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Solvation of Hydrocarbons by Aromatic Solvents: Origin of the Doubling of the Methylene ^1H Envelope for Long-Chain Hydrocarbons in 1-Chloronaphthalene

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ABSTRACT: Heteronuclear (^{13}C–^1H) shift-correlated two-dimensional NMR spectra are used to investigate aromatic solvent induced shifts (ASIS) for straight-chain hydrocarbons in 1-chloronaphthalene. All ^1H chemical shifts can be assigned. The pattern of ASIS demonstrates that the previously noted doubling of the methylene envelope for long-chain hydrocarbons in this solvent reflects subtle differences in solvation rather than slow gauche–anti interconversions. The ability of this 2D experiment to extract accurate ^1H chemical shifts from a complex spectral envelope makes it particularly useful for investigations of macromolecules.

A number of years ago, Liu observed that the methylene envelope in the ^1H spectrum of long-chain ($>C_{16}$) hydrocarbons is split into a doublet in 1-chloronaphthalene.[1] A number of subsequent publications have attempted to provide an explanation for this observation.[2-7] The most thorough investigation has been carried out by Ando and co-workers, who concluded, mainly on the basis of ^1H chemical shift calculations, that the second peak arose from an increased number of gauche conformations for long-chain hydrocarbons in 1-chloronaphthalene.[3,4] However, there are very serious problems with this explanation. For example, the methylene doublet is still observed at 120 °C. This indicates a barrier to gauche–anti conformer interconversion of at least 120 kJ mol^{-1}, far higher than any known barrier for C–C bond rotation.[6] Furthermore, the ^{13}C spectra for long-chain hydrocarbons in 1-chloronaphthalene are almost identical with those observed in $CDCl_3$.[6] If long-lived (on the NMR time scale) gauche conformers are present in 1-chloronaphthalene, one might expect to see two distinct ^{13}C peaks for each CH_2 group, due to the well established gauche γ shielding effect.[8] Finally, it has been observed that the low-field component of the ^1H doublet increases in relative area with increasing chain length.[2,6] However, rotational isomeric state calculations indicate a negligible variation in gauche–anti ratio with chain length for hydrocarbons longer than pentane.[9] These and other similar observations led us to conclude that the methylene doublet actually reflected different solvent (ring-current) effects on internal CH_2 groups and those near chain ends.[6] However, Ando et al. have recently reiterated their arguments in favor of persistent gauche conformations, supported by results of variable-pressure ^1H NMR measurements.[10]

Since the origins of this phenomenon are still in dispute almost 20 years after its initial observation, we decided to carry out an experiment that should provide a definitive explanation for the doubling of the methylene ^1H envelope. Heteronuclear shift-correlated two-dimensional NMR spectra allow simultaneous determination of ^{13}C and ^1H chemical shifts for directly bonded ^1H–^{13}C pairs.[11] Due to the greater ^{13}C chemical shift dispersion, this should allow one to extract from the methylene envelope the ^1H chemical shift(s) of each CH_2 group. This should either reveal two distinct ^1H chemical shifts for each CH_2 group,

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Table I
^{1}H Chemical Shifts for Eicosane in 90% 1-Chloronaphthalene/10% C_6D_6 and in $CDCl_3$ and Aromatic Solvent Induced Shifts for Eicosane and Other Straight-Chain Hydrocarbons

compound	parameter	C-1[a]	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
$C_{20}H_{42}$	δ_H(1-Cl)[b]	0.89_3	1.24_3	1.15_5	1.17_9	1.17_7	1.19_8	1.21_2	1.23_8	1.24_8	1.24_8
	$\delta_H(CDCl_3)$[b]	0.88_1	1.30_3	1.25_9	1.27_3	1.27_3	1.26_8	1.26_8[c]	1.26_8[c]	1.26_8[c]	1.26_8[c]
	$\Delta\delta$[d]	$+0.01_2$	-0.06_0	-0.10_4	-0.09_4	-0.09_1	-0.07_0	-0.05_6	-0.03_0	-0.02_0	-0.02_0
	$\Delta\delta(0.1)$[d]	$+0.01_4$	-0.06_2	-0.09_9	-0.09_4	-0.09_4	-0.06_6	-0.05_6	-0.01_8	-0.01_4	-0.00_9
$C_{16}H_{34}$	$\Delta\delta$	$+0.00_9$	-0.05_8	-0.08_6	-0.09_5	-0.09_0	-0.07_6	-0.06_7	-0.06_2		
$C_{12}H_{26}$	$\Delta\delta$	$+0.00_2$	-0.06_0	-0.09_5	-0.10_7	-0.08_3	-0.07_9				
$C_{10}H_{22}$	$\Delta\delta$	0.00_0	-0.07_6	-0.12_3	-0.14_6	-0.16_1					
C_8H_{18}	$\Delta\delta$	-0.02_4	-0.10_8	-0.16_9	-0.18_7						

