The Relative Signs of the ^1H–^1H Coupling Constants of Styrene Oxide

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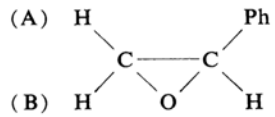
The NMR spectrum of styrene oxide has analyzed by Railly and Swalen[1] at 60 Mc. They reported that, though the position of the lines could be accounted for by two different nonequivalent assignments, J_{AC} and J_{BC}, with the same signs or different signs, the intensities were much more in agreement when J_{AC} and J_{BC} had the same sign, and that equivalent assignments could be obtained by positive or negative J_{AB} with positive (or negative) J_{AC} respectively. They arbitrarily chose both to be positive: $J_{AB}=+5.65$, $J_{AC}=+2.49$, and $J_{BC}=+4.04$ c.p.s.



On the other hand, the relative signs of the geminal and vicinal ^1H–^1H coupling constants are different in many organic compounds,[2] inconsistent with the prediction from the valence bond theory.[3] This suggests that the set of the coupling constants $-J_{AB}$, $+J_{AC}$, and $+J_{BC}$ (or $+$, $-$, $-$) would be correct, whereas the set of $+$, $+$, and $+$ (or $-$, $-$, $-$) would be wrong. In this communication, the result of our analysis, by means of which the correct set can be chosen, will be reported.

Since our calculations showed that the both sets could be practically distinguished from one another at frequencies below 20 Mc., the NMR spectrum of this compound was observed and recorded at 15 Mc. with a Varian 4300C spectrometer. It was found that the observed line-positions could be accounted for by the set of the coupling constants $+J_{AB}$, $+J_{AC}$, $+J_{BC}$ (or $-$, $-$, $-$) as shown in Fig. 1. This rather unexpected result may be ascribed to the specific structure of the three-membered ring of styrene oxide; it suggests that the signs of ^1H–^1H coupling constants are not definite for one type of a coupling of protons, as has been believed generally, but that they change depending on the chemical structure, for example, those in epoxides.

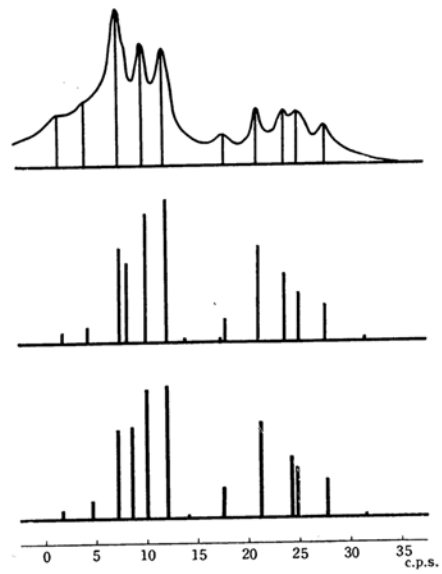


Fig. 1. The observed and calculated spectra of the ABC system of styrene oxide at 15 Mc.: the uppermost one is the observed spectrum and the middle and the lowest ones are the spectra calculated by using the sets $+J_{AB}$, $+J_{AC}$, $+J_{BC}$, and $-J_{AB}$, $+_{AC}$, $+J_{BC}$, respectively. The intensities of the observed lines are inaccurate because the spectrum was not recorded under the optimum conditions.

It is an interesting problem to determine whether the absolute signs of these coupling constants are positive or negative. Our conclusion on this point, as well as more detailed results of our analysis of the NMR spectrum of this compound, will be published elsewhere.

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3) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); H. S. Gutowsky, M. Karplus and D. M. Grant, ibid., **31**, 1278 (1959).