Alignment Effects in High Field Proton NMR Spectra of the Hydrogenated Fullerenes $C_{60}H_2$ and $C_{60}H_4$: Evidence for Residual Anisotropic Dipole−Dipole Couplings

Lawrence B. Alemany, Alexander Gonzalez, and W. E. Billups*

Department of Chemistry, Rice University, Houston, Texas 77251

M. Robert Willcott

Department of Radiology, The University of Texas Medical Branch, Galveston, Texas 77555-0793

Edward Ezell and Elliott Gozansky

Department of Human Biological Chemistry & Genetics, The University of Texas Medical Branch, Galveston, Texas 77555-1157

Received September 23, 1996 (Revised Manuscript Received June 9, 1997[⊗] *)*

500 MHz and especially 750 MHz ^1H NMR 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. Molecules with an anisotropic magnetic susceptibility are known to be partially aligned by a magnetic field. The 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. At 750 MHz, a splitting of 0.30 Hz results from a residual anisotropic dipole−dipole interaction between the two magnetically and chemically equivalent protons in $C_{60}H_2$. Similarly, a splitting of 0.74 Hz is observed for D_{2h}-$C_{60}H_4$. Neither of these splittings has been observed previously at lower field strengths. Some of the $C_{60}H_4$ isomers with two symmetry-equivalent H−C−C−H groups clearly 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 non-zero dipolar coupling constant) for the two H−C−C−H groups. Some of the signals from different isomers apparently overlap even at 750 MHz. At least two factors need to be considered in analyzing the unequal peak heights of the two AB quartets from a given isomer: (1) anisotropic relaxation and the resulting line width variations resulting from anisotropic motion and (2) line width variations resulting from cross correlation between $^1H-^1H$ dipole−dipole relaxation and ^1H chemical shift anisotropy relaxation or between ^1H CSA relaxation of one spin and ^1H CSA relaxation of another spin. More detailed experiments under carefully controlled conditions are required for a full analysis, particularly for the e isomer **5**. As noted previously, the choice of lock solvent clearly becomes much more important at very high field strengths.

Introduction

Molecules with an anisotropic magnetic susceptibility χ are partially aligned by a magnetic field; the orienting torque exerted on the molecules by the magnetic field is not completely counteracted by Brownian motion.[1−3] Consequently, anisotropic nuclear interactions are incompletely averaged, which results in spectra with additional fine structure. A decade ago, it was already recognized that partial alignment effects > 0.01 Hz could occur at a field strength greater than about 7 T (300 MHz ^1H).[4] However, because the magnitude of the interaction is very small, careful measurements either with a solute having a large magnetic susceptibility anisotropy $\Delta\chi$ or with a very high magnetic field are usually required for detecting partial alignment effects. Reviews on molecular alignment in high magnetic fields have appeared.[5,6] $^1H-^1H$ and $^1H-^{13}C$ dipolar coupling constants have been measured in small organic molecules,[1,6−8] a paramagnetic organometallic compound,[9] and porphyrins.[1,3] $^1H-^1H$ dipolar coupling constants have also been used to study the solution average conformation of a porphyrin−quinone cage molecule,[10] the flexibility of the linking moiety in diphenylethyne- or diphenylbutadiyne-linked porphyrin arrays in solution,[11] and aromatic−aromatic interactions.[12,13] Recently, multiple field (including 750 MHz ^1H), multidimensional NMR has been used to obtain $^1H-^{13}C$ dipolar couplings in structural studies of a DNA duplex and a DNA quadruplex,[14] $^1H-^{15}N$ dipolar cou-

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

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S0022-3263(96)01808-7 CCC: $14.00

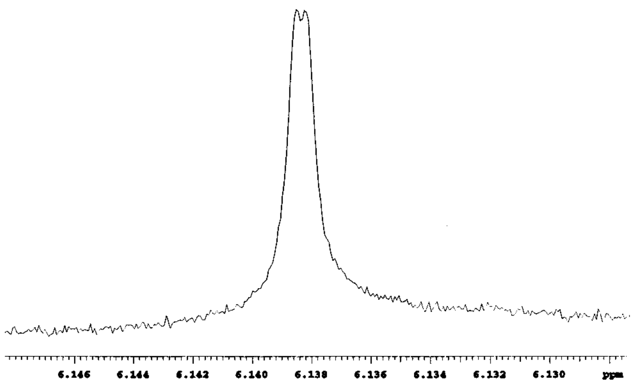
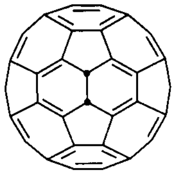


Figure 1. 750 MHz ^1H NMR spectrum of a dilute solution of $C_{60}H_2$ (**1**) dissolved in a 1:1 solution of C_6D_6:CS_2.

plings in structural studies of a paramagnetic protein,[15] and $^1H-^{15}N$[16a] and $^1H-^{13}C$[16b] dipolar couplings in structural studies of a diamagnetic protein. 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.

Results and Discussion

The 750 MHz ^1H spectrum of a dilute solution of $C_{60}H_2$ (**1**) dissolved in a 1:1 solution of C_6D_6:CS_2 is shown in Figure 1. Two signals at δ 6.14 separated by 0.30 Hz are evident (digital resolution = 0.10 Hz); no resolution enhancement was used. This splitting does not appear to be an artefact 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[17] as the cause of the pair of ^1H signals for $C_{60}H_2$.



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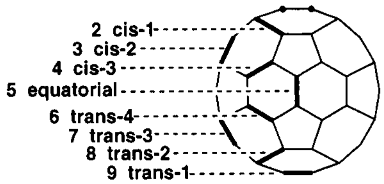
The two protons in $C_{60}H_2$ are chemically and magnetically equivalent and would be expected to give just a singlet. No ^{13}C isotope effect can account for the splitting observed in the 750 MHz spectrum. A residual dipole–dipole coupling appears to be the only reasonable explanation. For two equivalent protons, a splitting of 0.30 Hz corresponds to a dipolar coupling constant D_{HH} of 0.20 Hz,[3–6] which seems reasonable since the $^1H-^{12}C-^{13}C-^1H$ satellites in the ^1H spectrum of coronene at 600 MHz also exhibit D_{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 such a small splitting in a 1:1 solution of C_6D_6:CS_2. Prior studies of $C_{60}H_2$ in C_6D_6 at 300 MHz,[18] 400 MHz,[19] and 500 MHz,[20,21] in CS_2 at 500 MHz,[21] and in $C_6D_5CD_3$ at 200 MHz,[22] make no mention of any such splitting; indeed, a "sharp singlet" is sometimes reported.[18,20,22]

We are aware of only a few published ^1H spectra of solutions clearly exhibiting $^1H-^1H$ dipole–dipole splittings in a two-spin system.[1,3,6] In two cases,[3,6] the dipole–dipole splitting results from a pair of magnetically equivalent protons, just as in $C_{60}H_2$. Future work will involve obtaining a spectrum of the two isomers of $C_{70}H_2$[23] to see if at 750 MHz the isomer with two equivalent protons also gives a pair of signals arising from a dipolar coupling. Previous studies on $C_{70}H_2$ at 500 MHz[21] and at an unspecified field strength[23] reported only a singlet for this isomer.

