The NMR Spectra of Normal Alkanes and the Conformation of Linear Hydrocarbons in Aromatic Solvents

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ABSTRACT: A variety of NMR techniques have been employed to examine the source of the peculiar doubling in the ^1H NMR of the CH_2 envelope of *n*-alkanes, observed when these molecules are dissolved in certain aromatic solvents. ^{13}C chemical shift and T_1 measurements as well as ^1H chemical shift and T_1 and T_2 measurements indicate that this splitting is due to solvation effects associated with the chain ends and not due to unusual conformations imposed on the chains by their solvent environment.

In 1967 Liu published the first in a series of very careful observations of the proton magnetic resonance spectrum of *n*-alkanes in aromatic solvents.[1] He discovered a peculiar effect, that the singlet peak associated with the CH_2 groups of the chain is split into a doublet in 1-chloronaphthalene solutions for chains longer than 15 carbons. The effect was explored in some detail,[2] and in the early 1970's Ando repeated many of these experiments at higher (220 MHz) resolution,[4,5] confirming Liu's observations, and explored aspects of the phenomenon in more detail.

The nature of the phenomenon may be summarized as follows:[1-3] In 1-chloronaphthalene, both the methylene and methyl proton resonances are shifted with respect to the pure liquids or CCl_4 solutions. The extent of shift depends upon chain length, but not on concentration. For chains longer than 15 carbons, the methylene peak is seen to be a doublet. As the chain length increases, the downfield peak increases in intensity relative to its upfield partner. Raising the temperature causes the upfield peak to broaden, but even at 100 °C the two peaks do not coalesce. The magnitude of the chemical shift changes and the splitting of the methylene envelope are rather small, on the order of tenths of a ppm.

The explanation of this phenomenon which has emerged is at odds with the currently accepted picture of hydrocarbon chain conformation in ordinary solvents. Liu originally offered the speculation that "oligomers of polymethylene exhibit a sharp conformational transition as a function of chain length in certain bulky aromatic solvents".[2c] This was followed by a carefully reasoned analysis of the thermodynamics of chain folding,[3] in which it was pointed out that for a sufficiently unfavorable solvent–solute interaction (i.e., in terms of the Flory χ parameter), solute–solute interactions will predominate, and the molecule will collapse to a folded configuration which maximizes contacts between pairs of CH_2 groups. If the loop of the fold is solvated differently than the tail, ring current effects will be different. Splitting of the methylene resonances will occur. Ando and Nishioka interpreted the results differently.[4,5] They, too, saw the origin of the phenomenon as a conformational constraint imposed by the solvent. In their explanation, the chemical shift differences between protons involved in gauche bonds and those in trans bonds give rise to two peaks. In planar aromatic solvents, these forms are taken not to interconvert on an NMR time scale and thus are not averaged to a single peak.

Recently Barrales-Rienda[6] reported a similar phenomenon for *n*-alkyl maleimides in benzene solution. The terminal substituent is seen to accentuate the effect. Splitting of the methylene hydrogens into a doublet is seen for chains of ten or more carbons at 100 MHz resolution, whereas for the simple alkanes in benzene, it cannot be observed even at 220 MHz. These authors also support the ideas of Ando and Nishioka, that strong solute–solvent interactions diminish local segmental mobility of the chain. The rate of exchange among various conformations decreases, giving double peaks for alkanes sufficiently long.

We were attracted to the problem in part because the phenomena themselves are interesting, but also because the explanations currently proposed are at odds with one another and with currently accepted behavior of hydrocarbon chains in dilute solution.[7] Various techniques are available now, namely ^{13}C NMR and ^{13}C T_1 relaxation measurements, which are very sensitive to changes in conformation and rates of molecular motion. In this paper we present several new experimental results and offer some critical comments on possible explanations for the peculiar effect seen in the ^1H NMR spectrum of alkanes.

Experimental Section

^1H NMR spectra of the *n*-alkanes were carried out in Bordeaux on a Varian HA100 spectrometer, at 25 °C, which was used as well for determination of proton relaxation times. Measurements of ^1H NMR at 220 MHz were obtained using a Varian HR-220 spectrometer. ^{13}C spectra and ^{13}C spin–lattice relaxation times for all protonated carbons were obtained at 20.09 MHz and at 32 ± 2 °C on a Varian CFT-20 spectrometer. The T_1's for all carbons were determined simultaneously by the Inversion-Recovery Pulse method, modified by Levy and Peat (FIRFT).[8] The solutions, 0.5 M, were degassed by bubbling nitrogen through the solution for 1 min to remove dissolved oxygen. T_1 values are accurate to within ±5–15% with the T_1's for the terminal methyl group having the greatest error. For the determination of each T_1, 16–20 sets of measurements were used. Estimated accuracies for ^{13}C chemical shifts are better than 0.02 ppm.

