# High-resolution $^{13}$C N.M.R. Spectra of Solid Nitrogen-containing Compounds

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*Summary*. Carbon-13 n.m.r. spectra of glycine, alanine, and valine show splitting of the peaks for carbons bonded to nitrogen, thus giving a useful aid to assignment.

RECENT development of the techniques of dipolar decoupling, cross-polarization, and magic-angle rotation (M.A.R.) points the way to the routine use of high-resolution $^{13}$C n m r spectroscopy of powdered solids In general, it is anticipated that such spectra will be comparable with those for solutions Features peculiar to the solid state are therefore of considerable interest We report that carbon atoms bonded to nitrogen frequently do not give single sharp lines In particular, when $\geqslant$CNH$_3^+$ groups are involved, apparent doublet splittings are seen

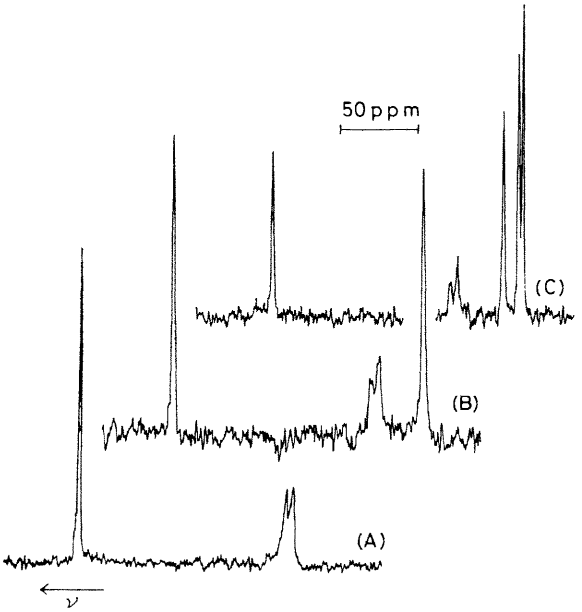

FIGURE 1 22 6 MHz $^{13}$C n m r spectra of some solid amino acids (A) glycine (B) L alanine (C) L valine Conditions contact time 1 ms (700 $\mu$s for B) recycle time 1 s (2 s for A) number of F I D s 8000 (4000 for C)

Figure 1 shows spectra for the amino-acids glycine alanine and valine, which are in the zwitterionic form[1] The sharpness of the carboxy carbon peaks shows that the spinning axis is well set to the magic angle The splittings are seen only for the C–N carbons and are *ca* 100 Hz We do not believe the doubling of the C–N peaks arises from chemical shift effects (*e g* from differing crystallographic sites in the unit cell) since the crystal structure of glycine is known[1] Dipolar coupling effects to $^{14}$N nuclei (which we estimate should give rise to a splitting constant of *ca* 1 kHz) would normally be expected to be averaged to zero by M A R , and elementary considerations of scalar coupling to $^{14}$N would predict triplets rather than doublets The explanation of the observed doublets is probably to be sought in the contradictory effects of quantisation for the quadrupolar $^{14}$N nucleus induced by the magnetic field $B_0$ and that produced by the internal electric field gradient It is probable that the limiting high field condition is not reached, and that under such circumstances M A R cannot average all the relevant interactions[2] Such a hypothesis would predict that the splitting should decrease at higher values of $B_0$ In addition, the bandshape for C–N carbons is likely to be greatly affected by the relaxation rate of the nitrogen We have found that carbons bonded to nitrogen can give rise to a range of effects in solid-state $^{13}$C n m r spectroscopy, sometimes resulting in difficulties of observation The $^{13}$C spectrum of solid tetraethylammonium bromide (Figure 2) apparently shows a single line for the methylene carbon, possibly because there is a low value for the electric field gradient at nitrogen in this molecule Once experience is gained in this area, appearances such as those shown in the Figures can be used as diagnostic tools for assignment purposes

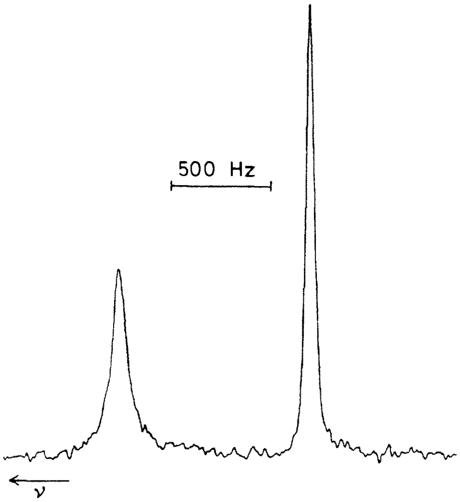

FIGURE 2 22 6 MHz $^{13}$C n m r spectrum of solid tetraethyl ammonium bromide Conditions contact time 5 ms recycle time 700 ms number of F I D s 6000 The width of the methylene carbon line which is to high frequency of the methyl peak is *ca* 80 Hz

A further feature of interest in the spectrum of valine is the separation of the methyl peaks of the isopropyl group (2 6 p p m ) This is to be compared with the value 1 2 p p m in solution[3] In the latter case there is partial averaging due to internal rotation, though complete averaging is not allowed because of the chiral nature of the situation Internal rotation is presumably 'frozen' in the solid, giving rise to the greater separation We believe this is the first reported instance of such a conformational effect about a C–C single bond in a solid state $^{13}$C spectrum, though cases involving a C–O bond are known[2,4] The spectra were obtained on a home-built spectrometer system operating at 22 6 MHz for $^{13}$C, using a novel design for M A R[5] About 100 mg of powdered compound were used in each case to obtain the spectra of Figures 1 and 2

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