation of the skewed phenylene rings with respect to each other. This is illustrated in *Figure 6*, where *cis*/*trans* refers to the geometry of the phenylene rings in relation to the fixed quinoid–imine ring, and *syn*/*anti* refers to the relative orientations of the phenylene ring hydrogens.

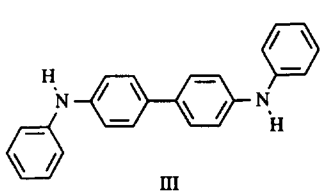
In terms of chain dynamics the introduction of quinoid–imine rings would be expected to have two important effects. First, it halves the number of rotational junctions in the chain, and secondly, it doubles the average length of stiff segment between the rotational junctions (stiff segments are now the doubly amine-bonded phenylene group (one ring), and the quinoid–imine group with its directly bonded phenylenes (three rings)—see *Figure 1*). These two effects would be expected to make the chain significantly stiffer and thus reduce the rate of conformation interchange. This is not to suggest that there is little or no motion in the chain; obviously motion is present otherwise relatively high-resolution spectra would not be obtained. Nevertheless, it seems that certain configurational properties of the chain may be relatively long-lived on the n.m.r. timescale, giving rise to distinct and characteristic signals.

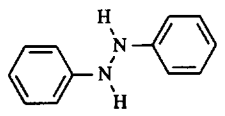
It is not possible to predict how many peaks should be observed in the emeraldine base spectrum on the basis of the above since the size of some of the effects is not known (or indeed if they are present at all), but it is possible to be convinced that the greatest number of peaks that might be observed for such a structure is in excess of one hundred. Thus, the complexity of the observed spectrum is consistent with the postulated structure for emeraldine base.

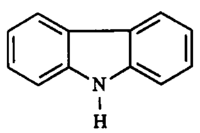
Before leaving this subject, there are two additional points that should be made. First, the quantitative spectrum shows that one in four of the rings is a quinoid–imine, but it cannot be claimed that it shows the quinoid–imine rings are entirely regularly distributed as every fourth ring on the chain. From the spectrum, it would seem that the majority of the rings follow this pattern, but the possibility of occasional disruptions (which would give rise to additional spectral complexity) cannot be ruled out. Secondly, minor peaks due to end-groups, minor substituents, solvent residues and the products of various possible side-reactions were identifiable in the spectrum of leucoemeraldine base and should therefore be expected in the emeraldine base spectrum but will be of too low an intensity for identification.

In order to try to evaluate some of the possible structures that might be giving rise to the minor peaks in the spectrum of leucoemeraldine base (*Figure 3*), the spectra of a series of model compounds were recorded. The model compounds were *N*,*N*′-diphenyl-*p*-phenylenediamine (I), *N*,*N*′-diphenylbenzidine (III), *N*,*N*′-diphenylhydrazine (IV) and carbazole (V):


I


III

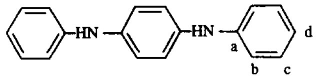
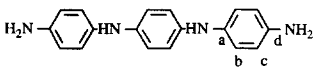
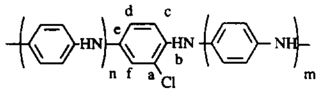
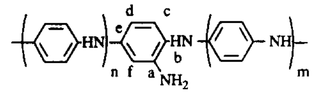
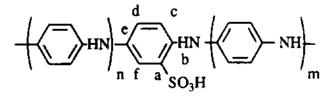
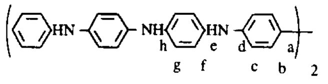
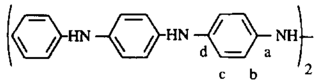
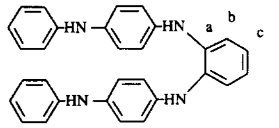
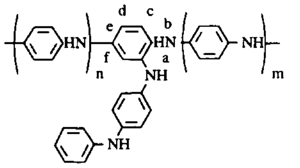
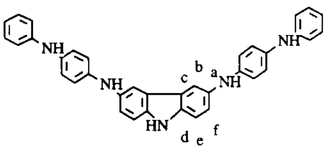
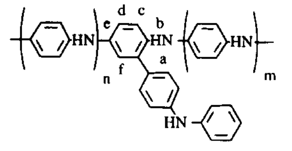

