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Proton Chemical Shifts of Molecular Complexes*

By

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Introduction

It is well known that iodine forms molecular complexes in some solvents of which molecules have π -electrons. Up to now, these molecular complexes have been studied by many techniques and recently the absorption spectra of visible ray and near ultra-violet region have been investigated in detail and then characteristic absorption spectra have been found¹⁾ in these complexes.

As to the origin of these absorption spectra and the nature of the chemical binding in these complexes, there have been many interpretations, but first Mulliken has succeeded²⁾ to give a reasonable explanation to them. He has concluded that molecular complexes are present because of the energy of stabilization resulting from the partial transfer of electrons from one to another of two molecules which formed the molecular complexes, and then the characteristic absorption spectra of these complexes are called the charge transfer spectra. Since then, the molecular complexes have been studied in many branches, for example, electronic spectra, X-ray diffraction, and infra-red or Raman spectra. And some studies by means of electron spin resonance have appeared recently, but now, nuclear magnetic resonance study of these complexes is not able to be found.

It may be expected that the change of electronic states of the molecules which is occurred as a result of formation of weak chemical binding in these complexes, would produce an effect on the chemical shifts of protons in these complexes, and therefore measurements were carried out on the chemical shifts of protons in solutions of iodine in aromatic substances as solvents.

As samples, some pure solvents and two iodine solutions in these solvents of which iodine-concentrations are different, were prepared and proton chemical shifts of pure solvents were compared with those of iodine solutions.

Experimental procedure

The proton resonance spectra were observed at 40 Mc, using a JNM-3 type high-resolution nuclear magnetic resonance spectrometer of Japan Electron Optics Laboratory Co., Ltd.

* A brief report of the measurements has been published in J. Phys. Soc. Japan 17 (1962) 1073.

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As the first series, benzene, toluene, and substituted toluenes were chosen as solvents and iodine was dissolved into them so as to have two concentrations, one was nearly iodine-saturated concentration for each solvent and the other was its half (but, for benzene, its one-third).

For measurements of the first series, the external reference using double-tube arrangements was employed and the sample solution was sealed in the inner tube and distilled water, as a reference substance, in the outer tube.

Next, as the second series, xylene derivatives were taken up as solvents and sample solutions were prepared as mentioned above for the first series. In this case, both the external and the internal references were employed. And as a reference substance, methylene chloride was chosen rather than water.

When the external reference was employed, a correction involving the difference between the bulk diamagnetic susceptibilities of the reference substance and the sample was applied, if the bulk diamagnetic susceptibility of the solvent was known.

The separation of the proton signal of the sample solution referred to the reference signal was obtained by employing the side band technique and the error of the present measurements did not exceed ± 0.05 ppm.

Results and Discussion

The results of the measurements for the first series are summarized in Table I. In the table, for *p*-chlorotoluene and *p*-bromotoluene, fine structures were observed for ring proton spectra as shown in Fig. 1 and Fig. 2, respectively, and therefore the chemical shifts of ring protons for these samples were not so accurate. Schaefer and Schneider have shown³⁾ that the resonance spectra of *meta*-protons in *p*-chlorotoluene and *p*-bromotoluene appeared at 0.05 and 0.07 ppm higher field than *ortho*-protons respectively. These separations between *meta*- and *ortho*-proton spectra are comparable order of spin-spin coupling constants between ring protons at 40 Mc and so complex spectra would be predicted for these compounds.

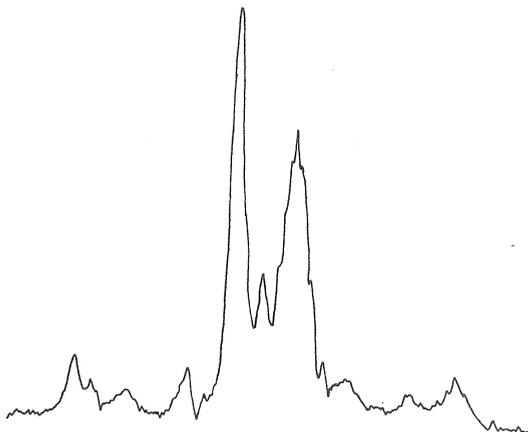


Fig. 1. Fine structures of ring protons in *p*-chlorotoluene.