In order 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 solute[6] 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.[2,5,24–26] Hydrogenated fullerenes are commonly studied in solutions of C_6D_6 or C_6D_6/CS_2, even though C_6D_6 has a non-negligible $\Delta\chi$,[24] because much more material dissolves than in $CDCl_3$ or CD_3COCD_3. $CDCl_3$ has a much smaller $\Delta\chi$ than does C_6D_6 (based on data for the protio isomers[5]). The $\Delta\chi$ of CD_3COCD_3 is presumably negligible; its quadrupolar coupling is much less than that in $CDCl_3$ or C_6D_6.[17a]

Eight isomers of $C_{60}H_4$ can result from two 1,2-additions across a bond common to two six-membered rings (a 6–6 bond). The shorthand nomenclature shown in the diagram presented below was devised by Hirsch *et al.*[42] and is commonly used to differentiate the eight isomers. The two dots indicate the location of the first addition.



Prior[21,27] ^1H spectra and our ^1H spectra of samples of $C_{60}H_4$ are consistent with semiempirical calculations[28]

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indicating that 1,2- rather than 1,4-addition is preferred for adding up to 12 hydrogen atoms to C_{60}. Recent geometry-optimized *ab initio* calculations[29,30] indicate, however, that the 1,2,4,15-$C_{60}H_4$ isomer (resulting from a 1,2-addition and a 1,4-addition) is lower in energy than all but one $C_{60}H_4$ isomer that results from two 1,2-additions across a 6−6 bond. However, neither previous work[21,27] nor our work clearly reveals any signals indicating the presence of the 1,2,4,15-$C_{60}H_4$ isomer (an ABCD spin system).

Another difference between calculations and experiment is provided by $C_{60}H_6$. The predominant isomer appears to be the highly symmetric 1,2,33,41,42,50-$C_{60}H_6$ apparently formed from 1,2,41,42-$C_{60}H_4$ (i.e., **7**).[31] However, **7** was not among the $C_{60}H_4$ isomers considered in calculating the relative energy of $C_{60}H_6$ isomers; only the two lowest energy $C_{60}H_4$ isomers, 1,2,3,4-$C_{60}H_4$ (**2**) and 1,2,4,15-$C_{60}H_4$, were considered.[29,30]

Highly expanded plots of the ^{1}H spectra of our sample of $C_{60}H_4$ dissolved in a 2:1 solution of C_6D_6:CS_2 reveal some splittings at 500 MHz and numerous splittings at 750 MHz (Figures 2−5). More highly expanded plots are required to clearly see some of the fine structure (Figures 6−9). A previous report[21] on the 500 MHz ^{1}H spectrum of $C_{60}H_4$ had indicated that a few pairs of signals were present. The presence of “two almost identical singlets of equal intensity” (frequency difference not given) was attributed[21] to conformationally inequivalent *meso* and (±) isomers of the D_{2h} isomer **9**. However, in light of our data (see below) and other[27] ^{1}H NMR data for $C_{60}H_4$, we believe that these two signals result from the two symmetry-equivalent protons in the e isomer **5**. Similarly, the same report[21] had indicated that a “secondary splitting of *ca.* 0.5 Hz can be seen” in each half of the AB quartet from another of the $C_{60}H_4$ isomers, but in light of our data (see below), we believe that the fine structure results from highly overlapping AB quartets from as many as three isomers. Indeed, it was this overlapping that led to our obtaining a spectrum at 750 MHz. All of the isomers shown in Figures 2−5 eluted in a single chromatographic fraction. Isomer **2**, with its distinctive AA′BB′ spectral pattern, eluted in another fraction.

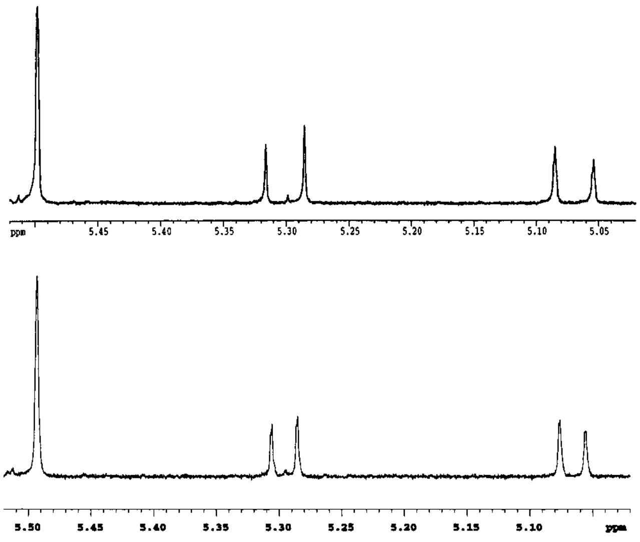

Figure 2. The δ 5.52−5.02 region in the 500 MHz (top) and 750 MHz (bottom) spectrum of $C_{60}H_4$ dissolved in a 2:1 solution of C_6D_6:CS_2. This region contains signals only from the e isomer **5** (an ABM_2 spin system) and constitutes 30% of the total intensity from $C_{60}H_4$ signals. 750 MHz: M_2 broad singlet, δ 5.493; nominal AB quartet centered at δ 5.180, $\Delta\delta = 0.229$ ppm, $J = 15.3$ Hz.