IV


V

These were used in conjunction with the measured chemical shift values for the major peaks in the leucoemeraldine base spectrum and published values for phenyl substituent effects[21] to calculate chemical shift values for postulated structures, the results of some of which are given in *Table 1*. While the quoted values are the result of a fairly crude procedure and should not be regarded as accurate to better than ±1 ppm, they do serve to make some interesting points when these calculated shifts are compared with the minor peaks observed in the spectrum of leucoemeraldine base (*Figure 3*). First, the presence of both types of end-groups (phenyl-capped and amine-capped) is consistent with the observed spectrum, as are chloride and sulphonate as substituents on the chain. The presence of benzidine and diphenylhydrazine type structures in the chain cannot be excluded, neither can the presence of *ortho*-substituted (rather than *para*-substituted) rings in the chain and carbon–carbon bonded branching points, but branching points due to amine-bonded rings seem unlikely, as do carbazole type structures in the chain and amine ring substituents, since no peaks are observed below 110 ppm. More sophisticated models will be required before definite assignments of the minor peaks can be made.

Finally, it was observed during the course of these investigations that the rate of dissolution of the emeraldine base in the solvent system was quite slow even following ultrasonic dispersion. Freshly prepared samples were of relatively low viscosity, but gave low signal-to-noise ratios in the spectra and fewer discernible features than in the normal emeraldine base spectrum presented in *Figure 2*. An example of these effects can be seen in *Figure 4*, where both spectra were obtained within

Table 1 Calculated shifts for postulated structures

Structure	Shifts (ppm)	Comments
	a = 144.9 b = 115.1 c = 129.1 d = 118.3	Observed
	a = 134.9 b = 115.9 c = 116.9 d = 136.5	Calculated for NH_2 substituent[21]
	a = 124.1 b = 137.8 c = 119.2 d = 115.9 e = 138.8 f = 118.2	Calculated for Cl substituent[21]
	a = 136.0 b = 124.0 c = 118.6 d = 107.8 e = 138.2 f = 104.4	Calculated for NH_2 substituent[21]
	a = 132.3 b = 134.7 c = 118.6 d = 121.1 e = 138.2 f = 115.1	Calculated for SO_3H substituent[21]
	a = 131.5 b = 126.2 c = 116.7 d = 142.0 e = 133.2 f = 118.5 g = 115.8 h = 136.0	Calculated for substituent derived from (I)
	a = 142.4 b = 112.5 c = 115.4 d = 133.7	Calculated for substituent derived from (I)
	a = 131.5 b = 115.7 c = 118.9	Calculated for substituent derived from (I)
	a = 134.2 b = 124.0 c = 118.4 d = 107.6 e = 138.0 f = 104.4	Calculated for substituent derived from (I)
	a = 134.9 b = 107.7 c = 123.0 d = 129.5 e = 110.7 f = 112.1	Calculated for substituent derived from (I)
	a = 131.5 b = 134.5 c = 116.7 d = 116.6 e = 136.3 f = 114.9	Calculated for substituent derived from (III)

a few hours of sample preparation. Over a period of about 12 h, the viscosity of the sample increased, but the number of resolvable features in the spectra increased also. After this time the samples apparently remained stable for several days. We interpret this as being due to the slow dissolution of material originally present mainly as finely dispersed solid, so that at short times after sample preparation the concentration of polymer actually in solution would be relatively low (low viscosity and low signal-to-noise ratio), but chain mobility for the material in solution would be relatively high, leading to rapid conformational interchange. As the concentration of material in solution increased, the viscosity and signal-to-noise ratio would increase also, but the rate of conformational interchange would decrease, giving rise to a greater number of distinct features in the spectrum. We report this here because we believe that it may be significant to other workers in, for example, the production of solvent-cast films.

