

Study of ^1H NMR Spectra of Alkyl 11-Maleimidoundecanoates and Conformational Changes in Benzene with Chain Length

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ABSTRACT: The intramolecular structure of a series of eleven alkyl 11-maleimidoundecanoates (EMIS) in solution was studied by high resolution ^1H NMR technique. A splitting in the NMR spectra of EMIS in benzene at 60°C was observed at octyl 11-maleimidoundecanoate (EMI 10-8), above which there exist two distinguishable NMR peaks for internal methylene protons situated in the outer part of the *n*-alkyl chain, and below which only a single peak was observed. The ^1H NMR signal of the same methylene protons taken in chloroform are not resolved as those NMR spectra in benzene solution. The effect of the hydrogenation of the *N*-maleimido ring on the NMR spectra of the internal methylene protons in both *N*-(*n*-alkyl)maleimides and EMIS was also studied. This fact exerts a great influence on the NMR spectra of *N*-(*n*-alkyl)maleimides because the disappearance of the doubling; however the splitting in hydrogenated EMIS is essentially the same as that found for EMIS. These results indicate that the appearance of a doubling in the *n*-alkyl chain of EMIS is strongly maintained by the presence of an ester function intercalated among the $-\text{CH}_2-$ groups.

KEY WORDS ^1H Nuclear Magnetic Resonance / Alkyl-11-maleimido-undecanoate Monomers / Splitting of Methylene Groups / Chain Length Effect / Solute-Solvent Interactions /

Some years ago, Liu¹⁻⁴ published a series of papers on the proton magnetic resonance spectra of *n*-alkanes in aromatic solvents. He found a splitting of the singlet peak associated with the methylene groups in certain bulky aromatic solvents for chains longer than fifteen carbons. He explained this effect by a sharp conformational transition as a function of chain length. This transition makes the solvation different for various parts of the chain and therefore, ring current effects are also different and cause this splitting.

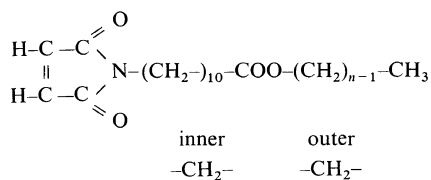
Later on, however, Ando and Nishioka⁵⁻⁸ repeated many of Liu's experiments at higher resolution, confirming his observations from an experimental point of view but interpreted the phenomenon as a conformational constraint imposed by the solvent. The two peaks are thus caused by chemical shifts differences between protons of *gauche* and *trans* bonds which do not interconvert on a nuclear magnetic resonance time scale.

From a theoretical point of view, apart from the calculations made by Ando and Nishioka,⁵⁻⁸ Liu and Ullman,⁹ by means of a simple statistical thermodynamic argument, have demonstrated the possibility of intramolecular chain folding by assuming the existence of low energy intramolecular conformations stable enough to overcome the tendency of chain molecules to assume a random arrangement in solution. According to these authors, this model may be employed to explain the NMR spectra of *n*-alkanes in some aromatic solvents. Later on, Tonelli¹⁰ demonstrated by the usual three state rotational isomeric state model that the sudden conformational transition between *n*-alkanes in the liquid state has no inherent intramolecular origin. Recently, the present authors¹¹ reported a similar phenomenon for *N*-(*n*-alkyl)maleimides in benzene solution. The effect of the *N*-maleimido ring causes the splitting at ten carbons instead of at sixteen, even in benzene

solvent which has no effect on *n*-alkanes. We interpreted our own experimental in terms of the mechanism developed by Ando and Nishioka,⁵⁻⁸ by assuming that the double peak can arise from a contribution of the methylene groups adjacent to *gauche* bonds which are incompletely averaged along the chain. The incomplete average is supposed to be due to a strong interaction between the *n*-alkyl chain of the *N*-(*n*-alkyl)maleimide and benzene molecules. This interaction arises from a 1:1 *exo*-stereospecific association between the *N*-maleimido ring and benzene molecules.

Much more recently, Winnik *et al.*¹² published a detailed but incomplete nuclear magnetic resonance study on *n*-alkanes and *n*-alkyl chains attached to chromophores dissolved in certain aromatic solvents. They concluded that the splitting is due to different solvation effects of the chain ends and in the middle of the chains and not to unusual conformations imposed on the chains by the solvent environments.

In the present paper, we study a homologous series of alkyl 11-maleimidoundecanoates, subsequently referred to as EMIS, from *n*=2 to *n*=22, including only the even members of the series. EMIS can be represented by the following structural formula,



n=2, 4, 6, 8, 10, 12, 14, 16, 18, 20, and 22.

