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^{13}C N.M.R. STUDY OF SITE EFFECT IN VAN DER WAALS INTERACTIONS

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In a recent ^{13}C N.M.R. study on a linear alkane (n-pentane), Tiffon and Doucet (1) showed that the screening constant σ_w, resulting from the Van der Waals solute-solvant interactions, varies markedly with the position of the carbon in the chain.

We now report much greater variations in sensitivity for sequences of sp^2 and sp^3 carbons substituted in various ways. These results shows the increased importance of the site effect in the sensitivity of the carbon atoms to Van der Waals interactions.

The study is carried out in non anisotropic solvents on various solutes (ramified alkenes and alkanes). For each carbon of each solute, the chemical shifts (δ) obtained (2) are correlated with the function proposed by Rummens (3-5) : $g^2 = \left[\frac{n^2 - 1}{2n^2 + 1}\right]^2$, where n is the refractive index of the solvent.

All the sp^3 carbons considered, for both alkane and alkene molecules, yield linear correlations (δ/g^2). This shows that the polar term σ_E of the screening constant is always nil for these nuclei, regardless of solute polarity, and that the Van der Waals term can be decomposed into a product having two factors : $\sigma_w = S^i \times g^2$ - one of which is characteristic of the solvent (g^2), and the other of the solute (S^i). Parameter S^i, the slope of the correlation, is peculiar to a given carbon of a given solute. This is well illustrated for the methyls of T.M.E., as shown in figure 1.

In the case of the sp^2 carbons, considering only those solvents which are inert with respect to the solute, we obtain again linear correlations which necessarily express the only Van der Waals effects. For the other polar or halogenated solvents, large deviations from these straight lines occur ; this reveals the superposition on the Van der Waals term of a polar term σ_E, or of another term σ_H corresponding to a specific interaction between the solvent and the double bond (hydrogen bond or charge transfer complex (6)). These specific terms will be discussed in detail in a subsequent article. An example of a (δ/g^2) correlation is shown in figure 1 for the sp^2 nuclei of T.M.E. .

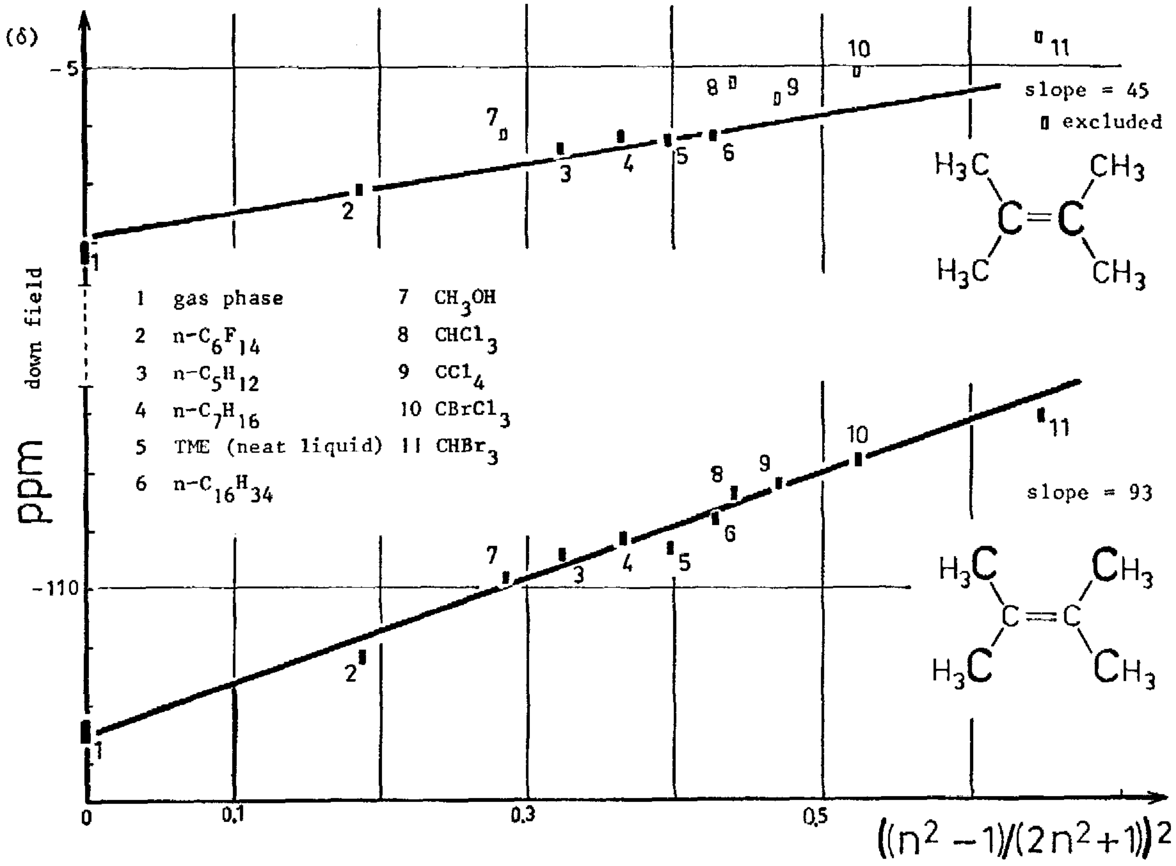
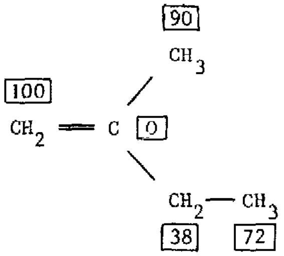
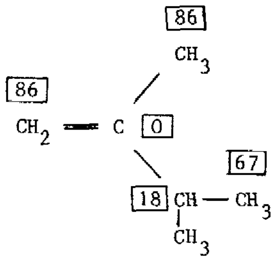


Figure 1

Thus, for all carbon atoms, a solute factor S^i can be defined from the slope of the correlation. This factor expresses the sensitivity of the carbon considered to Van der Waals effects. Results are given for each carbon of each solute molecule.



