Solvent Shift of Methyl Proton Nuclear Magnetic Resonance

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(Received June 27, 1960)

The solvent effect of high resolution proton magnetic resonance has been investigated by many workers[1-3], recently. We also reported that the HCN, —C≡CH, and $-CH_3$ protons show quite large solvent shifts[4]. In this paper, we will show the results of the investigations for methyl protons in various compounds.

Chemical shifts of the NMR spectra of methyl protons in a number of organic compounds dissolved in solvents such as benzene, pyridine, dioxane, and carbon tetrachloride were measured by the internal reference method. Each sample consists of solute, solvent, and cyclohexane as the internal reference, with a molar ratio of 1 : 9 : 0.25, and is sealed in a glass tube of 3.5 mm. O. D. The apparatus of the NMR measurement is the one constructed by one of the authors (S. F.), and is operated at 27 Mc. The details of this set-up were reported elsewhere[5]. The chemical shifts of the methyl protons of the samples were measured on the recorded charts as the separations from cyclohexane by taking the separation between toluene CH_3 and cyclohexane as 0.75 p.p.m. This value of the reference was determined by the side-band technique[6].

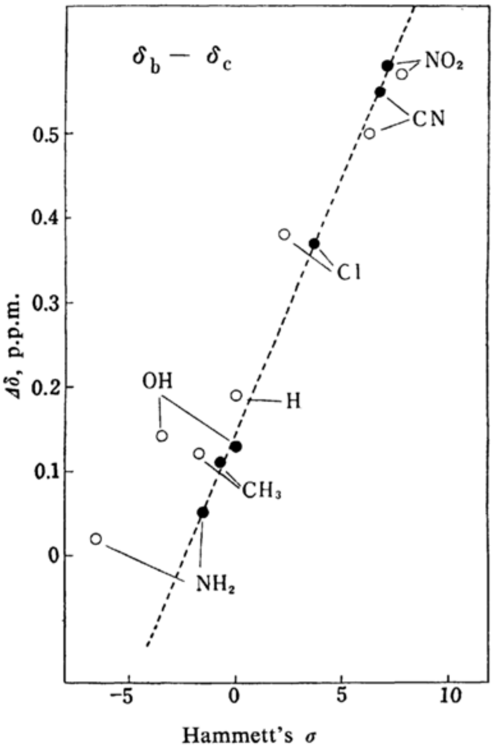

Fig. 1. Solvent shifts and Hammett's σ of substituted toluenes.

● meta ○ para

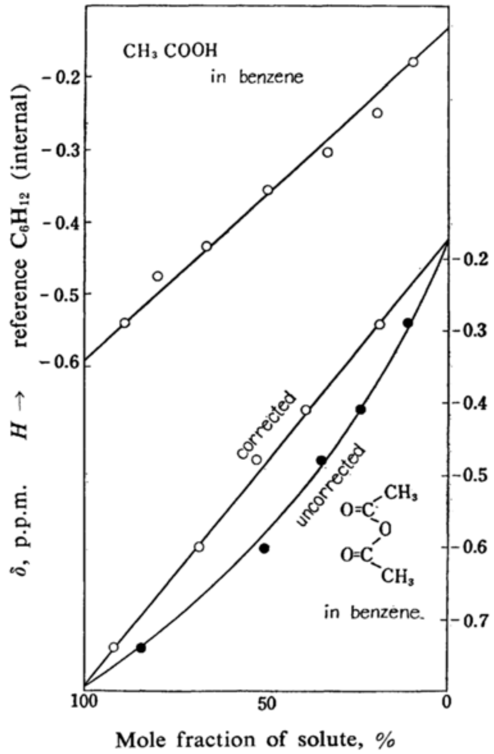

Fig. 2. Chemical shifts of CH_3 protons

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[1] As to the references of this effect before 1958, see, J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York (1959), pp. 400—432.

[2] E. B. Whipple, J. H. Goldstein, L. Mandell, G. S. Reddy and G. R. McClure, *J. Am. Chem. Soc.*, **81**, 1321 (1959).

[3] R. E. Glick, D. F. Kates and S. J. Ehrenson, *J. Chem. Phys.*, **31**, 567 (1959).