[a] Carbon for which chemical shift is tabulated. Symmetrically equivalent carbons (e.g., C-8 and C-9 in hexadecane) are listed only once. [b] ^{1}H chemical shifts (relative to internal tetramethylsilane in ppm) in 90% 1-chloronaphthalene/10% C_6D_6 (1-Cl) or $CDCl_3$ ($CDCl_3$). [c] ^{13}C chemical shifts for these methylene groups are not resolved in $CDCl_3$. Line width suggests identical ^{1}H chemical shifts. [d] Chemical shift change from $CDCl_3$ to 1-chloronaphthalene. $\Delta\delta(0.1)$ refers to 0.1 M solution for eicosane.

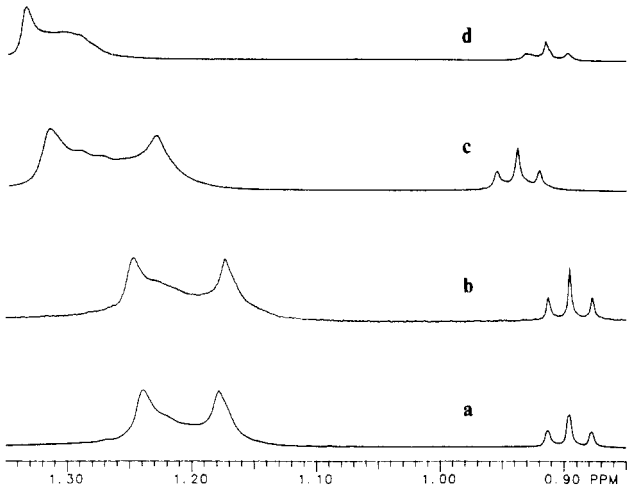

Figure 1. ^{1}H spectrum for eicosane in (a) 90% 1-chloronaphthalene/10% C_6D_6, (b) same solvent, 0.01 M solution, (c) 90% 1-methylnaphthalene/10% C_6D_6, and (d) C_6D_6. Unless otherwise indicated, solutions are 0.4 M in eicosane.

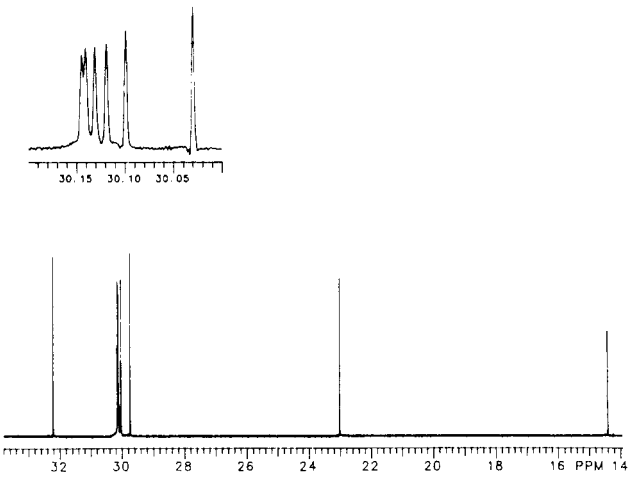

Figure 2. ^{13}C spectrum for eicosane in 90% 1-chloronaphthalene/10% C_6D_6. Insert shows expansion of internal CH_2 region of the spectrum.

corresponding to gauche and anti conformers, or a single peak reflecting the time-averaged environment of that group.

Results and Discussion

Initial spectra were obtained with 55 mg of eicosane in 0.5 mL of 90% (v/v) 1-chloronaphthalene/10% C_6D_6 (the latter providing the deuterium lock signal). A 400-MHz ^{1}H spectrum showed the expected methylene ^{1}H doublet (Figure 1a). Furthermore, all 10 nonequivalent carbons could be observed in the corresponding ^{13}C spectrum (Figure 2). Carbons C-1 through C-4 were assigned on the basis of previous assignments for straight-chain hydrocarbons.[12] The remaining carbons were assigned from partially relaxed spectra obtained with an inversion–recovery (180°–τ–90°) pulse sequence.[13] Assignments were based on the increase in ^{13}C spin–lattice (T_1) relaxation times from the middle to the end of the chain due to segmental motion.[6]

