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PROTON MAGNETIC RESONANCE SPECTRA OF RELATED SERIES OF HALOACETYLENES

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A variety of short chained haloacetylenes were recently prepared in this laboratory for various physico-chemical investigations (e.g. [3-7]). In the course of these studies we found it of interest to measure the proton chemical shift of the simple haloacetylenes $X-(C{\equiv}C)_n-R$ $(n=1,2;\ X = I, Br, Cl, F, H, CH_3;\ R = H, CH_3, CHO)$. PMR spectra of some of these compounds have been reported previously [8]. However, the data were obtained under varying conditions making an accurate comparison difficult.

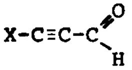
In this note we present the PMR spectra of twenty-two acetylenes, recorded under uniform [9] conditions. Table 1 summarizes the proton chemical shifts (solutions in deuterochloroform, - 50°C).

It is worth mentioning that in methylmonoacetylene (III (H)) the acetylenic and methyl protons exhibit identical δ-values [10]. Even more surprising is the same finding in methyldiacetylene (IV (H)).

In the following acetylenic as well as methyl proton chemical shifts are considered.

In the haloacetylene series (I) we observe a shift to *higher* field (decreasing δ-values) with *increasing* electronegativity of the halogen substituent. However, the opposite would be expected, if the dominating effect were the electron-with-

Table 1. Proton Chemical shifts of halogenated mono- and diacetylenes in deuterochloroform at - 50°C (δ-values with TMS as internal reference)[1].

Series	Compound[2] \ X	I	Br	Cl	F	H	CH_3
I	$X\text{-}C{\equiv}C\text{-}H$	2.23	2.21	1.94	1.63	2.01	1.88
II	$X\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}H$	1.89	1.99	2.00		2.06	1.97
III	$X\text{-}C{\equiv}C\text{-}CH_3$	2.06	1.88	1.84		1.88	1.80
IV	$X\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_3$	2.00	1.96	1.95		1.97	1.94
V	 $X\text{-}C{\equiv}C\text{-}C(=O)H$	9.17	9.18	9.19			

1) The spectra rerun at - 30°C show an excellent agreement with the data given, with displacements of the signals ≤ 0,02 ppm to lower fields.

2) Syntheses to be published elsewhere.

drawing power of the halogen atom, which would tend to deshield the protons. In the methylhaloacetylenes (III) and, within an extremely small range, also in the methylhalodiacetylenes (IV), the relative shifts parallel those of the haloacetylenes (I). The halodiacetylene series (II), however, shows a different trend.

If the chemical shifts of the series I to IV are plotted against the substituents in the order I, Br, H, Cl, CH_3, F (see Figure 1), series I, III and IV show a more or less continuous decrease of the δ-values. The decrease is most pronounced in the monoacetylene series (I), intermediate in the methylacetylene series (III) and only slight in the methyldiacetylene series (IV). This attenuated effect of the halogen substituent is to be expected, insofar as the halogens are further and further removed from the protons under consideration.

The irregular behaviour of the halodiacetylenes (II) as well as the unusual sequence of the substituents shown in Figure 1, indicate that at least two opposing effects must be at work in varying degrees.