(a)



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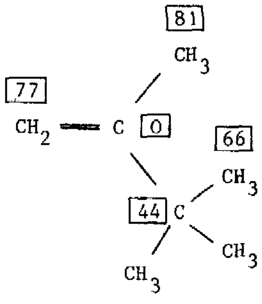
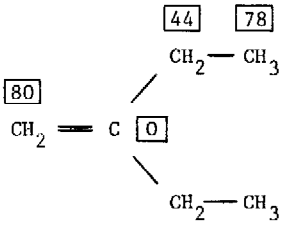


(c)



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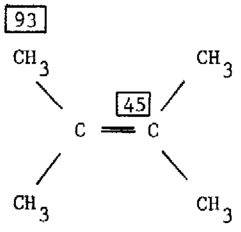
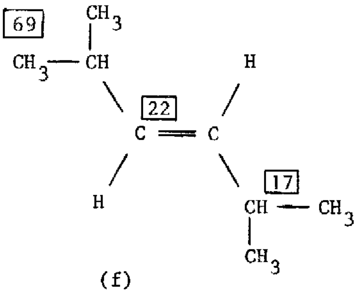
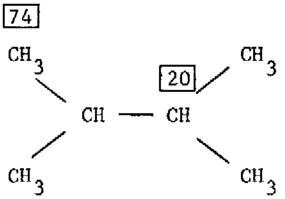


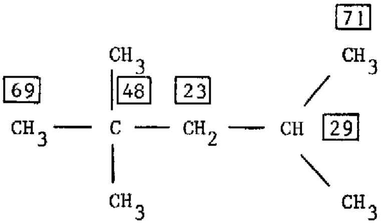
(e)



(f)



(g)



(h)

Analysis of these results brings out the following facts :

a) The sensitivity of an sp^2 or sp^3 nucleus with a given degree of substitution decreases when the size of the remainder of the molecule increases. This appears in solutes (a) (b) and (c) for the vinylic sp^2 carbons and for the sp^3 carbons of the methyls α to the double bond.

b) The sensitivity of differently substituted sp^3 atoms decreases in the order :

$$S^i_{-CH_3} > S^i_{-\overset{|}{\underset{|}{C}}-} > S^i_{-CH_2-} > S^i_{-CH\langle}$$

This sequence is not that which would be expected by extrapolation from data on n-pentane (1) on the sole basis of the accessibility of the sites to the solvent molecules. A possible explanation for this behaviour can be advanced on the basis of a suggestion by Buckingham et al.(7) to the effect that the local symmetry of the nucleus is involved. These authors mention the possibility of destroying a local symmetry by Van der Waals interactions, whence would arise a paramagnetic factor leading to greater sensitivity. Thus, the higher orbital symmetry of a quaternary carbon would account for the observation that the sensitivity is higher for this, than for a secondary or tertiary carbon. We should point out that the results observed for the above cited sequence of sp^3 carbons are in contradiction with the theoretical expression of the site parameter $S_{cont.}$, proposed by Rummens (5), for a spherical model. Indeed, for solutes (a), (b) and (c), respectively, the site factor $S_{cont.}$ would give the following qualitative classification (the distance from the site to the centre of mass decreasing and the molecular radius, constant or increasing, from the secondary to the quaternary carbon) : $S_{\substack{cont.\\(-CH_2-)}} > S_{\substack{cont.\\(-CH\langle)}} > S_{\substack{cont.\\(-\overset{|}{\underset{|}{C}}-)}}$. This classification is incompatible with the observed values of S^i.

c) The disubstituted sp^2 carbons of solutes (a), (b), (c) and (d) have sensitivity factors that are almost nil. The vinylic sp^2 nuclei of the same solutes are quite sensitive. In view of the non-negligible sensitivities observed for the substituted sp^2 carbons of solutes (e) and (f), steric effects cannot be considered to be the only cause of this difference in behaviour.

It may be significant, however, that in both cases where a substituted sp^2 carbon is solvent sensitive, the polarity of the double bond is zero. This would suggest that, for solutes (a), (b), (c) and (d), the polar character of the double bond is responsible for the insensitivity of the disubstituted sp^2 sites. The vinylic carbons tend to be negatively charged while the disubstituted sp^2 carbons are somewhat electron deficient. Thus for the negatively charged site, the increase in charge could enhance the possibility of deformation of the electronic environment by Van der Waals distorsions and, hence, lead to greater sensitivity. Conversely, electron deficiency on disubstituted nuclei would tend to diminish the sensitivity potential of these sites to the solvent.

We are continuing our study of these site effects with a view to a deeper understanding of Van der Waals interactions.

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(2) The chemical shifts are measured with respect to an external reference (benzene) and are corrected for the bulk magnetic susceptibility term. They are extrapolated to infinite dilution in each solvent, so as to avoid solute-solute interactions. The extrapolation is linear in volume fraction. In the case of tetramethylethylene (T.M.E.), chosen for its symmetric configuration, the shifts have been also determined in the gas phase.

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