A heteronuclear shift-correlated experiment was then carried out. Contour plots for the methylene region of the resulting 2D spectrum are illustrated in Figure 3. Individual ^{1}H chemical shifts were obtained by taking f_1 cross sections through the ^{13}C (f_2) frequency of each methylene signal. Results of the experiment are summarized in Table I. They reveal that there is a single ^{1}H signal associated with each methylene group, conclusively ruling out Ando's explanation of separate peaks associated with gauche and anti conformers. Rather, the ring-current effect of the aromatic solvent molecule must give rise to different magnetic environments for the different protons, depending upon their average position with respect to the aromatic rings.[6] However, the actual pattern of shifts is unusual in that the low-field envelope arises from protons bonded to C-2 and C-8–C-10 and the high-field envelope from C-3 to C-6 protons with C-7 protons showing intermediate chemical shifts. In order to separate out solvent

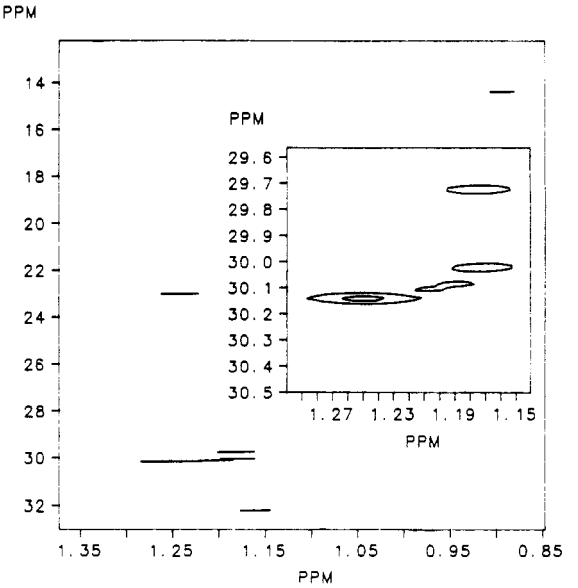

Figure 3. Heteronuclear (^{13}C–^{1}H) shift-correlated spectrum for eicosane in 90% 1-chloronaphthalene/10% C_6D_6. ^{1}H frequencies are along the horizontal with ^{13}C frequencies along vertical. Insert shows expansion of internal methylene region.

Table II
Aromatic Solvent Induced Shifts for Eicosane in Different Aromatic Solvents, Relative to Tetramethylsilane and to the Methyl Group of Eicosane

solvent	parameter	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
1-Cl[a]	$\Delta\delta$[b]	$+0.01_8$	-0.06_0	-0.10_4	-0.09_4	-0.09_1	-0.07_0	-0.05_6	-0.03_0	-0.02_0	-0.02_0
	$\Delta(\Delta\delta)$[c]	(0.000)	-0.07_2	-0.11_6	-0.10_6	-0.10_3	-0.08_2	-0.06_8	-0.04_2	-0.03_2	-0.03_2
1-CH_3[d]	$\Delta\delta$	$+0.05_6$	-0.02_5	-0.04_8	-0.03_5	-0.03_4	-0.00_5	$+0.01_4$	$+0.05_6$	$+0.05_6$	$+0.05_6$
	$\Delta(\Delta\delta)$	(0.000)	-0.08_1	-0.10_4	-0.09_1	-0.09_0	-0.06_1	-0.04_0	0.000	0.000	0.000
C_6D_6	$\Delta\delta$	$+0.03_9$	$+0.01_3$	$+0.01_8$	$+0.03_2$	$+0.03_7$	$+0.05_2$	$+0.06_5$	$+0.07_5$	$+0.07_5$	$+0.07_5$
	$\Delta(\Delta\delta)$	(0.000)	-0.02_6	-0.02_1	-0.00_7	-0.00_2	$+0.01_3$	$+0.02_6$	$+0.03_6$	$+0.03_6$	$+0.03_6$

[a] 90% 1-Chloronaphthalene/10% C_6D_6. [b] Change in ^1H chemical shift from $CDCl_3$ to indicated solvent. [c] Aromatic solvent induced chemical shifts expressed relative to the terminal methyl group. This connects for solvent effects on the reference. [d] 90% 1-Methylnaphthalene/10% C_6D_6.

