CHEMICAL SHIELDING ANISOTROPY OF ^{13}C AND ^{15}N IN ACETONITRILE*

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High resolution ^{13}C and ^{15}N NMR spectra have been obtained for powdered CH_3CN. The presence of resolved dipolar structure in the ^{13}C spectra permits the conclusion that the symmetry axis of the ^{13}C shielding tensor lies along the $C\equiv N$ bond direction.

The technique of proton-enhanced nuclear induction spectroscopy has proved useful for studying the anisotropy of chemical shifts of dilute isotopic species in solids [1–4]. When single crystals are available, rotation patterns can be used to obtain all six independent elements of the (effectively symmetric) chemical shielding tensor for each nucleus [3, 4]. Spectra of polycrystalline samples take the form of powder patterns from which the three principal elements of the shielding tensor are available [5, 6], but the orientation of the principal axis system with respect to crystallographic or molecular coordinates can obviously not be determined.

In this communication we wish to point out that some orientational information can be recovered even from powder spectra when the nucleus whose shielding is observed has a resolved dipolar or indirect coupling to another spin. This principle is not novel: it occurs in electron spin resonance spectroscopy where an electron may have an anisotropic g factor and a resolved anisotropic hyperfine coupling to a nucleus [7]. The chemical shielding and the spin–spin coupling both transform under rotations as second rank tensors, each having its own principal axis system.

Clearly, the form of the powder pattern depends upon the relative orientations of the shielding and coupling tensors. In NMR, as distinct from the usual ESR case, the spin–spin coupling is often completely dominated by dipolar coupling: such a coupling has the convenient feature that it is an axially symmetric tensor and that its symmetry axis has a known orientation in the molecular frame, i.e., it lies exactly along the line joining the two coupled nuclei. Thus the shape of the powder pattern contains information concerning the orientation of the internuclear vector with respect to the principal axis system of the chemical shielding.

A full analysis of this situation is complex and will be deferred to a later and more lengthy communication. In particular, when the two coupled nuclear spins are of the same species but have different chemical shieldings, the behavior of the spectrum is more complicated than in the usual ESR situation where the coupled species are always an electron and a nucleus. For the present, we content ourselves with displaying the spectrum shown in fig. 1 which shows the simultaneous presence of shielding anisotropy and dipolar coupling in its most primitive form. The upper part of the figure shows the proton-enhanced nuclear induction spectrum [2] of the ^{13}C in natural isotopic abundance in CH_3CN which has been enriched in ^{15}N. We expect the ^{13}C shielding to be axially symmetric, characterized by two shielding parameters $\sigma_\parallel$ and $\sigma_\perp$. The spin–spin coupling is expected to be purely dipolar, determined by the C–N internuclear distance R.

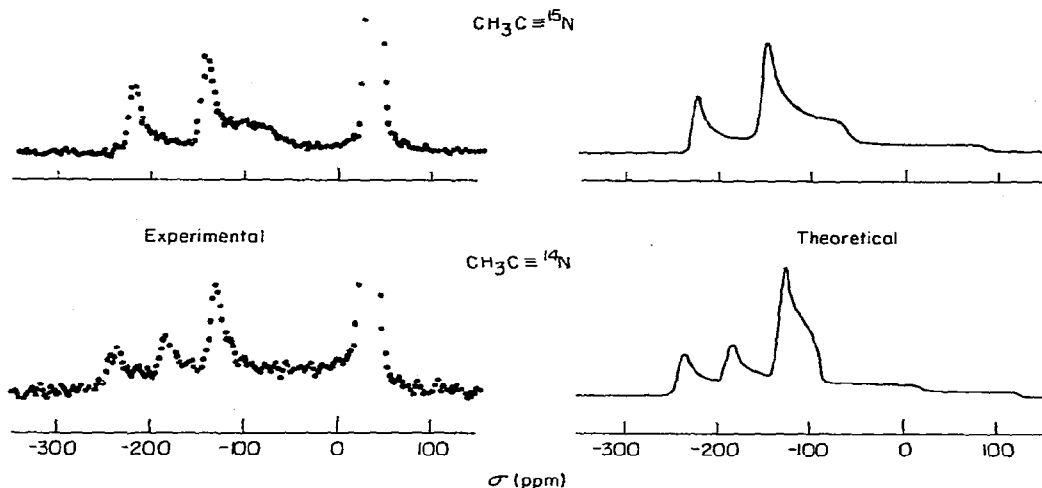An analysis of the spectrum under these assump-

Fig. 1. Theoretical and experimental ^{13}C spectra for ^{15}N enriched and normal acetonitrile at $-190°C$. Upfield sharp peak in the experimental spectrum is from the methyl carbon. Horizontal scale is in ppm relative to an external reference of neopentane.

tions leads to the values $\sigma_{\parallel} = 20 \pm 3$ and $\sigma_{\perp} = -184 \pm 3$ in ppm relative to methyl carbons in solid neopentane and $R = 1.182 \pm 0.04$ au which correspond to the theoretical spectrum shown. A previous microwave study of gaseous CH_3CN [8] found $R = 1.157$ Å. The discrepancy in these values of R appears to be outside experimental error. However, it is probably not profitable to speculate on whether this might be due to an actual difference in R between the gaseous and crystalline state, or possibly due to a contribution from anisotropic J-coupling.

The lower part of the figure shows the proton-enhanced ^{13}C spectrum of CH_3CN containing the normal complement of ^{14}N. The theoretical spectrum was calculated using the same parameters given above.

In the course of these experiments we also determined the ^{15}N chemical shielding anisotropy. This was done at $-190°C$ using proton-enhanced ^{15}N •

spectra from which we obtain the values $\sigma_{\parallel} = -366 \pm 5$; $\sigma_{\perp} = +122 \pm 8$ in ppm relative to $(NH_4)SO_4$.

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