Scheme 1.

The methylene groups of the side chain and those between nitrogen and ester group are designated as outer and inner methylenes, respectively. These compounds are similar to the *N*-(*n*-alkyl)maleimides studied previously but differ by the presence of an ester function intercalated in the *n*-alkyl chain. Previously¹¹ the validity of the magnetic resonance technique for estimating the dilute solution state of *N*-(*n*-alkyl)maleimides by ¹H NMR measurements was investigated. In the present case, we intend to put to a similar test the determinations of the methylene ¹H spectra on dilute solutions of EMIS

and also to join new information and to insight into the reasons for the splitting found in the methylene peak of *n*-alkyl chains by modifying the *n*-alkyl chain with a polar group. This group, through an enhancement of the solute-solvent interactions, might accentuate the effect causing the doubling.

EXPERIMENTAL

The synthesis and characterization of the alkyl 11-maleimidoundecanoates (EMIS) used in the present study are described in a previous paper.¹³ They are essentially very pure compounds containing no impurities which might possibly affect the high resolution magnetic resonance measurements. In thin layer chromatography experiments, all of these compounds gave unique spots.

N-(octadecyl)succinimide and octadecyl 11-succinimidoundecanoate were obtained by the catalytic hydrogenation of the corresponding homologous *N*-maleimides, using palladiated charcoal (Fluka A.G.) as catalyst and dioxane as solvent. ¹H NMR spectra were obtained with a Varian XL-100 spectrometer at 60°C with a temperature control attachment (Varian Associates, Palo Alto, California). Spectroscopic grade deuterated benzene (C₆D₆) and chloroform (CDCl₃) (Merck A.G.) were used as solvents. Hexamethylene disiloxane (0.5%) was used as internal standard. Dilute solutions (5% w/v) were used so as to eliminate any chemical shift contribution due to solute-solute interactions.

RESULTS AND DISCUSSION

In Figure 1 are shown the spectra of the *n*-alkyl side-chains in EMIS using C₆D₆ as solvent. Peaks I and II are due to the methyl and methylene protons respectively, except for the methylene groups adjacent to the imido and ester groups appearing at lower field. We can see that the -CH₂- protons show a single peak for compounds with a number of methylene groups in the external *n*-alkyl side chain *n*<8. When *n*≥8 two partially resolved peaks appear in the spectrum. No methylene groups -CH₂- of EMIS show any resolvable NMR peak in a dilute chloroform solution (5%). Only a single NMR peak was observed for -CH₂- of EMIS at any chain length. In Figure 2, the chemical shifts of the -CH₃ and -CH₂- groups in both C₆D₆ and CDCl₃ solutions are shown. In the CDCl₃ solution, δ_{-CH₂-}

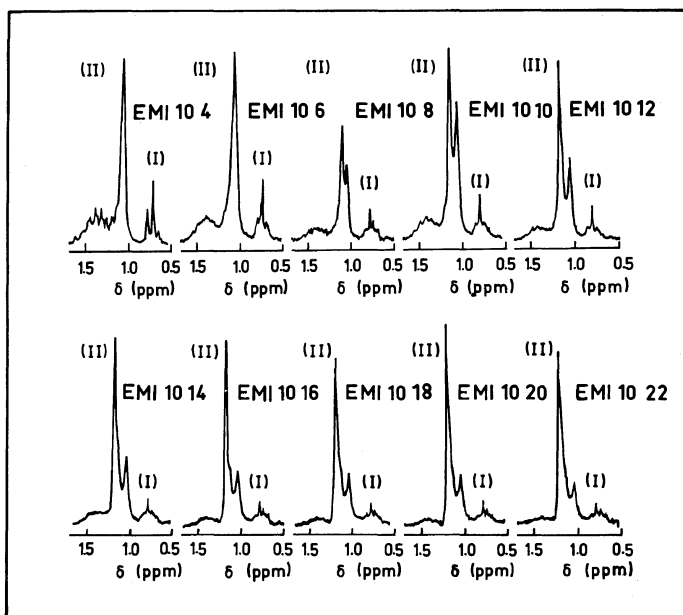


Figure 1. The ^1H NMR spectra at 100 MHz of alkyl 11-maleimidoundecanoates (EMIS) in 5.0% C_6D_6 solution at 60°C showing the portion between 0.5 and 1.5 ppm relative to internal hexamethylene disiloxane (0.5%).