effects from shifts that were intramolecular in origin, the same series of experiments was repeated for eicosane in $CDCl_3$, assuming that this solvent would give relatively small specific effects. Results are reported in Table I. In this solvent, all methylene protons except for C-2 protons occur in a narrow chemical shift range. A similar low-field C-2 ^1H chemical shift has been noted for pentane and attributed to C–C bond anisotropy effects.[14]

Chemical shift changes on going from $CDCl_3$ to 1-chloronaphthalene (i.e., aromatic solvent induced shifts (ASIS)) are also listed in Table I. The absolute magnitudes of these shifts must be interpreted with caution since there will also be a significant (negative) ASIS for the internal reference, tetramethylsilane.[15] Nevertheless, relative magnitudes of ASIS are still valid for determining relative screening effects. These show that C-3–C-5 protons are most strongly shielded on going from $CDCl_3$ to 1-chloronaphthalene while C-8–C-10 protons and methyl protons show ASIS similar to that for the reference tetramethylsilane.

Very similar ASIS are observed for hexadecane, dodecane, decane, and octane (see Table I). The only significant trend is one of increasingly negative ASIS with decreasing chain length. It is apparent from these data that the doubling of the methylene envelope is only observed for longer hydrocarbons simply because only they have sufficient methylene groups to allow the observation of differential shielding effects between internal methylene groups and those near chain ends. Hydrocarbons longer than eicosane show an increase in the relative area of the low-field component of the methylene doublet with increasing chain length,[2,6] indicating that they show ASIS patterns similar to that for eicosane.

To check for possible concentration effects, shift-correlated experiments were also carried out with a 0.1 M solution of eicosane. Observed ASIS were almost identical with those for the 0.4 M solution (Table I). Furthermore, a 0.01 M solution of eicosane in 1-chloronaphthalene gave a ^1H spectrum that was indistinguishable from that for the 0.4 M solution (see Figure 1). Thus concentration effects such as chain aggregation can be conclusively ruled out as the source of the differential shielding of internal and chain-end methylene groups. Previous alternative explanations such as chain folding[2] or increased numbers of gauche conformers[3,4,10] in 1-chloronaphthalene are also highly improbable. To begin, there are slight low-field ^{13}C shifts (ca. 0.3 ppm) for the methylene carbons of eicosane on going from $CDCl_3$ to 1-chloronaphthalene, while gauche steric interactions should cause significant high-field ^{13}C shifts.[8] Furthermore 1-chloronaphthalene is known to be a good solvent for long-chain hydrocarbons, since $\langle r^2 \rangle$, the mean-square end-to-end distance, is much larger for polyethylene in 1-chloronaphthalene than in Θ solvents.[16] In related work, the UV spectral shifts for naphthalene in hydrocarbon solvents have been interpreted in terms of a favorable interaction of the aromatic molecule with a $CH_2CH_2CH_2$ segment in an all-anti conformation.[17] In a more extreme case, it is known that long-chain hydrocarbons are adsorbed on graphite in an all-anti conformation.[18]

However, it is unlikely that our results and those of previous workers reflect a strong solvent–solute interaction. There should be a large negative ASIS for tetramethylsilane in 1-chloronaphthalene.[15] Allowing for this, one sees that we are actually dealing with a situation where all methylene protons are strongly shielded but where the effect is slightly greater for methylenes near chain ends. In other words, C-3–C-5 methylene protons have a slightly higher probability of being located near the "face" of an aromatic solvent molecule than that for internal methylene protons (and tetramethylsilane). This may reflect both a tendency for the solvent to promote extended conformations of the solute[17] and the way in which the solute is incorporated into the partially ordered solvent structure. Similarly, the recent results of Ando and Inouye[10] likely reflect small pressure-induced changes in solvation.

Previous workers have assumed unique solvent properties for 1-chloronaphthalene.[1-4,10] However, if our weak interaction model is correct, there should be only small and subtle changes in ASIS as one changes the shape and/or polarity of the solvent molecule. To check this, we have carried out measurements for eicosane in 1-methylnaphthalene and benzene. The methylene envelope is similar in shape for all three solvents (Figure 1). While absolute magnitudes of ASIS are different,[19] relative ASIS within a molecule are quite similar (Table II). The differences are greatest for benzene. Since 1-methylnaphthalene is almost the same size as 1-chloronaphthalene but closer in polarity to benzene, this suggests that solvent shape is more important than solvent polarity in determining ASIS for a nonpolar solute.

