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# Proton NMR Spectra of Methyl Alkanoates in Aromatic Solvents

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**Synopsis.** The splitting of methylene peaks in $^1$H NMR spectra was studied for long-chain methyl alkanoates in 1-chloronaphthalene as a function of the carbon number, $n_c$, of alkyls. With increase in $n_c$, the singlet peak of methylene is first split into a doublet and then into a triplet.

ASIS (Aromatic-Solvent-Induced Shift) phenomena in NMR have been widely accepted by organic chemists and applied successfully to conformational studies on organic molecules.

In 1967, a peculiar solvent effect by an aromatic solvent was reported by Liu.[1] He observed that methylene envelopes in $^1$H NMR spectra of long-chain hydrocarbons (the number of carbons$>$16) were split into doublets in 1-chloronaphthalene. Similar observations have been reported for other solute molecules with long alkyl chains. For example, Gonzalez de la Campa et al. reported on a series of *N*-alkylmaleimides[2] and alkyl 11-maleimidoundecanoates in benzene solution,[3] and Winnik et al.[4] also reported on the octadecyl ester of benzophenone-4-carboxylic acid in 1-chloronaphthalene. In $^1$H NMR spectra of these compounds, splittings of methylene signals were observed for shorter alkyl chains rather than for *n*-alkanes, and it was suggested that terminal substituted groups seemed to accentuate the splitting of methylene peaks of $^1$H NMR spectra, observed in aromatic solvent.

The first theoretical investigation was carried out by Ando and Nishioka.[5] They concluded that the splitting of peaks in aromatic solvent arose from increase in the number of gauche forms for long chain hydrocarbons. On the other hand, Winnik et al. applied $T_1$ measurements[4] and used the heteronuclear ($^{13}$C-$^1$H) shift correlated two-dimensional NMR spectroscopy.[6] They concluded that the splitting was due to a solvent effect associated with the chain end, and conclusively ruled out the presence of slowly interconverting gauche and trans conformations for long alkyl chains. Furthermore, several papers have been published to discuss the origin of these phenomena, without setting the issue.

In this paper, we intend to present another example of similar phenomenon to add to information so as to facilitate insight into the reason for the splitting found for methylene peaks of substituted alkyl chains.

## Experimental

Methyl alkanoate compounds with alkyl carbon ($n_c$=6 to 24) were used as solute substances. The compounds and solvents used were of the best available commercial grade. The samples were prepared in an about 0.5 M solution (1 M=1 mol dm$^{-3}$) of deuterated benzene or a mixed solvent of 90 vol% 1-chloronaphthalene/10 vol% deuterated benzene. NMR spectra were observed using a JEOL FX-100 NMR spectrometer operated at 100 MHz at ambient temperature, unless otherwise indicated.

## Results and Discussion

100 MHz $^1$H NMR spectra of a series of methyl alkanoates in 1-chloronaphthalene are shown in Fig. 1. The carbon number of alkyl chains, $n_c$, is in the range from 6 to 24. Triplet peaks at higher fields were assigned to their terminal methyl protons and the rest to methylene protons. The peaks which appeared in lower fields at about $\delta$ 3.4 and 2.2, were assigned to the methyl and methylene adjacent to the ester group, respectively, but they are not shown in Fig. 1. The small peaks at the lowest field were assigned to $\beta$ methylene protons to the carbonyl. A singlet methylene peak was observed for the compounds with $n_c$ ranging from 6 to 10. When $n_c$=12, one more partially resolved peak appeared in the spectrum as a shoulder. Then, there are two distinguishable peaks in the spec-

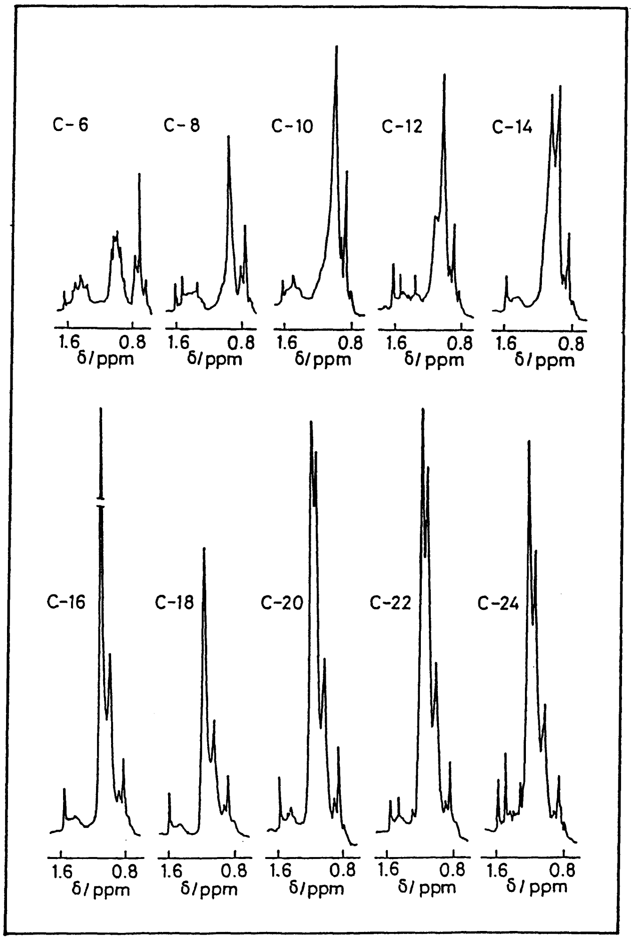

Fig. 1. The $^1$H NMR spectra at 100 MHz of methyl alkanoates in 90 vol% 1-chloronaphthalene/10 vol% deuterated benzene.

