

13C nuclear magnetic resonance chemical shifts of small hydrocarbons in the gas phase

Citation for published version (APA):

Ven, van de, L. J. M., & Haan, de, J. W. (1978). 13C nuclear magnetic resonance chemical shifts of small hydrocarbons in the gas phase. *Journal of the Chemical Society, Chemical Communications*, (3), 94-95. <https://doi.org/10.1039/c39780000094>

DOI:

[10.1039/c39780000094](https://doi.org/10.1039/c39780000094)

Document status and date:

Published: 01/01/1978

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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

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

THE basis of the empirical determination of substitution parameters for ^{13}C 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 ^{13}C 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 ^{13}C n.m.r. chemical shifts in relation to calculations we report here the ^{13}C 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 $(\text{CD}_3)_2\text{SO}$. 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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