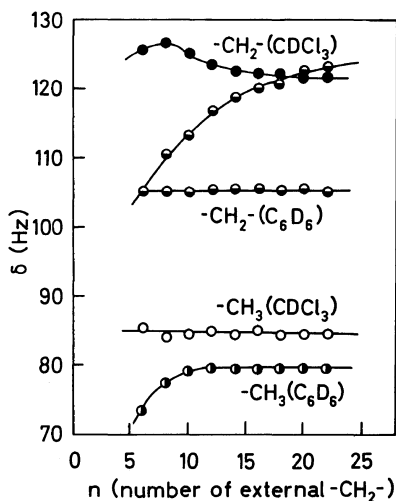


Figure 2. Plots of chemical shifts of $-\text{CH}_2-$ and $-\text{CH}_3$ protons of the *n*-alkyl chains of a series of alkyl 11-maleimidoundecanoates in C_6D_6 and CDCl_3 at 60°C vs. number of methylene groups in the outer part of the *n*-alkyl chain.

diminishes to a virtually constant value whereas $\delta_{-\text{CH}_3}$ remains constant throughout the series. In the C_6D_6 solution both $\delta_{-\text{CH}_2-}$ and $\delta_{-\text{CH}_3}$ increase with

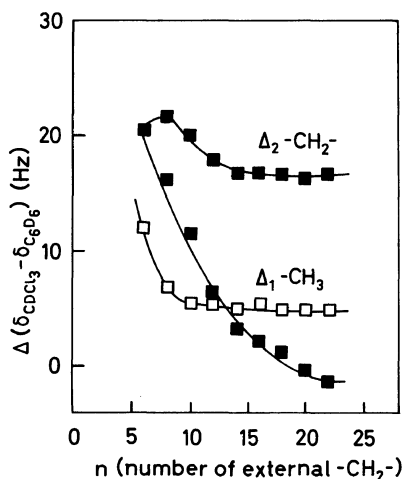


Figure 3. Plots of the relative solvent effect on the chemical shift $\Delta(\delta_{\text{CDCl}_3} - \delta_{\text{C}_6\text{D}_6})$ vs. number of methylene groups in the outer part of the *n*-alkyl chain of a homologous series of EMIS.

chain length but in the case of the $\delta_{-\text{CH}_3}$, the slope has an abrupt change when $n=8-10$. In order to compare the solvent effect due to the C_6D_6 on the chemical shifts of $-\text{CH}_3$ and $-\text{CH}_2-$ groups, the differences between the chemical shifts of $-\text{CH}_3$ and

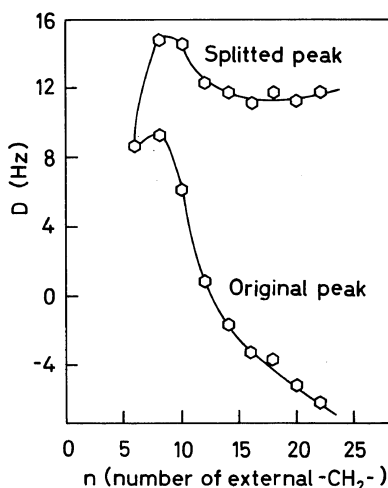


Figure 4. Plot of the differences between the relative solvent effects on chemical shifts of the internal $-\text{CH}_2-$ and of the end $-\text{CH}_3$ groups ($D = \Delta_2 - \Delta_1$) vs. number of methylene groups in the outer part of the n -alkyl chain of a homologous series of EMIS.

$-\text{CH}_2-$ in C_6D_6 and CDCl_3 are shown in Figure 3 as a function of the number of methylene groups in the outer part of the n -alkyl side-chain. From this Figure it can be seen that the $\Delta_{-\text{CH}_2-}$ is larger than $\Delta_{-\text{CH}_3}$ when $n < 13$ and becomes less than $\Delta_{-\text{CH}_3}$ when $n > 13$.

These results indicate that the relative solvent effect on chemical shifts is larger for the outer methylenes than for the final methyl group when $n < 13$. But for $n > 13$, the solvent effect on internal $-\text{CH}_2-$ protons becomes so small that it is even less than that of the terminal methyl protons. A representation of these differences $D = (\Delta_{-\text{CH}_2-} - \Delta_{-\text{CH}_3})$ as a function of chain length is shown in Figure 4. This plot is equivalent to the plot of $\Delta_{-\text{CH}_2-}$ shown in Figure 3 provided the chemical shift of the methyl protons is used as reference and is a good representation of the chain length effect. Comparison of these results with those obtained from N -(n -alkyl)maleimides¹¹ shows that the splitting appears at the same length of the n -alkyl chain considered from the methyl end. On the contrary, if we consider the origin in the N -maleimido ring, there is a great difference in the critical length needed to give place to the doubling of the methylene peak in both cases. It is surprising to observe that the substitution of the $-\text{CH}_2-$ by the ester group causes a deviation from the expected behaviour with respect

to n . This peculiar behaviour of EMIS is believed to be a consequence of the characteristic effect of the ester group, which can be superimposed on the ordinary chain length effect presented in the case of pure n -alkyl chains and alkanes as well.