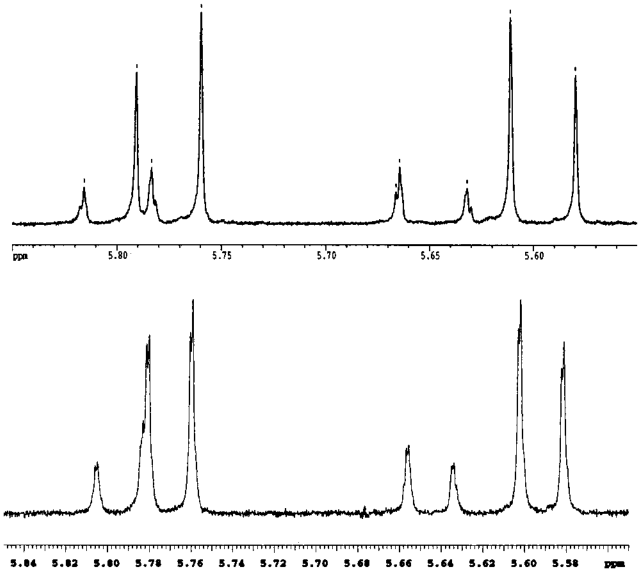

Figure 3. The δ 5.85−5.55 region in the 500 MHz (top) and 750 MHz (bottom) spectrum of $C_{60}H_4$ dissolved in a 2:1 solution of C_6D_6:CS_2. This region contains (at 750 MHz) two sets of AB quartets from one isomer (34% of the total intensity from $C_{60}H_4$ signals) and overlapping AB quartets from perhaps as many as three other isomers (13% of the total intensity from $C_{60}H_4$ signals). For the 34% component at 750 MHz: The AB quartets are centered at δ 5.682, $\Delta\delta = 0.177$ ppm, $J = 15.70$ Hz; the overlapping pairs of signals are separated by 0.93 Hz (most downfield pair), 0.92 Hz, 0.83 Hz, and 0.84 Hz (most upfield pair) (digital resolution = 0.09 Hz). Thus, the difference in the D_{HH} values for the two H−C−C−H groups is about 1.8 Hz. For the overlapping (13%) components at 750 MHz: AB quartets centered at about δ 5.720, $\Delta\delta \approx 0.148$ ppm, $J \approx 16.3$ Hz; the overlapping signals are separated by 0.83, not measurable, 0.84, and 0.93 Hz (digital resolution = 0.09 Hz).

The fine structure seen in the 750 MHz ^{1}H spectrum of $C_{60}H_2$ and in the 500 and 750 MHz ^{1}H spectra of $C_{60}H_4$ clearly cannot be attributed to J_{HH} coupling, nor can it be attributed to signals from unidentified isomers resolved only at 750 MHz. The latter possibility could be eliminated from the ^{3}He NMR spectrum of the corresponding chromatographic fraction of $^3He@C_{60}H_4$ (i.e., hydrides synthesized using $^3He@C_{60}$), which showed only five of the seven possible ^{3}He NMR signals,[32] all with reasonable ^{3}He chemical shifts for $^3He@C_{60}H_4$ species based on previous work.[33,34] These five signals correspond to the isomer in Figure 2, the major isomer and at least one minor isomer in Figure 3, the isomer in Figure 4, and the isomer in Figure 5. More highly expanded plots (Figures 8 and 9) of the weak ^{1}H NMR signals in Figure 3 suggest (see later) that these signals result from highly overlapping AB quartets from two or three isomers. For the ^{1}H chemical shifts of different isomers to be so similar implies that the ring currents

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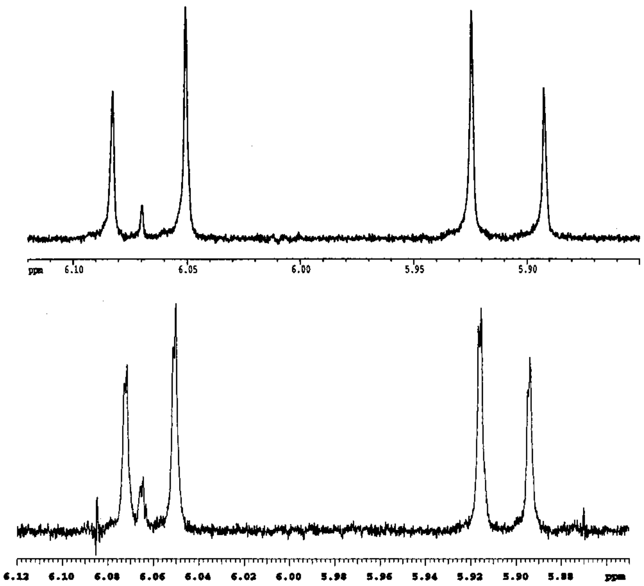

Figure 4. The δ 6.12−5.85 region in the 500 MHz (top) and 750 MHz (bottom) spectrum of $C_{60}H_4$ dissolved in a 2:1 solution of C_6D_6:CS_2. This region contains (at 750 MHz) two sets of AB quartets from one isomer (19% of the total intensity from $C_{60}H_4$ signals). At 750 MHz: The AB quartets are centered at δ 5.984, $\Delta\delta = 0.155$ ppm, $J = 16.2$ Hz; the overlapping pairs of signals are separated by 0.74, 0.84, 0.93, and ≈0.65 Hz (digital resolution = 0.09 Hz). Thus, the difference in the D_{HH} values for the two H−C−C−H groups is about 1.6 Hz.

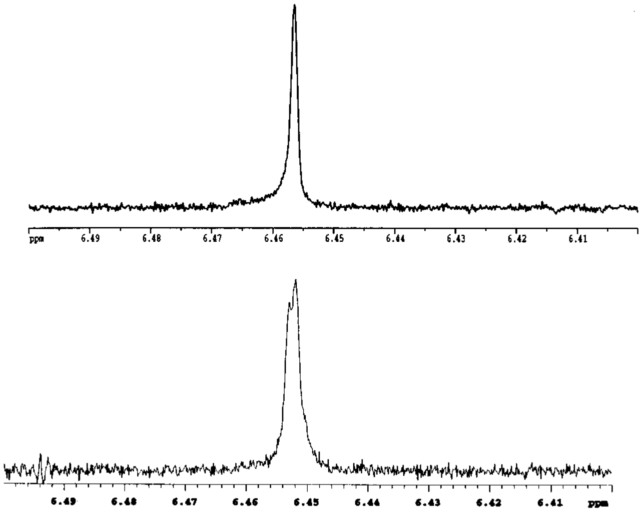

Figure 5. The δ 6.50−6.40 region in the 500 MHz (top) and 750 MHz (bottom) spectrum of $C_{60}H_4$ dissolved in a 2:1 solution of C_6D_6:CS_2. This region contains signals only from the D_{2h} isomer **9** and constitutes 4% of the total intensity from $C_{60}H_4$ signals. At 750 MHz, the overlapping signals are separated by 0.74 Hz.

