Association Shifts of NMR Spectra of Phenylacetylene[*]

By Naoya Nakagawa[**] and
Shizuo Fujiwara[***]

(Received October 15, 1960)

Solvent effects have recently attracted the attention of several workers in the investigations of the chemical shift phenomena of proton magnetic resonance in the -OH, -COOH, -NH, and $-SO_3H$ groups of organic compounds. The results of NMR measurements were interpreted in terms of proton exchange and of hydrogen-bond formation(1). Some of the most interesting results of these investigations are that obtained by Huggins, Pimentel and Shoolery(2), and by Korinek, Reeves and Schneider(3,4) for chloroform, which revealed us the fact that the association of the chloroform molecules can be studied by the proton resonance shifts of chloroform.

Since this technique is quite useful for the investigations of intermolecular interactions in liquid state, we made measurements of the solvent effects on the proton resonance shifts of phenylacetylene. The apparatus used for NMR measurements was constructed at the University of Electro-Communications and was operated at 27 Mc. In each of these samples, molecules are assumed to be associated with each other (self-association) or with solvent molecules; hence, the results of these measurements can be compared to those of chloroform.

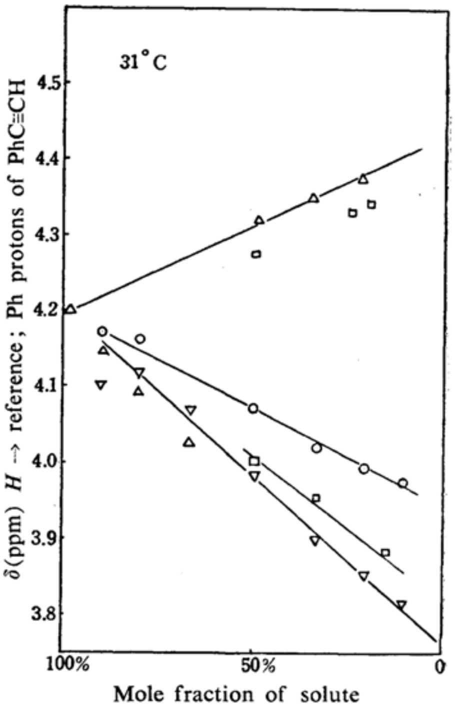

Fig. 1. Chemical shifts of C≡CH of PhC≡CH.
Solvent, △ C_6H_{12}, □ CCl_4
○ Et_3N, □ Me_2CO, ▽ Et_2NH,
△ EtOH

Fig. 1 shows the results of NMR measurements of the solvent effects for the ethinyl proton of phenylacetylene. The resonance position of the ethinyl proton is shifted to lower field by the addition of solvents such as Et_3N, Et_2NH, Et_2O, EtOH, and Me_2CO. This can be explained as being due to hydrogen bonding with nitrogen or with oxygen atoms of the solvent molecules. The high-field shift observed in the system with benzene is explained, as in the case of chloroform, by hydrogen bonding with the π-electrons of benzene. On the other hand, the high-field shifts observed in the system with carbon tetrachloride and with cyclohexane may be explained by assuming that the self-association of phenyl acetylene molecules is broken by the solvent molecules. This may be regarded as evidence for the proposition that the phenylacetylene molecules are associated with each other through interaction of the triple-bond π-electrons. This conclusion seems to be consistent with the finding of West in the infrared spectra of triple-bond compounds(5).

The authors thank to Mr. Hiroshi Shimizu of the University of Tokyo for valuable discussions.

Department of General Education
Nagoya University
Nagoya (N. N.)

Department of Chemistry
Faculty of Science
University of Electro-Communications
Chofu, Tokyo (S. F.)

---

[*] Presented at the Symposium of Structural Chemistry, the Chemical Society of Japan, Tokyo, September, 1959.

[**] Present address: University of Electro-Communications, Chofu, Tokyo.

[***] Present address: Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo.

1) J. A. Pople, W. G. Schneide and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill, New York (1959), p. 401.

2) C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, *J. Chem. Phys.*, **23**, 1244 (1955).

3) G. J. Korinek and W. G. Schneider, *Can. J. Chem.*, **35**, 1157 (1957).

4) L. W. Reeves and W. G. Schneider, ibid., **36**, 251 (1957).

5) R. West lectured at the Symposium of Electronic States of Molecules, the Chemical Society of Japan, September, 1959, Tokyo.