Also if we compare these results with the corresponding to n -alkanes, we can deduce the presence of two factors controlling the splitting: a) The existence of the N -maleimido ring or another suitable functional group, capable of strong interactions with the solvent, causes, as previously shown for N -(n -alkyl)maleimides, a shortening of the critical chain length necessary to produce the doubling of the methylene peak. In the case of EMIS, this shortening effect seems to be produced through the cooperative presence of the ester group which interacts preferentially with the aromatic solvents as shown by several authors.¹⁴⁻¹⁷ Moreover, the existence in the n -alkyl chains of these types of functional groups causes the splitting to come about in benzene solution whereas in the case of n -alkanes in benzene solution, splitting cannot be observed even at 220 MHz, although high n -alkanes show some skewed shoulders not present in carbon tetrachloride. b) Observation of the splitting is possible only in case of n -alkyl chains possessing at least one end of the chain free. Thus, in alkyl 11-maleimidoundecanoates, the existence of ten methylene groups situated between the N -maleimido ring and the ester group do not allow for any splitting, since the attainment of a critical length of $n \geq 8$ in the outer part of the n -alkyl chain is necessary for the splitting to occur. This fact seems to indicate the presence of two different types of behaviour of the methylene groups as a function of their position along the n -alkyl chain, namely, one position near the chain end and the other in the middle. The existence of a 1:1 *exo*-stereospecific association between aromatic rings and double bonds in N -maleimides has been suggested by the present authors as an explanation for the splitting at $n \geq 10$ in the case of N -(n -alkyl)maleimides.¹¹ The most important feature arising from EMIS is the evidence of the existence of two different types of interactions. Thus, we hydrogenated catalytically the 1,2-ethylenic bond of the N -maleimido ring in both N -(n -octadecyl)succinimide and octadecyl 11-maleimidoundecanoate to clarify the influence of the N -maleimido ring on this phenomenon and compared it with that found in the case N -(n -

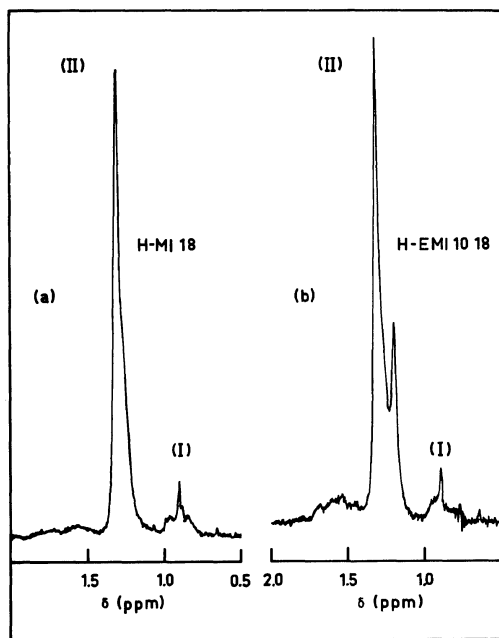


Figure 5. The ^1H NMR spectra at 90 MHz of (a) *N*-(*n*-octadecyl)succinimide and (b) octadecyl 11-succinimidoundecanoate in 5.0% C_6D_6 solution at 60°C showing the portion between 0.5 and 2.0 ppm relative to internal hexamethylene disiloxane (0.5%).

alkyl)maleimides.

In Figure 5 are shown the NMR spectra for the *n*-alkyl side-chain of *N*-(*n*-octadecyl)succinimide and octadecyl 11-succinimidoundecanoate. In the case of the *N*-(*n*-octadecyl)succinimide we can see that the hydrogenation was sufficient to cause doubling of the methylene peak to disappear. This striking result clearly indicates that the splitting in *N*-(*n*-octadecyl)maleimide [Figure 1 on ref 11] is due not only to specific interactions of the $-\text{CH}_2-$ groups with the solvent but also to the interaction between the benzene molecules and the *N*-maleimido ring throughout the 1:1 *exo*-stereospecific association. Since these two compounds have the same type of groups, the methyl group $-\text{CH}_3$ at the end, and within the chain, the seventeen $-\text{CH}_2-$, but they have different terminal groups on the other end, this must be the sole explanation for the different behaviour of both compounds with respect to benzene.