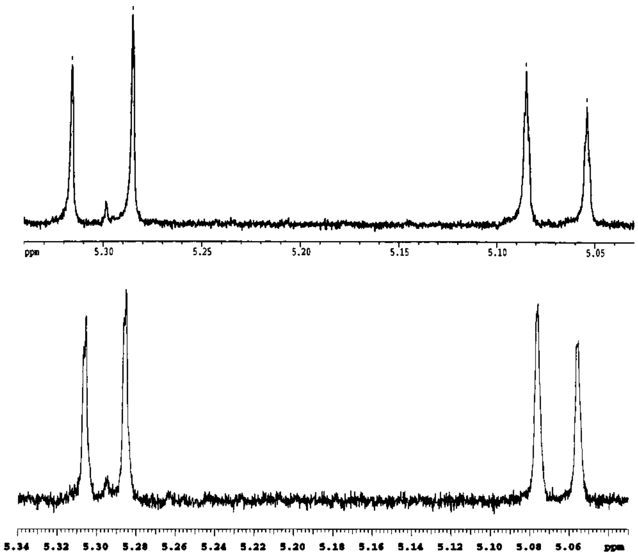

Figure 6. An expanded plot of just the nominally AB part of the 500 MHz spectrum (top) and 750 MHz spectrum (bottom) of the e isomer **5**.

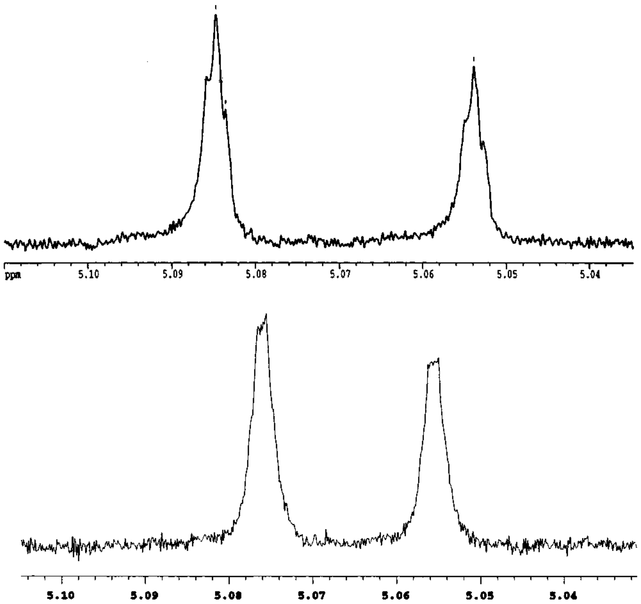

Figure 7. An expanded plot of just the upfield half (i.e., the signals from just one proton) of the nominally AB part of the 500 MHz spectrum (top) and 750 MHz spectrum (bottom) of the e isomer **5**.

in these isomers are correspondingly similar, which would cause their ^{3}He NMR chemical shifts to be nearly identical and thus, perhaps, unresolved. The low abundance of these isomers and the low S/N of the 11.7 T (381 MHz ^{3}He) NMR spectrum[32] make detection of weak ^{3}He NMR signals even more difficult. The absence of highly characteristic ^{3}He NMR signals from ^{3}He@C_{70} species[35−37] also argues against the possibility of hydrogenated C_{70} impurities causing the ^{1}H spectral complexity seen in Figures 2−9. An even stronger argument against such a possibility is that $C_{70}H_2$[23] and $C_{70}H_4$[21] are known to give ^{1}H NMR signals well upfield of those from $C_{60}H_2$ and $C_{60}H_4$.

The ^{3}He NMR spectrum of the chromatographic fraction of ^{3}He@**2** gave just one signal,[32] as expected. Thus, a total of six ^{3}He NMR signals was observed, just as in an unfractionated mixture of ^{3}He@$C_{60}H_4$ studied by another group at Yale and New York University.[33,34] The six signals are spread over 2.2 ppm in our sample (dissolved in 2:1 C_6D_6:CS_2) and over 2.5 ppm in the

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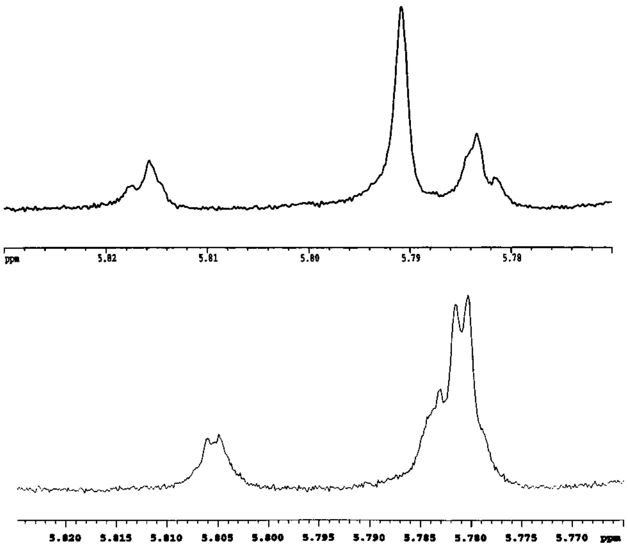

Figure 8. An expanded plot of the downfield half of overlapping AB quartets from as many as three isomers at 500 MHz (top) and 750 MHz (bottom).

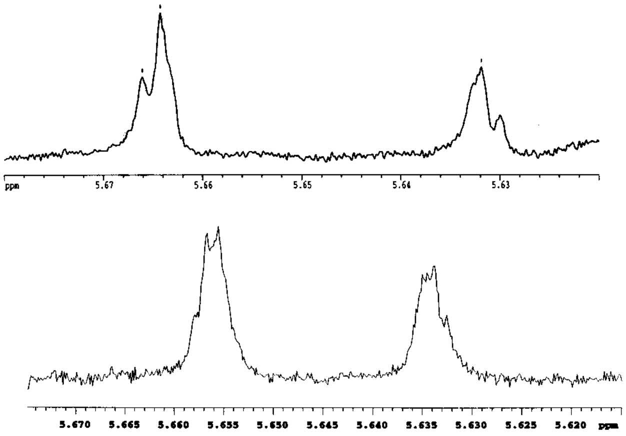

Figure 9. An expanded plot of the upfield half of overlapping AB quartets from as many as three isomers at 500 MHz (top) and 750 MHz (bottom).

unfractionated mixture (dissolved in 1-methylnaphthalene/CD_2Cl_2). The only ^3He signal assigned to a specific isomer is from the fraction of $^3He@\mathbf{2}$ dissolved in 2:1 C_6D_6:CS_2. While the chemical shifts relative to dissolved ^3He in the two solvent systems are not the same, the qualitative similarity of the ^3He NMR spectra is readily apparent. For example, in each case the two most upfield (and also the two most intense) signals are separated by just 0.05 ± 0.01 ppm and presumably result from the same two isomers. The Yale/NYU investigators[33,34] indicated that the intensity of the ^3He NMR signals is consistent with the isomer ratios derived from the ^1H spectrum and HPLC analysis of the crude reaction mixture. Thus, one can reasonably infer that the two most upfield and most intense ^3He NMR signals in our work result from the major isomer in Figure 3 (34% of the total) and the e isomer **5** in Figure 2 (30% of the total).