[4] N. Nakagawa and S. Fujiwara, to be published in *J. Org. Chem.*

[5] S. Fujiwara and H. Shimizu, in press in *J. Chem. Phys.*

[6] J. T. Arnold and M. G. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

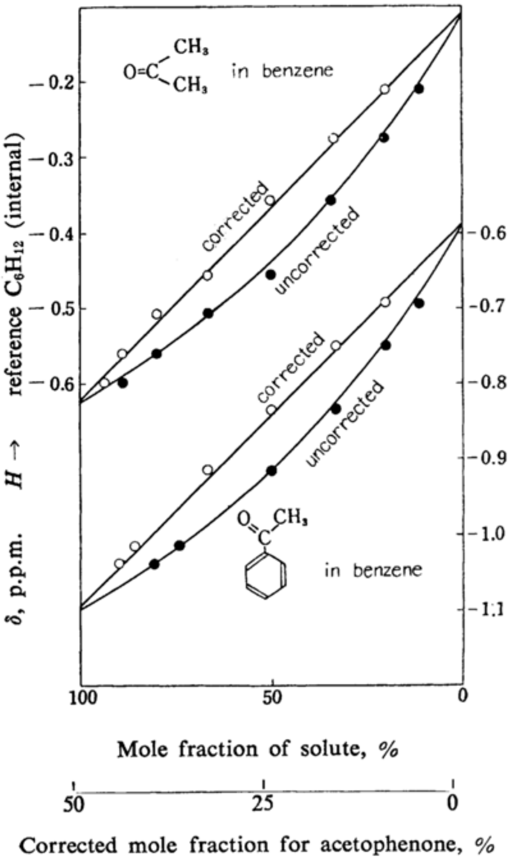

Fig. 3. Chemical shifts of CH_3 protons.

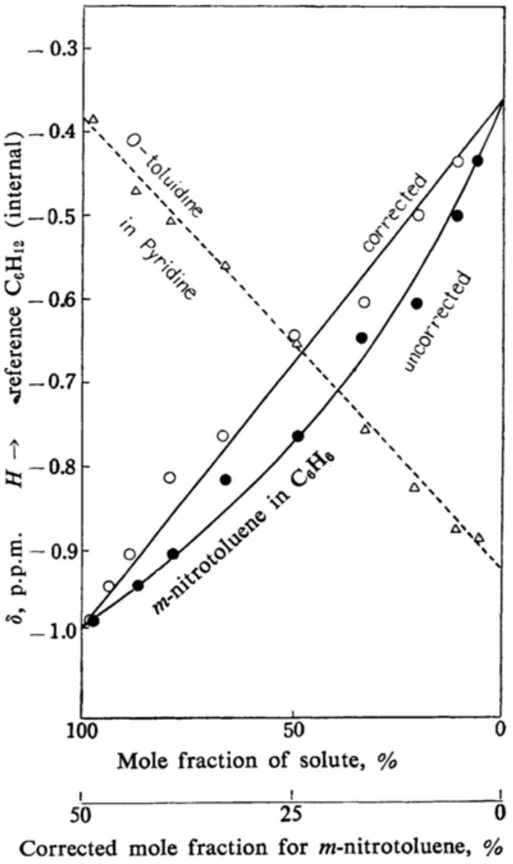

Fig. 4. Chemical shifts of CH_3 protons.

TABLE I. CHEMICAL SHIFTS OF METHYL PROTONS

Temperature: 11∼12°C
Concentration: solute: solvent: cyclohexane=1 : 9 : 0.25 (mol.)
Unit of chemical shift: p.p.m. from cyclohexane

Solute	Without solvent $-\delta_0$	In C_6H_6 $-\delta_b$	In C_5H_5N $-\delta_p$	In dioxane $-\delta_d$	In CCl_4 $-\delta_c$
Toluene	0.75	0.71	0.81	0.89	0.90
p-Nitrotoluene	—	0.50	0.90	1.01	1.07
p-Tolunitrile	0.90	0.50	0.87	0.97	1.00
p-Chlorotoluene	0.65	0.50	0.75	0.85	0.88
p-Xylene	0.71	0.72	0.83	0.79	0.84
p-Cresol*	0.70	0.66	0.91	0.77	0.80
p-Toluidine	—	0.73	0.82	0.70	0.76
m-Nitrotoluene*	0.99	0.48	0.93	1.03	1.06
m-Tolunitrile	0.87	0.42	0.82	0.93	0.97
m-Chlorotoluene	0.64	0.48	0.77	0.85	0.84
m-Xylene*	0.71	0.75	0.86	0.83	0.86
m-Cresol*	0.66	0.67	0.89	0.83	0.80
m-Toluidine	0.66	0.72	0.83	0.75	0.76

Table I (Continued)

o-Nitrotoluene	1.09	0.80	1.14	1.18	1.16
o-Tolunitrile	0.99	0.73	1.02	1.12	1.11
o-Chlorotoluene	0.78	0.71	0.85	0.91	0.93
o-Xylene	0.61	0.61	0.74	0.77	0.81
o-Cresol*	0.76	0.69	1.11	0.74	0.77
o-Toluidine	0.37	0.39	0.88	0.61	0.58
γ-Picoline	0.75	0.41	0.79	0.87	0.93
β-Picoline	0.76	0.46	0.81	0.87	0.88
α-Picoline	1.09	1.03	1.17	1.08	1.11
Acetone	0.65	0.24	0.66	0.62	0.67
Acetophenone	1.07	0.72	1.12	1.07	1.12
Acetic acid	0.60	0.17	0.80	0.52	0.62
Acetic anhydride	0.74	0.25	0.78	0.73	0.74
Methyl iodide	0.74	0.09	—	0.70	0.72
Acetonitrile	0.52	−0.43	0.52	0.51	0.53
Nitromethane	2.87	1.75	3.00	2.88	2.88

* Measurements for the compounds with asterisks were made at 17°C.