Results

The effect causing methylene peak doubling is not confined to 1-chloronaphthalene and 9-chloroanthracene. We have observed the effect for docosane in 1-methylnaphthalene, 1,4-dimethylnaphthalene, and in mixtures of toluene–naphthalene rich in the latter substance. In addition, significant nonsymmetric broadening of the methylene envelope is observed in the following solvents: mesitylene, xylene, ethylbenzene, and toluene. A well-

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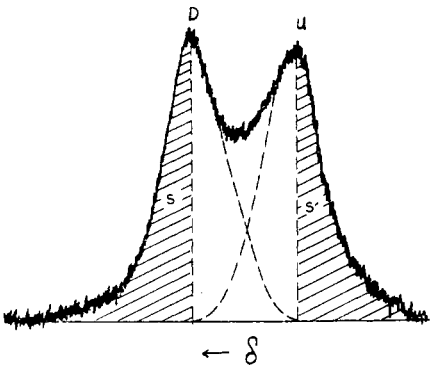


Figure 1. Methylene envelope of the ^1H NMR spectrum of *n*-eicosane in 1-chloronaphthalene with the data fit to the sum of two Lorentzian curves.

Table I
Widths at Half-Height (Hz) of Upfield (U) and Downfield (D) Components of the Doublet Associated with the ^1H CH_2 Envelope of Eicosane in 1-Chloronaphthalene

	T °C					
	26	35	53	65	91	121
$\Delta_{1/2}^{D}$	2.5	2.4	2.2	2.0	1.6	1.4
$\Delta_{1/2}^{U}$	3.6	3.4	3.3	3.2	4.6	5.2

defined shoulder appears in anisole and indene solutions. These results emphasize that it is the size and shape of the aromatic solvent, and probably the nature of the ring current associated with it, that are responsible for the changes in chemical shifts observed.

Temperature Effects. As reported by Liu[1,2] and by Ando and Nishioka,[4] we observe small changes in the splitting of the methylene doublet of *n*-eicosane as a function of temperature in 1-chloronaphthalene solution. If the methylene doublet is forced to fit the sum of two Lorentzian curves as shown in Figure 1, the chemical shift differences as a function of temperature are those shown in Figure 2. Line widths, determined as peak widths at half-height of the curves fit as in Figure 1, are collected in Table I. The most important feature of the data is the insensitivity of the relative chemical shifts and of the line widths to rather large changes in temperature. There is no evidence of coalescence of the doublet.

Proton Relaxation Times. Proton spin–spin relaxation times (T_2) and proton T_1 relaxation times were measured at 29 °C by the methods of Carr and Purcell.[9] Values obtained for a 5 mol % solution of docosane in CCl_4 are T_1 = 2.48 s and T_2 = 0.96 s. This difference is typical of that observed for many substances. It is unfortunately difficult to measure proton T_1 and T_2 values in proton containing solvents. Thus for 1 mol % docosane in 1-chloronaphthalene we observe T_1 = 4.27 s and T_2 = 1.78 s, virtually identical to the values obtained in pure 1-chloronaphthalene (T_1 = 4.27 s, T_2 = 1.70 s).

The proton T_2 relaxation time found for docosane in CCl_4 solution allows one to predict a width at half-height