The ^1H signals from all of the isomers are spread over 1.4 ppm (from about δ 5.05−6.45). Including isomer **2**, with its distinctive AA′BB′ spin system, increases the spread to 1.8 ppm (about δ 4.65−6.45). The ^1H chemical shifts of isomers of $C_{60}H_4$ vary for the same reason as do the ^3He chemical shifts of isomers of $^3He@C_{60}H_4$: the ring current in each $C_{60}H_4$ isomer is different,[33,34] although in some cases, this difference may be very small. Other ^1H NMR work[22,23] on $C_{60}H_2$ and $C_{70}H_2$ and ^3He NMR work on the $^3He@C_{60}$ and $^3He@C_{70}$ pair[38] and on the $^3He@C_{61}H_2$ and $^3He@C_{71}H_2$ pair[36] have similarly shown a significant change in the ring current in going from the C_{60} species to the corresponding C_{70} species.

The fine structure seen in the 750 MHz ^1H spectrum of $C_{60}H_2$ and in the 500 and 750 MHz ^1H spectra of $C_{60}H_4$ appears to be unique among spectra of derivatized C_{60} and C_{70}. $C_{60}H_4$ is the simplest bis adduct of C_{60} resulting from two 1,2-additions across a 6−6 bond. No such fine structure has apparently been reported in the 500 MHz ^1H spectral data of isomers of $C_{70}H_4$[21] or in the ^1H, ^{13}C, or ^{31}P spectral data of numerous more complex bis,[34,39−58] tris,[42−44,50,51] tetrakis,[44,50,51,59,60] pentakis,[59,61] hexakis,[44,59,61−66] heptakis,[66] and octakis[66] adducts of C_{60} or C_{70}. Similarly, we have not found any reports of such fine structure in spectra of mono adducts of C_{60} or C_{70}. Mono adducts with equivalent nuclei give the expected spectral patterns, the most notable of which may be the singlets from the equivalent ^{31}P, ^1H, ^{13}C, or ^{29}Si nuclei in $[(C_6H_5)_3P]_2Pt(\eta^2$-

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C_{60}),[67] the pyrazoline C_s-$C_{60}(CH_2N_2)$,[68] the methanofullerene C_s-$C_{60}CH_2$,[69] the methanofullerene C_s-$C_{60}C(CH_3)_2$,[70] the two pyrazolines C_s-$C_{70}(CH_2N_2)$,[71] the methanofullerene C_s-$C_{70}CH_2$,[71] C_{2v}-$C_{120}CH_2$ (the methylene-bridged dimer of C_{60}),[72] 1,2- and 1,4-$C_{60}(CH_3)_2$,[73] and 1,16-$C_{60}(SiR^1R^2R^3)_2$.[74] (These 1,4- and 1,16-adducts are mono adducts in the sense that, like the 1,2-adducts, they result from addition of two groups to C_{60}. Larger addends preferentially add in a 1,4- or, if necessary, 1,16-manner to minimize steric interactions.[75-78]) Adducts with inequivalent ^{31}P or ^1H nuclei give the expected spectral patterns, the most notable of which may be the $^2J_{PP}$ couplings exhibited by the inequivalent phosphorus nuclei in $C_{70}\{Pt(PPh_3)_2\}_n$, $n = 1-4$;[51] the $^2J_{HH}$ couplings exhibited by the inequivalent protons in the $C_{61}H_2$ and $C_{71}H_2$ 6,5-annulenes,[68,71] a $C_{70}CH_2$ methanofullerene different from that above,[71] and yet another $C_{70}(CH_2N_2)$ pyrazoline;[71] and the singlets exhibited by the inequivalent methyl groups in the 6,5-annulene $C_{61}(CH_3)_2$.[70]

We are aware of only two ^1H spectra of adducts of C_{60} obtained at 600 MHz[48,79] and are unaware of any ^1H spectra of adducts of C_{60} obtained at higher frequencies. The much greater complexity of the 750 MHz spectrum compared to the 500 MHz spectrum of our sample of $C_{60}H_4$ (Figures 2−5) and the apparent lack of spectral complexity for $C_{60}H_4$ in $C_6D_5CD_3$ at 400 MHz[27] suggest that the complexity is not related to J_{HH} coupling, is field-dependent, and is barely detectable at 500 MHz. Indeed, attempts at simulating[80] some of the multiplets in the 750 MHz spectrum by using various long range J_{HH} couplings in addition to $^3J_{HH}$ couplings do not yield any patterns similar to those observed. (For the e isomer **5**, $^6J_{HH} < 0.1$ Hz.[81]) Consequently, residual anisotropic $^1H-{}^1H$ dipole−dipole interactions resulting from partial alignment of the $C_{60}H_4$ molecules have to be considered.

In light of the $1/r^3$ dependence of 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 H−C−C−H group. However, incorporating a non-zero D_{HH} between such protons merely changes the frequency separation between lines 1 and 2 and between lines 3 and 4 of an AB quartet from J_{AB} to $J_{AB} + D_{AB}$; J_{AB} and D_{AB} can have the same or opposite signs,[3-6] but still only four signals result (Table 1).[5]

Table 1. Frequencies and Intensities for the 4 Lines of an AB Quartet under the Influence of Scalar and Dipolar Couplings[a]

line	frequency	intensity
1	$(J + D)/2 + C/2$	$1 - [(J - D/2)/C]$
2	$-(J + D)/2 + C/2$	$1 + [(J - D/2)/C]$
3	$(J + D)/2 - C/2$	$1 + [(J - D/2)/C]$
4	$-(J + D)/2 - C/2$	$1 - [(J - D/2)/C]$

[a] $C = [(\Delta\nu)^2 + (J - D/2)^2]^{1/2}$.