On the contrary, if now we compare octadecyl 11-maleimidoundecanoate with its hydrogenated

homologous *N*-succinimide shown in Figures 1 and 5, in which the *n*-alkyl chain is divided in two portions by the ester function, we can appreciate the fact that hydrogenation of the double bond of the *N*-maleimido ring does not have any specific effect on the NMR spectrum of the methylene groups. In this case, in addition to the specific interactions as in the case of *N*-(*n*-alkyl)maleimides, we have effects due to the ester group. This means that the interaction between the ester group and the aromatic solvent is strong enough to produce not only the splitting in the external part of the *n*-alkyl side-chain in the presence of the *N*-maleimido ring but also the splitting after its hydrogenation.

So far we have presented our experimental results and now we shall offer some possible explanations for the characteristic behaviour observed in the ^1H NMR spectra of EMIS. The *n*-alkanes are the simplest molecules which can be considered from a fundamental point of view. They contain no functional groups that can interact in a specific manner with the solvent. The splitting caused by the *n*-alkanes when $n \geq 18$ in large planar anisotropic solvents cannot definitely be due to any specific effect from strong interacting groups. By analogy, in the case of EMIS and *N*-(*n*-alkyl)maleimides,¹¹ one must consider that the occurrence of splitting is due also to the actual side chain length.

The dependence of splitting on the side chain length may be a feature to consider in regard to two types of interactions between bulky aromatic anisotropic solvents and the methylene chains. One, in the case of very short methylene chains, is produced by a certain type of interaction which is similar all over the chain. However, when the chain becomes longer, the interaction of the solvent with some of the methylenes is different from the others. This may be the controlling factor causing the methylene peak to split in two parts.

A detailed analysis in the case of *n*-alkanes shows¹⁸ that the new peak grown in relative intensity as the number of chain units increases, and can be identified with the peak of high molecular weight polyethylene. The second type of interaction predominates in the case of polyethylene.

All these interactions are modified by the existence of interacting groups, as previously shown by the present authors¹¹ and by Winnik *et al.*¹² Unfortunately, the latter made no study of the

dependence of this effect on the chain length and therefore, a comparison of results cannot be made.

The existence of two different types of interactions between the methylene chain and solvent molecules requires the presence of two different types of methylenes when the side chain has attained a certain length. In other words, the existence of two different types of conformation throughout the chain is necessary.

From a direct determination of end to end distances in a series of linear liquid *n*-alkanes ranging from C₆ to C₁₈, Brady *et al.*¹⁹ demonstrated that there is a fairly linear increase in the distance up to about C₁₀ and then a gradual decrease in slope, indicating that longer chains tend to assume a proportionately lower average end to end distance than do the shorter chains.

This results agree with those obtained by Schaufele²⁰ by means of laser vibrational scattering experiments and even with those obtained by Liu⁴ from ¹H NMR spectroscopy in benzene solution. Liu showed that the change in the relative solvent effect on the methylene chain with respect to *n* drastically deviates from the expected behaviour when *n*=9.

Keeping all the above in mind, we believe that the occurrence of the splitting after attainment of a certain length of the *n*-alkyl side-chain strongly indicates a second type of interaction caused by different conformational rearrangements of the chain. But, if the internal methylene groups vary gradually along the *n*-alkyl chain, a single dissymmetric NMR peak would then be expected for all internal methylene protons.

According to Liu¹ and our own experimental results, this premise is inconsistent with the observed results.

The length at which splitting is observed is actually controlled by the strength of the solute-solvent interactions. Both *N*-(*n*-alkyl)maleimides and EMIS show a splitting occurring at a shorter *n*-alkyl chain length than in the case of *n*-alkanes, owing to strong interacting groups. When the double bond of the *N*-maleimido ring is hydrogenated, which does not substantially modify the size or shape of the ring, the splitting disappears in the case of *N*-(*n*-alkyl)maleimides, but remains for EMIS since the existence of ester groups provides and maintains interactions strong enough to produce the splitting. It can be concluded that this effect is

due not only to a type of solute-solvent interaction, but also to a "conformational modification or bending" when a certain chain length is attained.

Such a type of "conformational modification or bending" is manifested by interactions among the *n*-alkyl chain and certain types of anisotropic solvents possessing planar structures. Schonhorn and Luongo,²¹ using model compounds, have observed infrared absorptions which can be attributed to the bending conformations in *n*-hydrocarbons.

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