Table II. "Solvent shifts" $\Delta\delta$ of methyl protons

Temperature: 11∼12°C
Concentration: solute : solvent : cyclohexane = 1 : 9 : 0.25 (mol.)
Unit: p.p.m. ±0.03 p.p.m.

Solute	$\Delta\delta\equiv\delta_b-\delta_p$	$\delta_b-\delta_d$	$\delta_b-\delta_c$	$\delta_p-\delta_d$	$\delta_p-\delta_c$	$\delta_d-\delta_c$
Toluene	0.17	0.18	0.19	0.01	0.02	0.02
p-Nitrotoluene	0.40	0.51	0.57	0.11	0.17	0.06
p-Tolunitrile	0.37	0.47	0.50	0.10	0.13	0.03
p-Chlorotoluene	0.25	0.35	0.38	0.09	0.13	0.04
p-Xylene	0.11	0.07	0.12	−0.04	0.01	0.05
p-Cresol*	0.25	0.11	0.14	−0.14	−0.11	0.03
p-Toluidine	0.08	−0.03	0.02	−0.11	−0.06	0.05
m-Nitrotoluene*	0.45	0.55	0.58	0.09	0.13	0.03
m-Tolunitrile	0.40	0.51	0.55	0.11	0.15	0.04
m-Chlorotoluene	0.29	0.38	0.37	0.08	0.07	−0.01
m-Xylene*	0.11	0.08	0.11	−0.04	0.00	0.03
m-Cresol*	0.23	0.17	0.13	−0.06	−0.09	−0.03
m-Toluidine	0.11	0.04	0.05	−0.07	−0.06	0.01
o-Nitrotoluene	0.33	0.37	0.35	0.04	0.02	−0.02
o-Tolunitrile	0.30	0.40	0.39	0.10	0.09	−0.01
o-Chlorotoluene	0.14	0.20	0.22	0.06	0.08	0.02
o-Xylene	0.13	0.16	0.19	0.03	0.07	0.03
o-Cresol*	0.42	0.05	0.07	−0.37	−0.35	0.02
o-Toluidine	0.49	0.22	0.20	−0.27	−0.30	−0.03
γ-Picoline	0.38	0.46	0.52	0.08	0.14	0.06
β-Picoline	0.34	0.41	0.41	0.06	0.07	0.01
α-Picoline	0.14	0.05	0.08	−0.10	−0.07	0.03
Acetone	0.42	0.38	0.43	−0.04	0.01	0.05
Acetophenone	0.40	0.35	0.40	−0.06	0.00	0.06
Acetic acid	0.64	0.35	0.45	−0.29	−0.19	0.10
Acetic anhydride	0.53	0.48	0.49	−0.05	−0.04	0.01
Methyl iodide	—	0.62	0.63	—	—	0.02
Acetonitrile	0.95	0.94	0.97	−0.01	0.01	0.02
Nitromethane	1.26	1.13	1.13	−0.13	−0.13	0.02

* Values for the compounds with asterisks are for 17°C.

The results of measurements are summarized as shown in Table I. In meta- and para-substituted toluenes, the solvent shifts of the methyl protons, $\Delta\delta$, which are defined as the difference between the chemical shifts in any two solutions of different solvents, are linearly correlated with Hammett's sigma values as shown in Fig. 1. If we assume that the solvent shift of cyclohexane is constant, and if this is also the case with respect to the samples listed in the same column of Table II, the observed values of $\Delta\delta$ will mainly refer to the solvent shifts of the methyl protons.

In the results of Tables I and II, we notice that the magnitudes of the solvent shifts of the methyl protons are increased with the acidity of the methyl protons of the solute molecule. For example, the $\Delta\delta$ value of *p*-nitrotoluene for the benzene–CCl_4 system is 0.57 p.p.m. and that of *p*-toluidine is 0.02 p.p.m. This result coincides with the behavior of the solute parameter x_i of the medium effect defined by Bothner-By⁷⁾.

According to the results of the measurements, we can conclude that the chemical shift of methyl proton in acetic acid is a linear function of the mole fraction solute (Fig. 2), as in the cases of nitromethane and of acetonitrile⁵⁾. In acetic anhydride, or in acetone, the linear relation is not obtained with the simple mole fraction of the solute, but a fine linearity is obtained by taking the corrected mole fraction as abscissa, where one methyl group of the solute is taken into account as one solute molecule (cf. Figs. 2 and 3). In the cases of acetophenone and *m*-nitrotoluene, similar corrections are also necessary, and we have used the corrected mole fractions as shown in Figs. 3 and 4, where the number of the phenyl groups of the solute has been taken into account for the calculation as well as the solvent benzene.

In the case of *o*-toluidine, the chemical shifts of the methyl protons linearly depend on the simple mole fraction of the solvent (cf. Fig. 4) and, moreover, the magnitudes of the solvent shifts are anomalously large (cf. Table II). Similar results are observed with *o*-cresole.

The authors' thanks are due to Mr. Hiroshi Shimizu of the University of Tokyo and Professor Hajime Kashiwagi of Nagoya University for valuable discussions.

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7) A. A. Bothner-By: Private communication. The present authors are very grateful to Dr. Bothner-By for sending them the reprint.