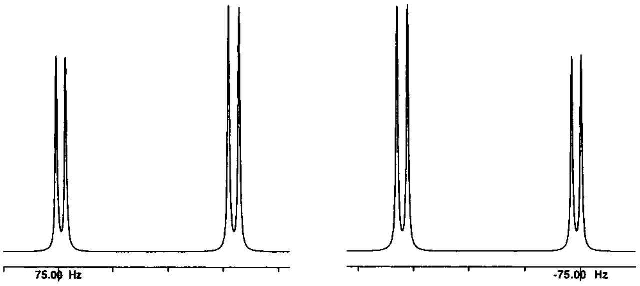

Figure 10. Simulated 750 MHz spectrum of two AB spin systems with the same chemical shifts (+66.4 Hz and −66.4 Hz) and the same $^3J_{HH}$ scalar coupling constant (15.7 Hz) but with different D_{HH} dipolar coupling constants (+0.9 Hz and −0.9 Hz). Thus, the frequency separation $J_{AB} + D_{AB}$ between lines 1 and 2 and between lines 3 and 4 is 16.6 Hz for one AB quartet and 14.8 Hz for the other AB quartet. Expanded plots from +80 Hz to +54 Hz and from −54 Hz to −80 Hz are shown. The simulation used Lorentzian line shapes and a line width at half-height of 0.20 Hz. The $\Delta\nu$, $^3J_{HH}$, and D_{HH} values are based upon the 750 MHz spectrum of the most abundant component shown in Figure 3.

For a given 4-line pattern, the relative intensities of the inner and outer signals depend on $^3J_{HH}$, D_{HH}, and the frequency difference $\Delta\nu$ between the two protons. However, incorporating two different dipolar coupling constants (or only one non-zero dipolar coupling constant) for the two H−C−C−H groups (D_{wx} for H_w−C−C−H_x and D_{yz} for H_y−C−C−H_z; assume $D_{wx} > D_{yz}$) in a given $C_{60}H_4$ isomer with C_2 or C_s symmetry results in two 4-line patterns with corresponding pairs of signals separated by $(D_{wx} - D_{yz})/2$ (since $[(J + D_{wx}) - (J + D_{yz})] = D_{wx} - D_{yz}$) (Figure 10). $D_{wx} \neq D_{yz} \neq 0$ if the angles of the H_w−H_x and H_y−H_z vectors relative to the magnetic alignment axis slightly differ. Furthermore, two different dipolar coupling constants result in the relative intensities of the four signals of the *WX* quartet differing from the relative intensities of the four signals of the *YZ* quartet. However, at 750 MHz (see Figures 3 and 4), the observed relative peak heights for the two 4-line patterns from the two H−C−C−H groups in a given isomer still differ from the simulated intensities (Figure 10). This difference in peak heights cannot be explained by using other values differing by 1.8 Hz for the two dipolar couplings constants (e.g., $D_{HH} = 1.8$ Hz and 0 Hz), as the intensity term $(J - D/2)/C$ changes by only about 0.3% compared to $D_{HH} = +0.9$ Hz and −0.9 Hz. (Within experimental error, the D_{HH} values appear to be equal and opposite based upon the chemical shifts and peak separations in the 500 and 750 MHz spectra.) In contrast, at 500 MHz (see Figures

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3 and 4), only one AB quartet appears for each isomer; the intensity of the two inner signals is the same; and the intensity of the two outer signals is the same—all as expected. At this point, we believe that the different peak heights of signals separated by $(D_{wx} - D_{yz})/2$ in the 750 MHz spectra most likely result from anisotropic motion and cross correlation effects.

Inequivalent line widths resulting from inequivalent spin–spin relaxation times $[\nu_{1/2} = 1/(\pi T_2)]$ for H_w and H_x compared to H_y and H_z in **2**–**8** would result in different peak heights. Anisotropic motion causes relaxation to depend on the orientation of the internuclear vector relative to the magnetic alignment axis.[82] However, such anisotropic relaxation is not possible in **9** because of its higher symmetry. A previous example of such anisotropic relaxation can be found in the inequivalent T_2 values for the two *N*-acetyl methyl groups at the N termini of the alamethicin dimer in methanol solution; these two methyl groups are inequivalent in terms of the angle subtended by them with respect to the long axis of the dimer.[83]

In addition, we cannot rule out the possibility of variation in line widths between lines 1 and 2 and between lines 3 and 4 of an AB quartet resulting from cross correlation between ^{1}H–^{1}H dipole–dipole relaxation of spins A and B and ^{1}H chemical shift anisotropy (CSA) relaxation of spin A[84–90] at 750 MHz. Cross correlation is extremely sensitive to rotational anisotropy,[91a] and the spectral density $J_{ABA}(\omega)$ of this cross correlation is proportional to the field strength and to the ^{1}H CSA.[85] Furthermore, even if the CSA spectral density of spin A is only a small fraction of the dipole–dipole spectral density, the dipole–dipole/CSA cross term $J_{ABA}(\omega)$ can be significant.[85] However, trying to measure any variation in line widths between lines 1 and 2 and between lines 3 and 4 is complicated by the presence of extensively overlapping pairs of signals resulting from the unequal dipolar coupling constants. Probing the possibility of cross correlation between ^{1}H–^{1}H dipole–dipole relaxation and ^{1}H CSA relaxation is well beyond the scope of this initial work. Such cross correlation within a H–C–C–H group of $C_{60}H_4$ at 750 MHz is certainly plausible, since this cross correlation has been shown at 500 MHz for two ortho aromatic protons in a salicylate ion in a viscous aqueous solution with cetyltrimethylammonium bromide[84] and at field strengths ranging from 300–720 MHz for two ortho aromatic protons in a dilute solution of 2,3,4,3′,4′,5′-hexahydroxybenzophenone.[85–87,89,90] (For the salicylate ion, the more downfield component of the doublet is much broader.[84] Similarly, for the AX spin system in the benzophenone derivative, the differences in the transverse relaxation time for the two components of each doublet show that the more downfield component relaxes faster in each doublet.[86,90])

Similarly, we cannot rule out the possibility of variation in line widths between lines 1 and 2 and between lines 3 and 4 of an AB quartet resulting from cross correlation between ^{1}H CSA relaxation of spin A and ^{1}H CSA relaxation of spin B[92,93] at 750 MHz. The CSA of spin B can apparently contribute unequally to the line width of each of the two A-spin signals via the B-spin CSA autocorrelation and the cross correlation between CSA relaxation of spin B and CSA relaxation of spin A.[93] There has to be a resolved *J* coupling between spin A and spin B for this auto and cross correlation to be in effect.[93]

We cannot account for unequal peak heights in the 750 MHz spectrum of the purely dipolar-coupled protons in the A_2 spin system in **9** (Figure 5) but equal heights for the analogous A_2 spin system in **1** (Figure 1). Only a singlet is observed in the 500 MHz spectra of **1** or **9**. Considerably more unequal peak heights have been observed in another purely dipolar-coupled A_2 spin system (the methylene group of a cyclopentenone ring in a porphyrin in which $D_{HH} = 1.32$ Hz at 600 MHz).[3]