CONCLUSIONS

We have shown that it is possible to obtain high-quality solution-state ^{13}C n.m.r. spectra of polyanilines, and that the information content of these spectra is very much greater than that of solid-state spectra. We have shown that the vast majority (>95%) of the material present in a sample of leucoemeraldine base has the postulated structure (*para*-substituted phenylene rings linked by amine groups). We have shown that emeraldine base has the same skeletal form as leucoemeraldine base (*para*-substituted six-membered rings linked by nitrogens), and that the observed spectrum is consistent with the postulated structure despite its considerable complexity. It is also clear from the data that there are defects in the structure, and although these cannot be identified with certainty they may be present at a concentration of up to 5 mol% of the repeat units. The evidence does not favour branching at amine-bonded ring sites but does not exclude branching at carbon–carbon bonded ring sites, or trisubstituted nitrogens. End-groups form part of the 'defect' resonances, but do not account for all of them.

ACKNOWLEDGEMENTS

We would like to thank Mrs J. M. Say for technical assistance.

REFERENCES

1 Runge, F. F. *Ann. Phys. (Lpz.)* 1834, **31**, 513
2 Fritzsche, J. *J. Prakt. Chem.* 1840, **20**, 453; 1843, **28**, 198
3 Willstatter, R. and Moore, C. W. *Chem. Ber.* 1907, **40**, 2665
4 Green, A. G. and Woodhead, A. E. *J. Chem. Soc.* 1910, **97**,2388; 1912, **101**, 1117
5 Furukawa, Y., Ueda, F., Hyodo, Y., Harada, I., Nakajima, T. and Kawagoe, T. *Macromolecules* 1988, **21**, 1297
6 Sandberg, M. and Hjertberg, T. *Synth. Met.* 1989, **29**, E257
7 Shacklette, L. W., Wolf. J. F., Gould, S. and Baughman, R. H. *J. Chem. Phys.* 1988, **88**, 3955
8 Wu, F. L., Wudl, F., Nowak, M. and Heeger, A. J. *J. Am. Chem. Soc.* 1986, **108**, 8311
9 Wudl, F., Angus, R. O., Lu, F. L., Allemand, P. L., Vachon, D. J., Nowak, M., Liu, Z. X. and Heeger, A. J. *J. Am. Chem. Soc.* 1987, **109**, 3677
10 Devreux, F., Bidan. G., Syed, A. A. and Tsintavis, C. *J. Physique* 1985, **46**, 1595
11 Hjertberg, T., Salaneck, W. R., Lundstrom, I., Somasiri, N. L. D. and Macdiarmid, A. G. *J. Polym. Sci., Polym. Lett. Edn.* 1985, **23**, 503
12 Menardo, C., Nechtschein, M., Rousseau, A., Travers, J. P. and Hany, P. *Synth. Met.* 1988, **25**, 311

13 Hagiwara, T., Yamaura, M. and Iwata, K. *Synth. Met.* 1988, **26**, 195

14 Kaplan, S., Conwell, E. M., Richter, A. F. and Macdiarmid, A. G. *J. Am. Chem. Soc.* 1988, **110**, 7467

15 Monkman, A. P. and Adams, P. *Synth. Met.* 1991, **41–43**, 891

16 Richter, A. F., Ray, A., Ramanathan, K. V., Manohar, S. K., Furst, G. T., Opella, S. J., Macdiarmid, A. G. and Epstein, A. J. *Synth. Met.* 1989, **29**, E243

17 Bendall, M. R. and Pegg, D. T. *J. Magn. Res.* 1983, **53**, 272

18 Spiess, H. W. *Colloid Polym. Sci.* 1983, **261**, 193

19 Schaefer, J., Stejskal, E. O., McKay, R. A. and Dixon, W. T. *Macromolecules* 1984, **17**, 1479

20 Abraham, R. J., Haworth, I. S., Bunn, A. and Hearmon, R. A. *Polymer* 1990, **31**, 728 and references therein

21 Kalinowski, H.-O., Berger, S. and Braun, S. 'Carbon-13 NMR Spectroscopy', Wiley, Chichester, 1988, p. 313