Table 1. The Least Carbon Numbers of Alkyl Chains, $n_c$, at which the Splitting of Methylene Proton Signals is Observed

| Solute | Solvent | Doublet | Triplet | Ref. |
|---|---|---|---|---|
| Normal alkanes | 1-Clnap[a)] | 17 | | 1 |
| | Benzene | None | | 7 |
| *N*-Alkyl maleimides | Benzene | 12 | | 2 |
| Alkyl 11-maleimido-undecanoates | Benzene | 12 | | 3 |
| Methyl alkanoates | 1-Clnap[a)] | 12 | 20 | b) |
| | Benzene | 12 | | b) |
| 1-Chloroalkanes | 1-Clnap[a)] | 18 | | b) |
| | Benzene | None | | b) |

a) 1-Chloronaphthalene. b) Present investigation.

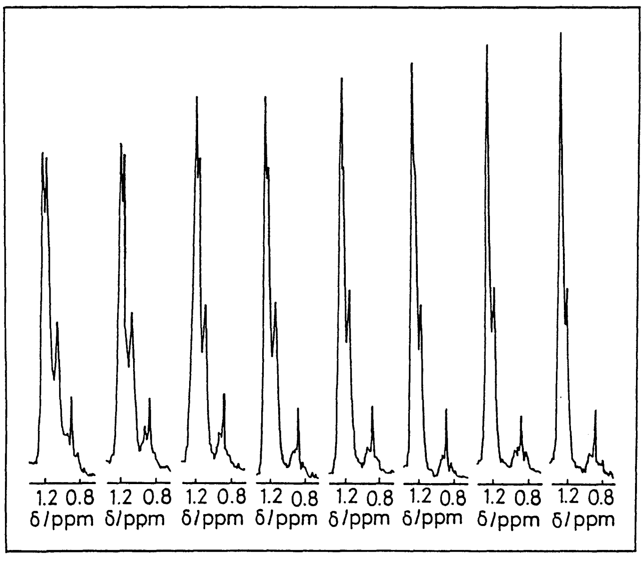

Fig. 2. The $^1$H NMR spectra of methyl eicosanoate in 1-chloronaphthalene solution at various temperatures; 25, 38.8, 55.0, 70.3, 85.3, 99.7, 115.5, and 129.5 °C from left to right, respectively.

tra of the compounds for $n_c=12$ to 18. When $n_c \geqslant 20$, the lower field peak further split into a doublet, and a distinct triplet peak was recognized. A peak splitting at $n_c=12$ was also observed in benzene solutions but no splitting at $n_c=20$ in 1-chloronaphthalene was observed in benzene, as shown in Table 1, which shows a list of the splitting behavior for substituted alkanes in aromatic solvent. This splitting at $n_c=12$ has substantially the same character as observed in the case of a series of *N*-alkylmaleimides[2)] and alkyl 11-maleimidoundecanoates[3)] in benzene solutions. On the other hand, the second splitting of the lower field peak observed in 1-chloronaphthalene solutions for $n_c \geqslant 20$ was not observed in the case of benzene solutions. The splitting for $n_c \geqslant 20$ seems to be consistent with the results obtained by Liu[1,7)] for a series of alkanes. He reported that the splitting was observed only in 1-chloronaphthalene solutions[1)] but not in benzene solutions for alkanes.[7)] We considered that the nature of the origin of this splitting of the peak of the methylene envelope for $n_c \geqslant 12$ is different from that of the splitting effect in the case of alkanes.

The splitting for $n_c=12$ seems to be strongly dependent on the presence of the ester function. In the series of 1-chloroalkanes in 1-chloronaphthalene solutions, the splitting was not observed for $n_c$ less than 18. This behavior is the same as in the case of alkanes.

$^1$H NMR spectra of methyl eicosanoate of $n_c=20$ in 1-chloronaphthalene solutions at various temperatures are shown in Fig. 2. The chemical shift differences among the three peaks in the methylene envelope decrease with temperature raise, and the two lower field peaks for the methylene coalesce at about 100 °C. This temperature is lower than that reported for *n*-alkanes. Winnik et al.[6)] calculated the energy barrier to be 120 kJ mol$^{-1}$ for *n*-alkanes by assuming the two site exchange. They suggested that this value was too large for the constraint of the interconversion between gauche and trans conformers to account for the splitting phenomena.[5)] In this study, the energy barrier for methyl alkanoates was calculated to be about 80 kJ mol$^{-1}$ using the coalesce temperature method.[8)] This value is less than the value reported for alkanes but still large for the ordinary interconversion energy. However, in order to make further discussion on the results of our observation, it may be desirable to establish a new molecular model for the solvent-solute interaction.

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