Remarkable changes in conformations of *n*-alkanes with their carbon numbers and aromatic solvents

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Based on magnetic anisotropy in NMR, it is found that preferred conformations of *n*-alkanes in aromatic solvents (C_6D_6 and 1-chloronaphthalene) are dependent both on their carbon numbers and on the solvents used. A short-chain alkane, hexane, tends to adopt extended conformations in both C_6D_6 and 1-chloronaphthalene. In contrast, a long-chain alkane, dodecane, in 1-chloronaphthalene prefers to take open conformations, though in C_6D_6 taking U-shaped conformations. A 'conformational change model' is proposed on the basis of the NMR results.

Analysis of preferred conformations of a solute molecule in solution is essential to the understanding of chemical and biological events therein. These are related to the ability of a molecule to act as a chemical signal and to recognize other molecules – the ability resulting from attractive intermolecular interactions between the respective molecules. There is now much experimental evidence that attractive interactions operate between such nonpolar groups as alkyl ones: (1) equilibrium measurements for 1,3,5-trineopentylbenzene conformation reveal that the most favored conformation is one in which the three *tert*-butyl groups lie on the same side of the benzene ring;[1] (2) the equilibrium between the two-bond shift isomers of cyclo-octatetraenes favors the 1,4-isomer over the 1,6-isomer;[2] (3) in the conformational analysis of 1-phenylalkan-2-ols, an alkyl group has been suggested to be brought close to the aromatic ring;[3] (4) the enthalpies of the attractive interactions of a phenyl group with a variety of chemically and biologically interesting molecules were precisely evaluated by means of gas–liquid partition chromatography;[4] (5) the X-ray studies of a series of liquid alkanes labelled at the ends with highly scattering bromine atoms showed that the longer chains tend to assume lower average end-to-end distances than do the shorter ones;[5] (6) based on detailed NMR studies, it was found that the degree of folding of alkanes in solution (i) depends on the strength of the dispersion force of the solvent[6] and (ii) increases with increasing chain length.[7]

There exist some studies on conformations of alkanes in solvents.[8,9] No reports have, however, been published on conformations of alkanes in aromatic solvents by use of magnetic anisotropy of the solvents.

It is now recognized that large shifts of proton signals for a solute molecule are induced by magnetic anisotropy of π-electron systems in the solvent molecules.[10] Magnetic anisotropy 'apparently' amplifies differences in chemical shifts. It can therefore be said that magnetic anisotropy is probably the most effective experimental method for studying the influence of weak intermolecular interactions between solute and aromatic solvent molecules on conformations of alkanes therein. Another method for evaluating weak intermolecular interactions is the NOE. This method is rather less accurate due to the necessity of determination of changes in signal intensity.

In this paper, we suggest that alkanes in 1-chloronaphthalene alter markedly in conformation with their carbon number (6 and 12).

Results and discussion

In this work, C_6D_6 and 1-chloronaphthalene were used as aromatic solvents, and $CDCl_3$ or CCl_4 as a non-aromatic one. 1-Chloronaphthalene (liquid at room temperature) was chosen on the basis of the fact that this compound induces a higher field shift than does benzene.† Further, alkanes with various carbon numbers (5 to 15) were employed as solutes.

Proton spectra of octane in aromatic and non-aromatic solvents

Fig. 1 shows ^{1}H NMR spectra of octane in $CDCl_3$, C_6D_6, and 1-chloronaphthalene at 23 °C. In going from $CDCl_3$ to 1-chloronaphthalene, the Me signal (a triplet) is shifted to higher field (*i.e.*, low frequency, small chemical shift).

The same is true for the CH_2 signals: an '*apparent*' sharp peak with a small multiplet in $CDCl_3$ is split obviously into a broad multiplet and an '*apparent*' sharp peak in 1-chloronaphthalene. The CH_2 groups giving the former multiplet are termed 'CH_2 groups proximate to the terminal Me groups [CH_2(PR)]', and those producing the latter sharp peak are termed 'CH_2 groups remote from the terminal Me groups [CH_2(RE)]'.

