

¹³C Nuclear Magnetic Resonance Chemical Shifts of Small Hydrocarbons in the Gas Phase

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Summary Gas phase ¹³C n.m.r. chemical shifts of small hydrocarbons are given and discussed briefly.

THE basis of the empirical determination of substitution parameters for ¹³C n.m.r. chemical shifts is formed by the shifts of the series of normal and branched alkanes and (hetero-) substituted derivatives. The chemical shifts of the alkanes were measured at a relatively early stage.¹ The results seemed to indicate that rather constant chemical shift differences could be observed between consecutive members of a homologous series and that these differences could be 'translated' into substituent parameters α , β , etc., without large deviations as long as no geminal or vicinal disubstituted alkanes were considered.²

On the other hand, theoretical calculations of ¹³C n.m.r. chemical shifts are still confined to rather small molecules. The older measurements (*vide supra*) included such compounds as methane, ethane, and ethene. Methane was measured as a dilute solution in cyclohexane of enriched material. Details for ethane and propane were not given;

most of the other measurements were obtained from neat liquids.^{1,2} The solvent effects were estimated to be relatively small. Recently it has been shown that solvent effects can become quite large for certain solvents with large dielectric constants.³ Even binary hydrocarbon mixtures show marked solvent effects.⁴ For these reasons and also in view of the obvious importance of 'unperturbed' experimental ¹³C n.m.r. chemical shifts in relation to calculations we report here the ¹³C n.m.r. chemical shifts of methane, ethane, propane, ethene, and propene in the gas phase at *ca.* 0.5 atm. Results are given in the Table.

The results indicate that the solvent effects on methane must have been rather large; in the previous work^{1b} the methane resonance was 45.6 p.p.m. upfield from (CD₃)₂SO. Under the conditions of our experiments it seems unlikely that intermolecular interactions will be very important.⁵ Intramolecular effects, such as interference of vibrational and rotational modes with bond angles and distances and thence with chemical shifts, may still play a minor role at 40 °C.⁶

TABLE. ^{13}C N.m.r. chemical shifts in p.p.m. downfield with respect to methane.^a

Compound	C(1)	C(2)	C(3)
Ethane	14.07	14.07	
Propane	24.16	25.83	
Ethene	129.79	129.79	
Propene	123.22	142.48	26.21

^a The methane resonance signal is 52.69 p.p.m. upfield from the ^{13}C signal of $(\text{CD}_3)_2\text{SO}$, which served as an external deuterium lock. All measurements were performed at 40 °C in cylindrical sample tubes.

The shift difference between methane and ethane is *ca.* 14.1 p.p.m. rather than 8–10 p.p.m. as reported previously.^{1–3} Also, some of the α - and β -effects deduced by comparing the pairs ethane–propane and ethene–propene differ from those used previously. For the alkanes an α -effect of +11.76 p.p.m. is now obtained, to be compared with +11.9 p.p.m.^{1b} or with the more commonly used value of +10.2 p.p.m.² For the alkenes the α -effect is +12.69 instead of +10.3 p.p.m.² The β -effect in propane

with respect to ethane is now +10.09 *vs.* +11.5 p.p.m.;^{1b} in propene we find –6.57 instead of –7.8 p.p.m.^{1b} A theoretical approach to ^{13}C n.m.r. chemical shifts should take these facts into account.

Of some further interest finally is a reversion in the initial assignments of the signals of isobutane in the liquid phase. Signal multiplicities in retain-*J* experiments as well as relative intensities in a decoupled spectrum indicate clearly that the lower-field signal is to be assigned to the methyl carbon atoms. A more detailed account of our work, including ^{13}C gas to liquid shifts of a number of alkanes (up to and including C_6) and substituted ethenes (up to C_4 inclusive) is in preparation.⁵

This investigation was supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

(Received, 12th September 1977; Com. 953.)

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