In summary, the heteronuclear shift-correlated spectra have allowed us to conclusively rule out the presence of slowly (on the NMR time scale) interconverting gauche and anti conformers for hydrocarbons in 1-chloronaphthalene. At the same time, the ability of this experiment to "pick out" the chemical shift of each proton from a complex spectral envelope makes it possible to obtain a detailed picture of very subtle solvent effects. This information should represent a considerable challenge to theoreticians interested in a solvent–solute interaction involving hydrocarbons. In more general terms, the heteronuclear shift-correlated experiment is ideally suited for investigations of polymer microstructure since ^{13}C spectra of polymers are typically much better resolved than ^1H spectra.[20]

Experimental Section

All compounds and deuterated solvents used in this investigation were obtained from Aldrich and were used without further

purification. All NMR spectra were obtained on a Varian XL-400 spectrometer operating at 399.93 MHz for ^1H and 100.56 MHz for ^{13}C at a probe temperature of 18 ± 1 °C. Unless otherwise indicated, spectra were obtained for 0.4 M solutions of hydrocarbon in the appropriate solvent.

Heteronuclear shift-correlated spectra were obtained with a version of this experiment that provides ^1H–^1H decoupling.[21] Typical spectra were obtained with a 240-Hz spectral width in the f_1 (^1H) domain and 2000-Hz spectral width for f_2 (^{13}C). Forty time increments were used with zero-filling in 256 in f_1 while 2048 data points were collected in f_2 with zero-filling to 4096. Sixty-four transients were collected for each time increment and, with a relaxation delay of 1.0 s between increments, total measuring time was 1.1 h. Pseudoecho processing[22] was applied in both domains to ensure maximum resolution. Repeat measurements indicated that ^1H chemical shifts could usually be determined with a precision of 0.005 ppm, i.e., 2 Hz.

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Registry No. $C_{16}H_{34}$, 544-76-3; $C_{12}H_{26}$, 112-40-3; $C_{10}H_{22}$, 124-18-5; C_8H_{18}, 111-65-9; eicosane, 112-95-8; 1-chloronaphthalene, 90-13-1; 1-methylnaphthalene, 90-12-0.

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Matrix Effects on the Diffusion of Long Polymer Chains†

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ABSTRACT: The diffusion of long chains of molecular weight M (M-chains) into matrices of molecular weight P is studied by forward-recoil spectrometry. The matrix molecular weight P ranged from very short unentangled chains below the critical molecular weight for entanglement M_c to long highly entangled chains. Whereas the tracer diffusion coefficient D^* of the M-chains is independent of P for sufficiently large P in the entangled regime ($D^* \sim M^{-2}$), it rapidly increases with decreasing P for P less than a characteristic molecular weight P^* which increases slowly with M. This behavior is consistent with theoretical predictions that $D^* = D_{rep} + D_{cr}$. Here D_{rep} is the diffusion coefficient due to the reptation of the M-chain, and D_{cr} is an additional matrix contribution to the diffusion of the M-chain that arises from the simultaneous diffusion of the surrounding P-chains (constraint release). We find that D_{cr} scales approximately as $M^{-1}P^{-3}$. In the unentangled regime ($P < M_e$) studies were conducted at different temperatures where the fractional free volume of each matrix was equal to a constant, 0.042. Here the tracer diffusion coefficient scales approximately as $D^* \sim M^{-(0.5-0.6)}P^{-1}$, a result that is consistent with the chain diffusing as a coil of hydrodynamic radius $R \sim M^{-(0.5-0.6)}$ in a viscous environment whose viscosity scales as P.

Introduction

Current theories predict that the center of mass diffusion of a polymer chain of molecular weight M in an entangled polymer matrix of molecular weight P may occur by three different processes: reptation,[1,2] constraint release (tube renewal),[3-6] or Stokes–Einstein[5,6] diffusion. Which type of behavior is observed is expected to depend on the values of P and M.

The theory of Doi and Edwards[7] predicts that the diffusion of the chain of molecular weight M (M-chain) in a high molecular weight matrix occurs by reptation. Here motion of the chain is restricted to a tubelike region that is defined by the topological constraints of the neighboring matrix chains. As it crawls along the primitive path that its "tube" defines, its lateral motions are assumed to be prohibited on the time scale $\tau_{rep}(M) \sim M^3$, the time for it to diffuse out of the tube. If the constraints defining this tube remain relatively immobile on the time scale $\tau_{rep}(M)$, then the tracer diffusion coefficient D^* of this chain depends only on its molecular weight M so that

$$D^* = D_{rep}(M) = D_0 M^{-2} \quad (1)$$

where D_0 is independent of M. There is considerable experimental evidence that supports this prediction.[8-15]

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