Proton resonances of alkanes in aromatic solvents

In Fig. 2 are plotted the CH_2(RE) and Me resonances (δ) against the number of carbon atoms (m) in alkanes in 1-chloronaphthalene and in C_6D_6. When the value of m changes from 5 to 8, the CH_2(RE) proton resonances in 1-chloronaphthalene shift to higher fields. On the other hand, the resonances are shifted to lower fields when m goes from 8 to 15. These results clearly indicate that a break point exists at m = 8 in the m–δ plots, suggesting that the alkanes would differ in conformation,

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† There is a slight difference in magnetic anisotropy (χ) between benzene (-89.4×10^{-29} J T^{-2} mol^{-1}) and naphthalene (-84.8×10^{-29} J T^{-2} mol^{-1}).[11] Naphthalene has, however, a larger region causing highfield shift than does benzene, because of its larger π-electron surface area. Naphthalene derivatives (1-Me-, 1,2-diMe-, 1-Cl-, 1-Br-, and 1-I-naphthalenes) examined here all give similar solvent effects on alkanes.

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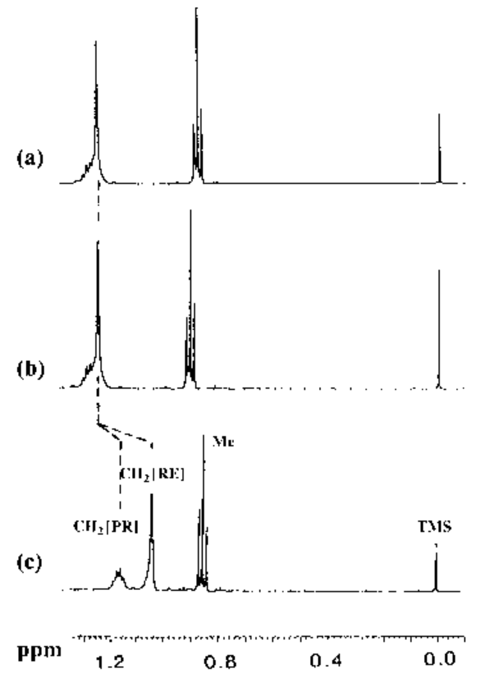

Fig. 1 ^{1}H NMR spectra of octane in $CDCl_3$ (**a**), C_6D_6 (**b**), and 1-chloronaphthalene (**c**) at 23 °C.

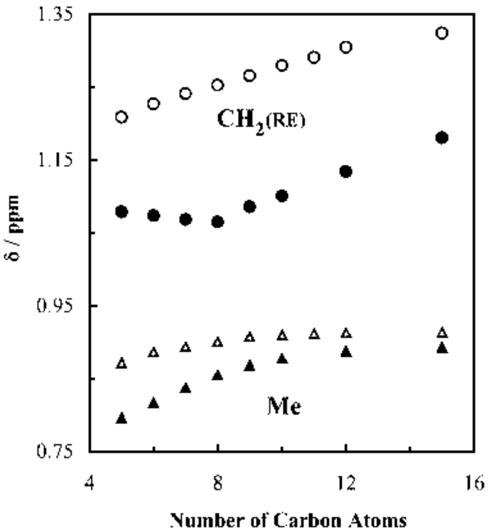

Fig. 2 Dependence of ^{1}H NMR chemical shifts (δ) for alkanes on their carbon number (m) at 30 °C. ○, CH_2(RE) protons in C_6D_6; ●, CH_2(RE) protons in 1-chloronaphthalene; △, Me protons in C_6D_6; ▲, Me protons in 1-chloronaphthalene.

depending on whether m is larger than 8 or smaller. In this connection, it should be noted that, in $CDCl_3$ and CCl_4, the δ-values for the CH_2 protons remain almost unaltered with varying m.[6] ‡