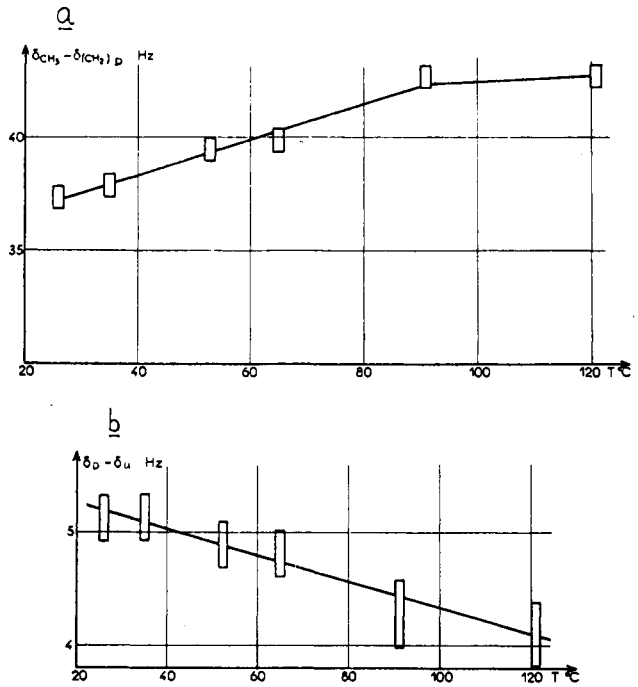


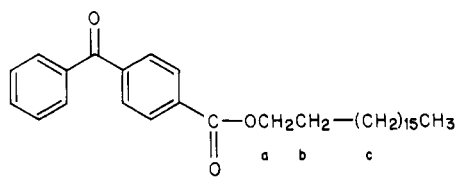
Figure 2. Change in chemical shifts as a function of temperature for *n*-eicosane in 1-chloronaphthalene: (a) $\delta_{CH_3} - \delta_{(CH_2)downfield}$; (b) $\delta_{(CH_2)downfield} - \delta_{(CH_2)upfield}$.

for the methylene singlet of 0.3 Hz. The measured width at half-height is 1.6 Hz. The peak width is not limited by the resolution of the Varian HA 100 instrument. Even in carbon tetrachloride, the methylene protons are not identical, and the peak observed seems to be due to the superposition of a number of similar resonances.

^{13}C Spectra. Values are collected in Table II of the chemical shifts of the resolvable carbons for *n*-octane, *n*-octadecane, and *n*-eicosane, in CCl_4 and 1-chloronaphthalene solutions, relative to an external Me_4Si standard. The maximum chemical shift difference in the two solvents is 0.1 ppm.

The T_1 relaxation times (Table III) are in accord with values found for the hydrocarbon chains in nonaromatic solvents of similar viscosity.[11] Thus these measurements show no pronounced effects of 1-chloronaphthalene on segmental motion of the alkane.

Chain Attached to a Chromophore. The 220-MHz ^1H-NMR spectrum of the octadecyl ester of benzophenone-4-carboxylic acid, 1-18, in 1-chloronaphthalene, is shown in Figure 3. The methyl group appears as a



1-18

Table II
^{13}C Chemical Shifts (in ppm) for *n*-Alkanes in Dilute Solution

CH_3-CH_2-CH_2-CH_2-(CH_2)-CH_2-CH_2-CH_2-CH_3
1 2 3 4 int

	in carbon tetrachloride					in 1-chloronaphthalene				
	C_1	C_2	C_3	C_4	C_{int}	C_1	C_2	C_3	C_4	C_{int}
octane	14.8	23.4	32.6	30.0		14.7	23.3	32.5	29.9	
octadecane	14.8	23.4	32.6	30.1	30.4	14.8	23.4	32.6	30.1	30.5
eicosane	14.8	23.4	32.6	30.1	30.4	14.7	23.4	32.6	30.1	30.5

[a] Relative to Me_4Si external.

Table III
^{13}C T_1 Relaxation Times (in s) for *n*-Alkanes in Dilute Solution

CH_3-CH_2-CH_2-CH_2-(CH_2)-CH_2-CH_2-CH_2-CH_3
1 2 3 4 int

	in carbon tetrachloride			in 1-chloronaphthalene		
n-alkane	[8]	[18]	[20]	[8]	[18]	[20]
C_1	8.80	5.70	4.72	5.14	4.12	3.60
C_2	7.92	4.76	4.04	4.47	2.47	2.17
C_3	7.15	4.04	3.62	3.94	1.93	1.79
C_4	6.41	2.98	2.65	3.58	1.33	1.19
C_{int}		1.94	1.71		0.97	0.69

well-resolved triplet at 0.8 ppm, and as expected, the protons on the CH_2(a) adjacent to the ester oxygen appear downfield at δ 4.2. The methylene envelope, which appears as a singlet in CCl_4 solution, now appears as a minimum of four different resonances.

