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Observation of Alignment Effects in High-Field Proton NMR Spectra of Hydrogenated Fullerenes: Evidence for Residual Anisotropic Dipole–Dipole Couplings

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Received October 7, 1996

^1H NMR (500 MHz and especially 750 MHz) spectra of the hydrogenated fullerenes C_{60}H_2 and C_{60}H_4 reveal much unexpected fine structure that apparently results from the partial alignment of the molecules in the magnetic field.^{1–3} Molecules with an anisotropic magnetic susceptibility are known to be partially aligned by a magnetic field. Consequently, anisotropic nuclear interactions are incompletely averaged. The alignment effect is much more pronounced at 750 MHz because the order parameters describing the molecular orientation are proportional to the square of the magnetic field. Multiple field (including 750 MHz ^1H), multidimensional NMR has been used recently to obtain dipolar couplings in structural studies of DNA⁴ and proteins.^{5,6}

Our work illustrates alignment effects, with a resulting elimination of C_2 or C_s symmetry, in 1D ^1H NMR spectra of very simple spin systems. Such alignment effects will clearly become more commonly observed as 17.6 T (750 MHz ^1H) and higher field strength magnets become more available. The 750 MHz ^1H spectrum of a dilute solution of C_{60}H_2 dissolved in a 1:1 solution of C_6D_6 – CS_2 reveals two overlapping signals (separation 0.30 Hz without resolution enhancement; digital resolution 0.10 Hz) of equal intensity at δ 6.14 (Figure 1). The two protons in C_{60}H_2 are chemically and magnetically equivalent and would be expected to give just a singlet. A residual dipole–dipole coupling appears to be the most reasonable explanation of the splitting. The splitting does not appear to be an artifact of poor shimming, as the reference TMS signal is a singlet with a line width at half-height of 0.20 Hz. The TMS singlet also rules out frequency jumping caused by deuterium quadrupolar coupling splitting the C_6D_6 lock signal as the cause⁷ of the pair of ^1H signals.

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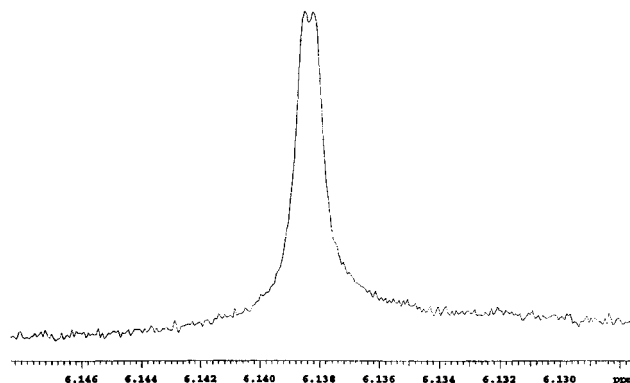


Figure 1. The δ 6.128–6.148 region in the 750 MHz spectrum of C_{60}H_2 dissolved in a 1:1 solution of C_6D_6 – CS_2 .

We are aware of only a few published ^1H spectra of solutions clearly exhibiting ^1H – ^1H dipole–dipole splittings in a two-spin system.^{1,3,8} For two equivalent protons, a splitting of 0.30 Hz corresponds to a dipolar coupling constant D_{HH} of 0.20 Hz,^{3,8,9} which seems reasonable since the ^1H – ^{12}C – ^{13}C – ^1H satellites in the ^1H spectrum of coronene at 600 MHz also exhibit $D_{\text{HH}} = 0.20$ Hz.¹ Because the magnitude of the dipolar coupling constant varies with the square of the field strength,^{1–3} a splitting of 0.13 Hz would be predicted at 500 MHz. However, we were unable to detect this splitting. Prior studies of C_{60}H_2 at 200–500 MHz using various solvents^{10–13} mention no splitting; indeed, a “sharp singlet” is sometimes reported.^{10–12,14}

To detect the splitting in the 750 MHz ^1H spectrum of C_{60}H_2 , a solvent such as C_6D_6 that is also partially aligned by the magnetic field resulting in alignment transfer from solvent to solute⁸ is required. No splitting of the C_{60}H_2 signal is observed in solutions of CDCl_3 or CD_3COCD_3 . In general, the anisotropy and asymmetry of the magnetic susceptibility are affected by the concentration and solvent.^{2,9}

Unexpected fine structure that apparently results from the partial alignment of the molecules in the magnetic field has also been observed with C_{60}H_4 isomers. Thus, some of the C_2 or C_s C_{60}H_4 isomers with two symmetry-equivalent H–C–C–H groups¹⁵ give two highly overlapped AB quartets at 750 MHz (separation <1 Hz) because of two different ^1H – ^1H dipole–dipole coupling constants (or only one nonzero dipolar coupling constant) for the two H–C–C–H groups.¹⁷ Such dipolar coupling is not detected at 500 MHz. The much greater complexity of the entire 750 MHz spectrum compared to the 500 MHz spectrum and the apparent lack of spectral complexity for C_{60}H_4 in $\text{C}_6\text{D}_5\text{CD}_3$ at 400 MHz¹⁶ suggest that the complexity is not related to J_{HH} coupling, is field-dependent, and is barely detectable at 500 MHz. In light of the $1/r^3$ dependence of

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(14) Similarly, the splitting of 0.74 Hz observed for D_{2h} C_{60}H_4 (two pairs of hydrogens added at double bonds on opposite sides of C_{60}^{15}) at 750 MHz has not been observed at lower field strengths.^{13,16}

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(17) A reviewer has suggested that these observations might be explained by the presence of unidentified isomers. To eliminate this possibility, the hydrides were synthesized using ^3He @ C_{60} . ^3He NMR spectroscopy was used to show that unidentified isomers were not present.¹⁸

dipole–dipole couplings and the spherical C_{60} surface, the only reasonable ^1H – ^1H dipole–dipole interactions in a dilute solution can be between protons within a $\text{H}-\text{C}-\text{C}-\text{H}$ group. A more detailed discussion considering these factors (as opposed to those previously advanced¹³ to explain small splittings in the spectrum of $C_{60}\text{H}_4$) will follow.

As 17.6 T and higher frequency magnets become more available, it becomes necessary to keep in mind the possibility of detecting residual anisotropic ^1H – ^1H dipole–dipole couplings and cross correlation between ^1H – ^1H dipole–dipole relaxation and ^1H chemical shift anisotropy relaxation^{19–24} even in relatively simple organic compounds (e.g., ethanol²⁵), especially

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if a lock solvent partially aligned by the magnetic field is used. Ideally, one would use a low concentration of solute in a nonaligning solvent⁸ exhibiting a single, narrow ^2H signal allowing excellent shimming.^{7a} The anisotropic dipole–dipole couplings and cross correlation effects result in additional spectral complexity but provide an opportunity, as noted earlier, to obtain structural information not present in lower field spectra.

Acknowledgment. The Rice 500 MHz NMR facility was established with the support of NIH Grant RR05759 and the W. M. Keck Foundation. We gratefully acknowledge financial support from the National Science Foundation (Grant CHE-9406952) and the Robert A. Welch Foundation. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. A.G. gratefully acknowledges Lucent Technologies for a Fellowship. The University of Texas Medical Branch (UTMB) investigators thank the Sealy and Smith Foundation for financial support. We thank Dr. David G. Gorenstein, Director of the Sealy Center for Structural Biology at UTMB, for his interest and support of this work.

JA963493+

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