These results can be explained as follows. In general, conformations of alkanes can be said to be controlled by two competitive types of attractive interactions: (i) *intermolecular* interactions between the CH_2(RE) protons and the aromatic solvent molecules (*attractive intermolecular alkyl–aromatic interactions*) and (ii) *intramolecular* interactions among CH_2(RE) groups proximate to one another (*attractive intramolecular alkyl–alkyl interactions*). When m ranges from 5 to 8, the number of CH_2(RE) groups of an alkane contacting with 1-chloronaphthalene molecules thus increases, thereby strengthening the attractive intermolecular alkyl–aromatic interactions. This would result in higher field shifts for the CH_2(RE) proton resonances. In contrast, when m increases from 8 to 12, the number of the CH_2(RE) groups increases so remarkably that the attractive intramolecular *alkyl–alkyl interactions* would become stronger relative to the attractive intermolecular alkyl–aromatic interactions. This would result in lower field shifts for the CH_2(RE) proton resonances.

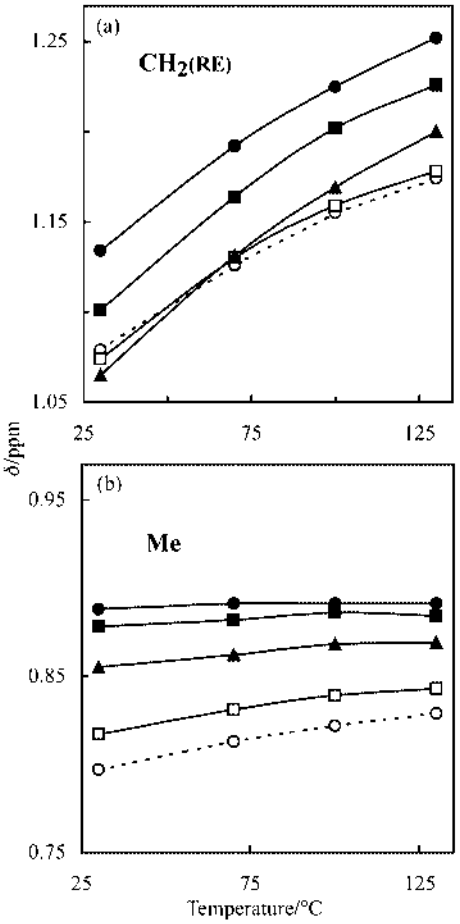

Fig. 3 Temperature dependence of the δ-value for CH_2(RE) (**a**) and Me protons (**b**) of alkanes in 1-chloronaphthalene. ○, C_5H_{12}; □, C_6H_{14}; ▲, C_8H_{18}; ■, $C_{10}H_{22}$; ●, $C_{12}H_{26}$.

For the CH_2(PR) protons (the data not shown in Fig. 2 for simplicity), changes in the δ-values with m are more slight than those for the CH_2(RE) protons. Furthermore, the Me proton resonances have been shown (i) to be shifted to higher fields in 1-chloronaphthalene (as well as in C_6D_6)[7] as m decreases from 10 to 5 and (ii) to be kept nearly constant in the two aromatic solvents when m decreases from 15 to 10.

Temperature dependence of proton resonances for alkanes in 1-chloronaphthalene

Fig. 3 shows the temperature dependence of the δ-value for the CH_2(Re) and Me protons in alkanes in 1-chloronaphthalene, with the value of m being changed. The CH_2(Re) proton resonances have turned out to shift to higher field as temperature is reduced. A fascinating aspect of the data in Fig. 3 is that the degree of highfield shift for the CH_2(Re) protons is larger when $m = 12$ than when $m = 5$.

The data in Fig. 3a can be understood by a view that the decrease in the δ (*i.e.*, highfield shift) for the CH_2(Re) protons with decreasing temperature would be induced by 'apparent' strengthening of the attractive intermolecular alkyl–aromatic interactions.