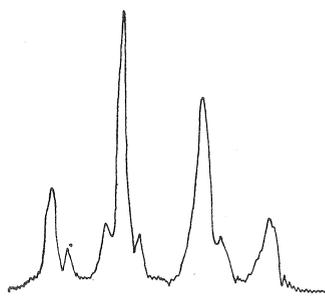


Fig. 2. Fine structures of ring protons in *p*-bromotoluene.

A correction for bulk diamagnetic susceptibilities of the reference substance and the sample was made according to the following expression,

$$\delta = \delta_{obs} + (2\pi/3) (\chi_v^{ref} - \chi_v),$$

where δ and δ_{obs} are the corrected and the observed chemical shifts, and χ_v^{ref} and χ_v are the bulk diamagnetic susceptibilities for the reference substance and the sample.

For iodine-solutions, their bulk diamagnetic susceptibilities were evaluated by the relation

$$\chi_v(\text{sol.}) = \phi(\text{I}_2) \cdot \chi_v(\text{I}_2) + \phi(\text{solv.}) \cdot \chi_v(\text{solv.}),$$

where $\phi(\text{I}_2)$ and $\phi(\text{solv.})$ are the volume fractions, and $\chi_v(\text{I}_2)$ and $\chi_v(\text{solv.})$ are the volume susceptibilities of iodine and the solvents, respectively. For some of the solvents, diamagnetic susceptibilities, which were not known, evaluated* with the aid of those of the related compounds and Pascal's constants.

Table I. Proton chemical shifts of benzene- and substituted toluene-iodine solutions. (In ppm from water as external reference, and corrected for bulk diamagnetic susceptibility.)

Solvent	I ₂ -conc. (mol-%)	Proton chemical shift, (H-H _r)/H _r	
		Ring proton	Methyl proton
benzene	0.0	-1.92	—
	1.4	-1.94	—
	4.1	-1.98	—
toluene	0.0	-1.84	+3.06
	2.0	-1.83	+3.07
	3.9	-1.86	+3.06
<i>o</i> -chloro- toluene	0.0	-2.01	+2.79
	1.4	-2.00	+2.77
	2.9	-1.98	+2.79
<i>m</i> -bromo- toluene	0.0	-1.79	+3.06
	1.6	-1.83	+3.03
	3.2	-1.83	+3.03
<i>p</i> -chloro- toluene	0.0	(-2.00 -1.93)	+2.87
	0.8	(-2.00 -1.94)	+2.87
	1.5	(-2.02 -1.96)	+2.88
<i>p</i> -bromo- toluene	0.0	(-2.10 -1.86)	+2.90
	2.4	(-2.12 -1.86)	+2.91
	4.8	(-2.11 -1.86)	+2.89

* We are indebted to Dr. J. Maruha of Chemical Department of this University for suggesting the method to estimate the unknown susceptibilities.

From Table I, differences of the chemical shifts which were dependent upon the concentrations of iodine were not able to be found within the experimental errors. This fact means probably that in the molecular complexes formed in iodine-solutions with these solvents, the relative large change of electronic states which is able to affect the chemical shifts of solvents, is not occurred.

Benesi and Hildebrand have shown¹⁾ that the iodine-mesitylene complex is a much tighter one than the iodine-benzene complex. Therefore, as the second series, xylenes were chosen as solvents and sample solutions were prepared in which concentrations of iodine are the same as the first series. Now, methylene chloride was used as the reference substance, because the position of the spectrum of water, which was used in the first series as the reference, is sensitive to the change of the temperature and impurities contained. And also, in this series, both the internal and the external references were employed and in the case of the latter, the bulk diamagnetic susceptibility corrections were applied, as in the first series, for the samples of which susceptibility was known.