Appearing furthest downfield are the protons on CH_2(b) [pentuplet, J = 7 Hz, identified by decoupling the spin–spin interaction with CH_2(a)]. The "envelope" appears as three broad peaks, whose relative intensity changes with the length of the chain. These effects are similar to what one might observe in CCl_4 solution in the presence of a Lanthanide shift reagent.[10]

The aliphatic portion of the ^{13}C NMR spectrum of 1-18 in 1-chloronaphthalene is virtually identical with its counterpart in CCl_4 solution. Seven aliphatic carbons can be resolved in CCl_4 and nine in 1-chloronaphthalene at 25 MHz. The chemical shifts are not sensitive to concentration for concentrations less than 1 molar. ^{13}C chemical shifts and T_1 relaxation times for this molecule are shown in Table IV. Again the T_1 values are consistent with changes dependent only on the viscosity of the aromatic solvent.[11]

Discussion

Neither the ^{13}C NMR chemical shifts nor the T_1 relaxation times reported above are consistent with restricted motion or discrete conformations imposed by the solvent. ^{13}C chemical shifts are very sensitive to conformational changes, such as axial vs. equatorial methyl substitution in cyclohexane derivates.[12] Thus one would anticipate different chemical shifts as large as several parts per million for $^{13}CH_2$ in gauche and in trans conformations.[13] That peak doubling is not observed suggests that these rotamers are in rapid equilibrium on an NMR time scale.

The barrier to rotation in butane, pentane, and other normal alkanes is approximately 3 kcal/mol in the gas phase and in simple solutions.[7] The temperature dependence of the methylene doublet in 1-chloronaphthalene is also incompatible with the hypothesis of rotamers which do not interconvert. The doublet seen for the methylene envelope in the proton spectrum broadens but does not coalesce at 120 °C. This corresponds to a rotational barrier of at least 30 kcal/mol assuming the doublet is due to different rotamers of a hydrocarbon chain. Solvation is unlikely to provide a tenfold increase to the barrier to rotation about C–C single bonds.

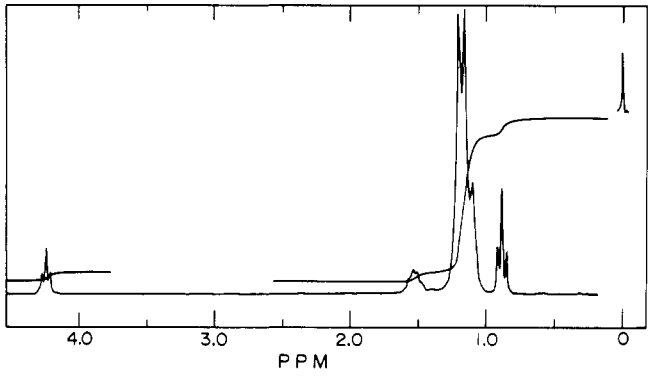
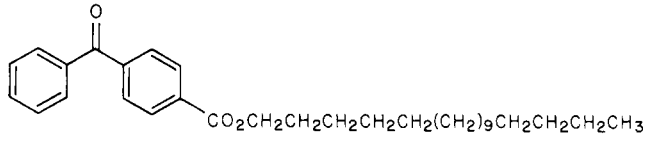


Figure 3. 220 MHz ^1H NMR spectrum of benzophenone-4-$CO_2(CH_2)_{17}CH_3$ in 1-chloronaphthalene showing the portion between 0 and 5 ppm relative to internal Me_4Si.

The same argument can be directed at the concept of chain folding for *n*-alkanes. Because of the pentane effect, it takes 11 CH_2 groups for a chain to reverse 180° upon itself to allow the remaining carbons to align all-trans for the maximum nonbonded interaction. For a 20-carbon chain the "stabilization energy" considering 1-chloronaphthalene to be a poor solvent for alkanes is at most 1 or 2 kcal/mol,[3] and this enthalpy of interaction competes with the entropy gain of the random coil. That extent of interaction could not sustain a folded configuration at 120 °C. Furthermore, 1-chloronaphthalene is generally considered to be a "good" solvent for polyethylene, in that values of $\langle r^2 \rangle$, the mean-squared end-to-end distance, are much larger in 1-chloronaphthalene than in a variety of Θ solvents.[14] The ^{13}C NMR data are also inconsistent with the idea of a folded chain with severely restricted motion. The T_1 values for both the linear alkanes and 1-18 show normal patterns for segmental motion of alkyl groups.[11,15] A folded chain with close CH_2 contacts might also be expected to exhibit high field shifts associated with close steric contacts.[12]