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‡ Dispersion force varies slightly with the solutes and solvents, as indicated by the n_D^{20}-values: 1.445 ($CDCl_3$), 1.460 (CCl_4), 1.474 (C_6D_6), 1.357 (C_5H_{12}), 1.398 (C_8H_{18}), and 1.432 ($C_{15}H_{32}$).

Table 1 The ASIS ($\Delta\,\delta_C$, ppm)[a] for alkanes in 1-chloronaphthalene

Alkane	$C_{(1)}$[b]	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$
C_6H_{14}	0.00[a]	−0.05	−0.12			
C_8H_{18}	0.04	−0.02	−0.10	−0.05		
$C_{12}H_{26}$	0.06	0.04	−0.03	0.06	0.04	0.05

[a] The ASIS value is that relative to the terminal Me carbons [$C_{(1)}$] in hexane. The 'minus (−)' thus indicates a highfield shift relative to the δ for the $C_{(1)}$ in hexane. [b] The '$C_{(1)}$' represents the terminal Me carbons, '$C_{(2)}$' represents the carbon atom bonded to the Me carbon, and so on.

For the Me protons, the temperature dependence of the δ-value is far smaller than that for the CH_2(RE) protons. Furthermore in $CDCl_3$ and CCl_4, the CH_2 resonances remain unchanged with both temperature and *m*.[12]

Carbon chemical shifts for alkanes in 1-chloronaphthalene

Carbon chemical shifts ($\Delta\,\delta_C$) for alkanes are listed in Table 1 where 1-chloronaphthalene is an aromatic solvent and $CDCl_3$ is a non-aromatic solvent. Chemical shift in an aromatic solvent (δ^A) is usually represented as the 'aromatic solvent-induced shift' (ASIS, $\Delta\,\delta_C$) [$= \delta^A - \delta^N$] where δ^N is the chemical shift in a non-aromatic solvent.[13]

The ASIS value for $C_{(3)}$, the third carbon from the terminal one, is smallest (*i.e.*, highest field) among all methylene carbon atoms in hexane.§ This finding suggests that the $C_{(3)}$ atom (central carbon atom) in *n*-hexane would be most tightly surrounded by 1-chloronaphthalene molecules among all of the methylene carbon atoms, thus resulting in strengthening of the attractive intermolecular interactions between the central CH_2 group and the aromatic solvent molecules.

Possible conformations of hexane in aromatic solvents

As is evident from the data in Fig. 2, the CH_2(RE) protons in 1-chloronaphthalene resonate at higher fields in going from pentane to octane. Moreover, the central carbon [$C_{(3)}$] of hexane in 1-chloronaphthalene shows the highest field shift among all methylene carbon atoms (Table 1).

In this connection, it has been suggested that hexane tends to adopt extended conformations both in non-aromatic solvents[5] and in C_6D_6.[7]

From the NMR results and discussions mentioned above, possible conformations of hexane in C_6D_6 and 1-chloronaphthalene are proposed (Fig. 4). In both solvents, hexane prefers to take *extended* conformations.

Possible conformational changes of dodecane with the aromatic solvents

We reported that alkanes come to take U-shaped conformations as their carbon numbers become larger.[6] Furthermore, the degree of folding of alkanes in C_6D_6 has been suggested to increase with an increasing number of carbon atoms (*m*).[7]

On the basis of the NMR results and discussions mentioned above, we propose possible conformations of dodecane in C_6D_6 and 1-chloronaphthalene (Fig. 5). In C_6D_6, dodecane tends to take *U-shaped* conformations (Fig. 5a), since the solvent molecules cannot enter the cavity formed by its interior CH_2(RE) chains due to the stronger attractive intramolecular alkyl–alkyl interactions relative to the attractive intermolecular alkyl–aromatic interactions. On the other hand, in 1-chloronaphthalene, dodecane prefers to adopt *more open* conformations (Fig. 5b), since the solvent molecules interact more strongly with interior CH_2(RE) groups due to the stronger attractive intermolecular alkyl–aromatic interactions probably resulting from larger surface area of the solvent molecule.