For a purely dipolar-coupled A_2 spin system, the transverse relaxation can be multiexponential.[94–96] In the absence of *J* coupling, but in the presence of direct dipole–dipole/CSA cross correlation, the off-diagonal term $R_{1313} - R_{2424}$ is nonzero (where the eigenstates are $|1> = \alpha\alpha$, $|2> = \alpha\beta$, $|3> = \beta\alpha$, and $|4> = \beta\beta$, and thus, $R_{\alpha\beta\alpha\beta}$ is the line width of the coherence $|a> \leftrightarrow |b>$).[93] Unequal line widths imply unequal peak heights. The two signals are partially resolved in our work only because of the residual ^{1}H–^{1}H dipole–dipole coupling. We also note that a distance-independent CSA autocorrelation term results, via the direct dipole–dipole/CSA cross correlation, in a second-order effect on the decay rates.[93] Transverse and longitudinal relaxation measurements and 2D DQF-NOESY experiments would provide additional information,[85,86,90,97] and experiments with still better field homogeneity and digital resolution might better define the lineshapes to facilitate a more detailed analysis, including a consideration of any orientation-independent, field-dependent, second-order dynamic frequency shift[16a,91b,98] (also termed a cross-correlation-induced *J* coupling[99]) for each signal of an AB quartet. Such a detailed analysis may be necessary for the complex signals, even at 500 MHz, from the inequivalent protons in the e isomer **5**. As discussed earlier, in light of the ^{3}He NMR spectrum of ^{3}He@$C_{60}H_4$,[32] the complexity of the ^{1}H signals in Figures 6 and 7 cannot reasonably be attributed to the presence of more than one isomer. The complexity of the upfield ^{1}H signals resulting from just one proton in the nominally AB quartet (Figure 7) relative to the downfield signals resulting from the other proton (Figure 6) suggests that the upfield signals result from the proton closer to the two other nominally equivalent protons (the M_2 protons

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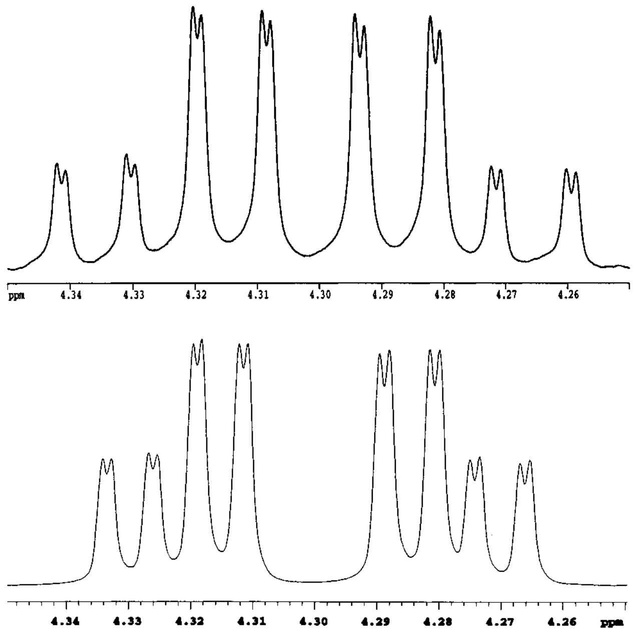


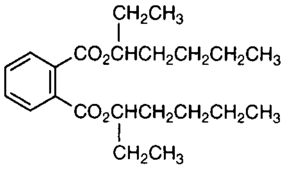
Figure 11. An expanded plot of the OCH_2CHRR' methylene proton region in a dilute solution of 1,2-bis(2-ethylhexyl)phthalate (**10**) dissolved in C_6D_6 at 500 MHz (top) and 750 MHz (bottom).

of this ABM_2 spin system). Unlike the 500 MHz AB quartets in Figures 3 and 4, the 500 MHz AB quartet in Figure 6 has inner signals of unequal height and outer signals of unequal height. The ABM_2 spin system is unique to the e isomer **5**; the integrated intensities (as opposed to peak heights) are in the expected 1:1:2 ratio; and the shift assignments are consistent with previous work in $C_6D_5CD_3$.[27]

Comparing the chemical shifts of various isomers of $C_{60}H_4$ dissolved in a 2:1 solution of C_6D_6:CS_2 (Figures 2−5) with the chemical shifts in $C_6D_5CD_3$[27] shows that the signals in C_6D_6:CS_2 are consistently 0.12−0.14 ppm further downfield. Comparing the chemical shifts in C_6D_6:CS_2 with the chemical shifts in C_6D_6[21] shows that the signals in C_6D_6:CS_2 are 0.15−0.16 ppm further downfield in most cases, but seem to be 1.11 ppm further downfield for the D_{2h} isomer **9** (δ 6.45 vs δ 5.34) and seem to be the same for the two symmetry-equivalent protons (the singlet) in the e isomer **5** (δ 5.49). Furthermore, for **5**, the chemical shift difference between the singlet and the center of the nominal AB quartet is 0.31 ppm in $C_6D_5CD_3$[27] or in C_6D_6:CS_2 but is 0.46 ppm in C_6D_6.[21] (Note, however, that the chemical shift assignment of this AB quartet in C_6D_6 was not obvious when the work was done[21] but is now possible in light of the subsequent work in $C_6D_5CD_3$[27] and C_6D_6:CS_2.) Taken together, these data indicate that the signal at δ 5.34 in C_6D_6[21] (not at δ 5.49) is the singlet in **5**, which results in a chemical shift difference between the singlet and the center of the nominal AB quartet of 0.31 ppm. With the signal at δ 5.34 in C_6D_6 no longer assigned[21] to the D_{2h} isomer, the apparent discrepancies for the data in C_6D_6 are explained. Thus, the "two almost identical singlets of equal intensity"[21] at δ 5.34 in C_6D_6 should be attributed to the two symmetry-equivalent protons in **5**. In our work (Figure 2), the M_2 protons in **5** give an unusually broad singlet (line width = 1.8 Hz at 750 MHz).