It might be of interest to point to the fact that introduction of a second

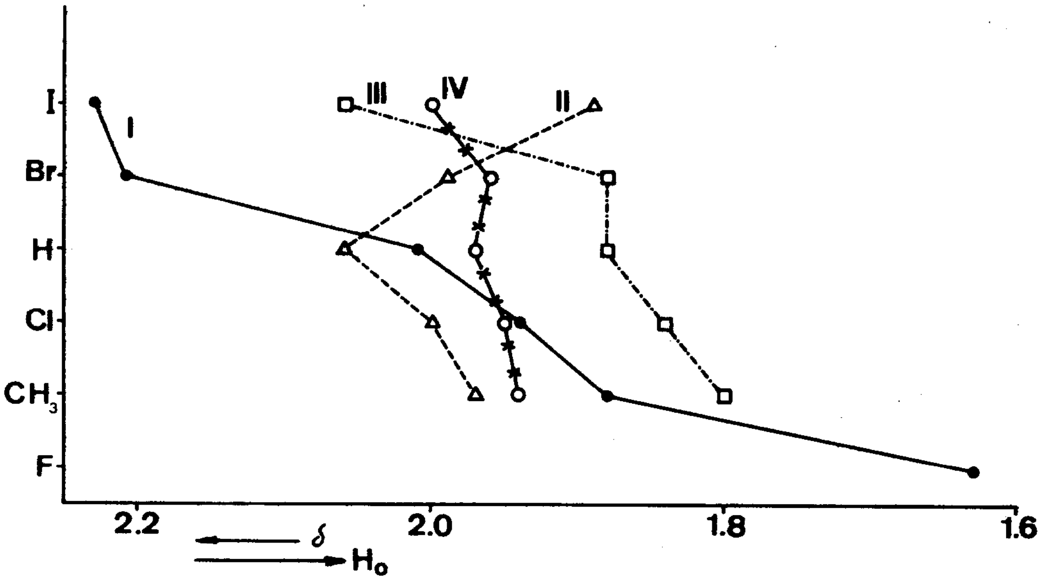


Figure 1. Displacement in chemical shifts of series I - IV, according to the chosen sequence of substituents: I, Br, H, Cl, CH_3, F.

triple bond into the carbon chain moves the signal down to lower fields. Comparison of the halogen-free compounds I(H) with II(H), and III(H) with IV(H), yields a down-field displacement (positive increment $\Delta\delta$) in the chemical shift of $\Delta\delta$ = 0.05 and 0.09, respectively. Furthermore, introduction of a third triple bond as in triacetylene $H-(C\equiv C)_3-H$ moves the shift *further* down-field by an increment $\Delta\delta$ = 0.08, which is comparable to that of diacetylene, whereas a fourth acetylenic bond as in tetra-acetylene, $H-(C\equiv C)_4-H$, leaves the shift unaltered relative to that of triacetylene. In these two samples diacetylene was added as reference [11].

Finally, the aldehydic proton in the halopropioloaldehyde series (V) is shown to remain practically uninfluenced by the halogen substituent. This contrasts strongly with the rather halogen-sensitive, equally distant methyl protons in the methylhaloacetylene series (III).

An explanation in terms of the electronic structure of these compounds is left open for discussion.

Experimental

The PMR spectra were recorded on a VARIAN HA-100 D spectrometer. The purity of all samples was checked with a mass spectrometer. An appropriate amount of sample was vacuum transferred into a tube containing the solvent, which was cooled in liquid nitrogen. The tube was sealed off and the contents were allowed to melt at low temperatures. Since most of the compounds are extremely reactive gases, weighing of the samples for preparation of strictly equimolar solutions had to be neglected. However, we believe that the variations in chemical shift caused by the actual differences in concentration are within the limits of experimental accuracy. The chemical shifts given are an average of three measurements.

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References and notes

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[3] E. Heilbronner, V. Hornung and Else Kloster-Jensen, Helv. Chim. Acta 53, 331 (1970).

[4] E. Heilbronner, V. Hornung and Else Kloster-Jensen, Helv. Chim. Acta 53, 1073 (1970).

[5] Else Kloster-Jensen, C. Pascual and J. Vogt, Helv. Chim. Acta 53, 2109 (1970).

[6] P. Gerber, H. Labhart and Else Kloster-Jensen, Helv. Chim. Acta 54, 2030 (1971).

[7] G. Bieri, F. Brogli, E. Heilbronner and Else Kloster-Jensen, J. Electron Spectroscopy and Related Phenomena, in press.

[8] a) H. Heel and W. Zeil, Z.f. Elektrochem. 64, 962 (1960);
b) L. Lunazzi, D. Macciantelli and F. Taddei, Mol. Phys. 19, 137 (1970).
c) For a survey see among others H. Suhr: Anwendung der kernmagnetischen Resonanz in der org. Chemie, Springer Verlag 1965,p.160, and ref. cit. therein.

[9] For small variations in concentration see Experimental.

[10] J.N. Shoolery, L.F. Johnson and W.A. Anderson, J. Mol. Spec. 5, 110 (1960).

[11] E. Kloster-Jensen, Angew. Chem. 84, 483 (1972); Angew. Int.Ed. 11, 438 (1972).