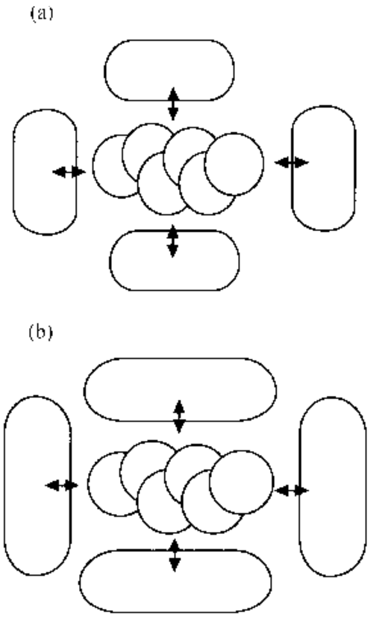

Fig. 4 Schematic drawings of possible conformations of hexane in benzene (**a**) and 1-chloronaphthalene (**b**). The 'circle' represents a Me or methylene group and the 'ellipse' represents an aromatic solvent molecule.

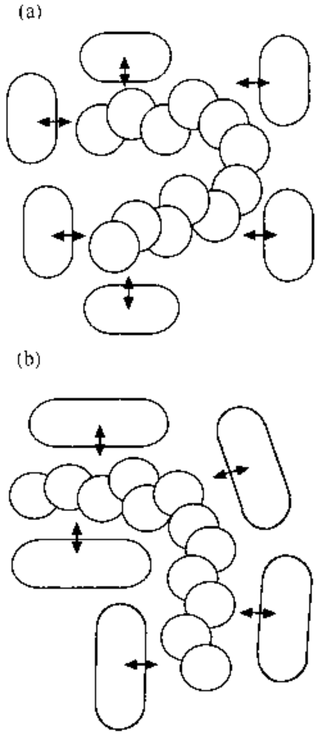

Fig. 5 Schematic drawings of possible conformations of dodecane in benzene (**a**) and in 1-chloronaphthalene (**b**). The symbols are as in Fig. 4.

Conclusions

The present work indicates that magnetic anisotropy in NMR provides a very useful method for estimating the strength of solute–solvent interactions, namely, alkyl–aromatic interactions between alkanes and aromatic solvents. The experimental results described above might be better explained by the 'conformational change model' proposed here: (1) hexane has a tendency to take extended conformations in both C_6D_6 and 1-chloronaphthalene; (2) dodecane in C_6D_6 prefers to take U-shaped conformations, while in 1-chloronaphthalene adopting more open conformations. In order to estimate the

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§ In this relation, it should be noted that in C_6D_6 as an aromatic solvent, the ASIS value for the $C_{(1)}$ in hexane is smallest.[7]

strength of the intramolecular dispersion force among $CH_2(RE)$ groups within a single alkane molecule, *ab initio* calculations will be necessary.

Experimental

Materials were of spectroscopic or analytical grade. The spectra of alkanes in $CDCl_3$, CCl_4, C_6D_6, and 1-chloronaphthalene were recorded at a ^1H frequency of 499.743 MHz and at a ^{13}C frequency of 125.663 MHz using a Varian Unity Plus 500 FT-NMR spectrometer. Concentrations of samples were *ca.* 0.01 mol%. Typical conditions for Unity Plus 500 FT-NMR were as follows: (1) digital resolution of 0.366 Hz and number of pulses of 100 for ^1H and (2) digital resolution of 0.833 Hz and number of pulses of 2000 for ^{13}C. Chemical shifts (δ) for alkanes are represented relative to that for TMS. The split signals of alkanes in 1-chloronaphthalene were assigned by the decoupling method.

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