A striking feature of the ^1H NMR of *n*-alkanes in 1-chloronaphthalene is the chain length dependence of the shape of the methylene doublet. As the chain length

Table IV
^{13}C Chemical Shifts (ppm) and T_1 Relaxation Times (s) for Solutions of



	C_1	C_2	C_3	C_4	C_5	C_{int}	C_{15}	C_{16}	C_{17}	C_{18}
					Chemical Shifts[a]					
0.5 M CCl_4	65.6	29.6	26.8	30.1		30.4		32.6	23.4	14.9
0.5 M 1Cl-N[b]	65.7	29.3	26.6	29.9		30.4	30.0	32.5	23.3	14.7
0.25 M 1Cl-N	65.7	29.2	26.5	29.9	30.2	30.4	30.0	32.6	23.3	14.7
					T_1 Relaxation Times					
0.5 M CCl_4	0.38	0.48	0.59	1.12		0.93		2.85	3.73	5.23
0.5 M 1Cl-N	0.14	0.23	0.28	0.25	0.35[c]	0.48	0.51	1.08	1.76	3.35

[a] Relative to external Me_4Si. [b] 1-Chloronaphthalene. [c] Obtained at 0.25 M.

increases, the downfield peak increases in intensity and the upfield peak decreases in relative intensity. This fact suggested to us that the effect might reflect differential solvation of the chain ends and the chain interior by the aromatic solvent. Toward that end it was particularly interesting to consider the ^1H NMR spectrum of linear polyethylene, reported in Liu's first paper. In that spectrum only a single broad line is observed. Chain folding implies for a long polymer many loops and many tails. For polyethylene the doublet should persist. Its absence is further evidence against nonrandom chain configuration.

If, however, a doublet is observed in the ^1H NMR of the *n*-alkanes because the ends are differently solvated than the center, all aspects of the phenomenon can be rationalized. The chain ends experience, on the average, a slightly different magnetic environment than the center of the chain because the detailed nature of the solvation interaction affects the degree of shielding and deshielding due to the 1-chloronaphthalene. The presence of a bulky aromatic chromophore at one end of the chain leads to differential solvation of the two ends. The induced chemical shifts differ at the two ends, and as in 1-18, a more complicated splitting is observed. The critical length for observing the doublet depends, of course, on the number of carbons at each end considered to be solvated differently than the chain interior. If the terminal CH_3 and four CH_2 groups experience the solvation effects associated with the chain ends, then a 10-carbon chain will show negligible splitting and a 16-carbon chain would have four CH_2 groups differently solvated. The ^{13}C chemical shift data are consistent with this explanation. Since the carbons of the alkyl chain will not be in as close proximity to the solvent as the alkyl hydrogens, ring current effects should be smaller for the carbons, consistent with the very small solvent shifts shown in Table II. Slightly larger solvent shifts are noted for the carbons close to the aromatic chromophore in 1-18, consistent with the differential solvation inferred from the ^1H chemical shifts.

Thus it appears that all of our data and that of previous workers[1-4,6] can be accounted for in terms of (relatively small) differences in solvation of alkyl chain ends and chain interiors in aromatic solvents. It is unnecessary to invoke either severely folded alkane conformations or severely restricted rotation about individual bonds in aromatic solvents.

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Cross-Linking of Polymers with a Primary Size Distribution

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ABSTRACT: A univariate Stockmayer distribution has been obtained for the condensation of polymer chains with an initial size distribution. The technique involves the use of the theory of cascade processes. The final molecular size distribution is shown to be a compound distribution. The expression for weight average size is in agreement with Stockmayer. Initial weight average and distribution can be recovered from this distribution. In the special case of the compound Borel–Poisson distribution, multimodality can be detected.

There are at least three general theories dealing with polymer size distributions in the condensation of polymer chains with an arbitrary initial size distribution: The first, formulated by Stockmayer,[2] is based on Flory's theory[3] of condensation and follows a classical combinatorial argument. The second one, proposed by Charlesby,[4] uses distribution moments and moment ratios to describe gelation. The third theory is given by Saito,[5] who used a continuous size distribution and a phenomenological kinetic argument. These theories arrive at the same number average and slightly different expressions for the weight averages, but their distributions differ to a considerable extent.

Among these theories, the Stockmayer distribution is multivariate.[2] It is originated from the Flory–Stockmayer distribution for the condensation of polyfunctional mo-

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