The same report[21] also indicated that a "secondary splitting of *ca.* 0.5 Hz can be seen" in each half of the AB quartet from another of the $C_{60}H_4$ isomers, but we believe that the fine structure results from highly overlapping AB quartets from as many as three isomers. The relevant signals are centered at δ 5.57 in C_6D_6[21] and at δ 5.72 in C_6D_6:CS_2 (Figures 8 and 9). At 500 MHz, the four groups of signals are at δ 5.815 and δ 5.783 (Figure 8) and at δ 5.664 and δ 5.632 (Figure 9). The 500 MHz spectrum shows that the downfield signals (Figure 8) are roughly mirror images of the upfield signals (Figure 8). (The signals are not plotted on the same vertical scale in Figures 8 and 9; they are in Figure 3.) The complexity of these four groups of signals suggests, but does not prove, that these signals result from highly overlapping AB quartets from two or three isomers. Unfortunately, the 750 MHz spectrum does not provide a definitive indication; the resolved signal from one species at δ 5.791 at 500 MHz overlaps signals of interest from other species at 750 MHz, and additional fine structure may result at 750 MHz from $^1H-^1H$ dipole−dipole couplings.

The common plasticizer 1,2-bis(2-ethylhexyl)phthalate (**10**) was a contaminant found in several samples (based on a comparison of the ^1H spectra of the samples with the ^1H spectrum of an authentic sample of **10**) as well as in previous work.[21] The ^1H spectrum of this phthalate is also interesting. The inequivalent methylene protons adjacent to the oxygen constitute the AB part of an ABX spin system and would therefore be expected to give two 4-line AB patterns.



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However, at 500 and 750 MHz, 8 *pairs* of overlapping signals appear (Figure 11) for a dilute solution of **10** in C_6D_6, $CDCl_3$, or CD_3COCD_3. The 1.5-ppb frequency difference within any pair of signals is constant within experimental error (Table 2), which indicates that D_{AB} is zero within experimental error, i.e., there is no detectable residual anisotropic dipole−dipole interaction. Rather, the 8 pairs of signals result from the two diastereomers of **10** (each alkyl group has a chiral center). Each diastereomer gives two 4-line AB patterns; corresponding 4-line patterns from the two diastereomers are offset from each other by only about 1.5 ppb. The separation between signals 1 (most downfield) and 5, 3 and 7, 9 and 13, and 11 and 15 from one diastereomer and the separation between signals 2 and 6, 4 and 8, 10 and 14, and 12 and 16 (most upfield) in the other diastereomer is constant in hertz within experimental error (10.96 ± 0.03 Hz) and is just the familiar J_{AB} separation for the outer pairs of signals in an AB quartet. Even with the C_6D_6 partially aligned by the magnetic field, the anisotropic magnetic susceptibility of **10** is too small to detect under the conditions used. In contrast, the methylene protons in rigid five-membered rings (fluorene[6] and several porphyrins[1,3]) have readily detectable dipolar couplings (with D_{HH} in the porphyrins ranging from 1.06−1.77 Hz at 600 MHz). With a difference of only 1.5 ppb for the ^1H chemical shift of the OCH_2 group in the two diastereomers of **10**, trying to resolve two sets of ^{13}C signals, even for the spatially proximate

Table 2. Frequency Difference (in ppb) within the 8 Pairs of Signals from the Inequivalent Methylene Protons in the OCH_2CHRR' Group in 10 Dissolved in C_6D_6

field strength	pair 1[a]	pair 2	pair 3	pair 4	pair 5	pair 6	pair 7	pair 8[b]
500 MHz[c]	1.38	1.36	1.32	1.34	1.48	1.52	1.52	1.54
750 MHz[d]	1.43	1.41	1.43	1.43	1.57	1.71	1.56	1.56

[a] Most downfield pair of signals. [b] Most upfield pair of signals. [c] Digital resolution = 0.077 Hz (0.15 ppb). [d] Digital resolution = 0.049 Hz (0.065 ppb).

^{13}C nuclei near the chiral centers, should prove challenging, even under very high resolution conditions.[100]

Summary

Additional work will be required to fully understand all of the phenomena presented in this paper. Nevertheless, as 17.6 T and higher frequency magnets become more available, it becomes necessary to keep in mind the possibility of detecting, even in relatively simple organic compounds (e.g., ethanol[101]), residual anisotropic $^1H-^1H$ dipole−dipole coupling, cross correlation between $^1H-^1H$ dipole−dipole relaxation and ^1H CSA relaxation, or cross correlation between ^1H CSA relaxation of one spin and ^1H CSA relaxation of another spin—especially if a lock solvent partially aligned by the magnetic field is used. Ideally, one would use a low concentration of solute in a nonaligning solvent[6] exhibiting a single, narrow ^2H signal allowing excellent shimming.[17a] The anisotropic dipole−dipole couplings and cross correlation effects result in additional spectral complexity but provide an opportunity, as illustrated in the Introduction, to obtain structural information not present in lower field spectra. Obtaining such information requires appropriate acquisition and processing conditions, especially with spin systems yielding more complex spectra than the isolated two-spin systems discussed in this work.

Experimental Section

The synthesis and isolation of the $C_{60}H_2$, $C_{60}H_4$, and $^3He@C_{60}H_4$ samples have been reported.[102] 1,2-Bis(2-ethylhexyl)phthalate was from Lancaster Synthesis (Windham, NH). Solutions were neither degassed nor sealed before study in high precision Wilmad 528PP tubes. Spectra were recorded under ambient conditions (about 23 °C) on a Bruker AMX500 (at Rice) and with temperature control (20 °C) on a Varian UNITY*plus*750 (at UTMB). Calibrated 90° pulses and a digital resolution of 0.077 Hz (0.15 ppb) at 500 MHz and a digital resolution of 0.093 Hz (0.12 ppb) at 750 MHz were used unless noted otherwise. No line broadening or resolution enhancement was used. Samples were refrigerated between spectroscopic analyses in order to minimize solvent evaporation and decomposition[81] of the hydrogenated fullerenes. The slight differences in temperature and concentration resulted in small (i.e., ppb) chemical shift differences for a given isomer at the two field strengths; the spectra in the figures are deliberately arranged so that the signals are aligned.

Acknowledgment. The Rice 500 MHz NMR facility was established with the support of NIH grant RR05759 and the W. M. Keck Foundation. The Rice investigators thank the Department of Biochemistry & Cell Biology for providing access to the 500 MHz spectrometer and, in particular, thank Dr. William K. Wilson for instruction in its use and access to the gNMR software program. We gratefully acknowledge financial support from the National Science Foundation (CHE-9112530) and the Robert A. Welch Foundation. Acknowledgment 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 UTMB investigators thank the Sealy and Smith Foundation for financial support and Dr. Joe Schwartz for assistance at the beginning of this study. All the investigators thank Dr. David G. Gorenstein, Director of the Sealy Center for Structural Biology at UTMB, for his interest and support of this work. L.B.A. also thanks Dr. Donald E. Woessner of the University of Texas Southwest Medical Center for his interest in this work and reviewing a draft manuscript. We thank the referee for a careful review and helpful comments.

JO961808Y

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