Table II. Proton chemical shifts of xylene-iodine solutions.

(In ppm from methylene chloride.)

Solvent	I ₂ - conc. (mol- %)	Proton chemical shift, (H-H _r)/H _r			
		Internal CCl ₂ H ₂ reference		External CCl ₂ H ₂ reference*	
		Ring proton	Methyl proton	Ring proton	Nethyl proton
<i>o</i> -xylene	0.0	-2.16	+2.68	-1.33	+3.61
	2.3	-2.12	+2.73	-1.35	+3.61
	4.6	-2.14	+2.71	-1.36	+3.60
<i>m</i> -xylene	0.0	(-2.14 -2.05)	+2.63	(-1.13 -1.07)	+3.62
	2.4	(-2.09 -2.05)	+2.63	(-1.14 -1.09)	+3.63
	4.7	(-2.09 -2.06)	+2.64	(-1.13 -1.09)	+3.61
<i>p</i> -xylene	0.0	-2.10	+2.63	-0.90	+3.83
	2.3	-2.10	+2.64	-0.94	+3.80
	4.6	-2.06	+2.69	-0.97	+3.76
mesitylene	0.0	-1.32	+1.44	-2.35	+1.29
	3.3	-0.89	+1.91	-1.89	+1.74
	6.5	-0.50	+2.33	-1.45	+2.16
pseudo-cumene	0.0	-2.02	+2.66 +2.73	-0.89	+3.76 +3.90
	2.7	-1.99	+2.69 +2.76	-0.94	+3.72 +3.86
	5.4	-2.00	+2.68 +2.74	-1.00	+3.67 +3.77

* For *o*- and *m*-xylenes, corrected for bulk diamagnetic susceptibility, and uncorrected for others.

The results of the measured chemical shifts of protons in solvents of iodine-xylene solutions are shown in Table II. Of this table, complex fine structures

were observed for ring-proton spectra of *m*-xylene as shown in Fig. 3, and so the observed chemical shifts for these spectra were not so reliable. Also, for methyl proton spectra of pseudocumene (1, 2, 4-trimethylbenzene), doublet lines were obtained with intensities of 1 : 2.

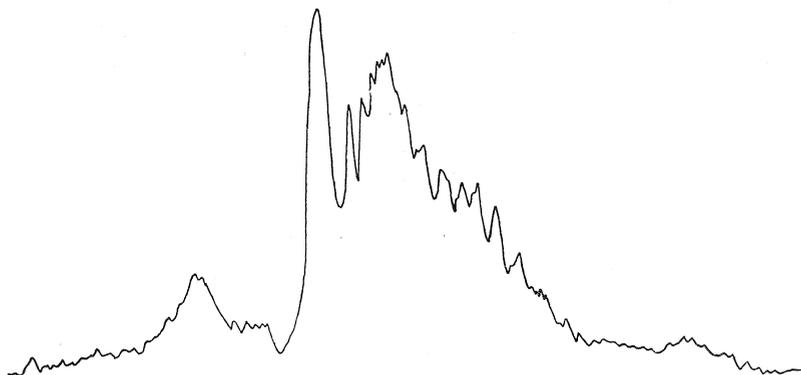


Fig. 3. Fine structures of ring protons in *m*-xylene.

For these samples, except *o*- and *m*-xylenes, the correction for the bulk diamagnetic susceptibilities was not applied, since the susceptibilities of these were not found.

Compared the obtained chemical shifts in the case of the internal reference with those in the external reference which were corrected for the differences of bulk diamagnetic susceptibilities for *m*- and *o*-xylenes, respectively, it is found that there are discrepancies amounting about 0.8 to 1.0 ppm between them. This indicates that the correction for bulk diamagnetic susceptibility is only a part of corrections which are required when chemical shifts of the internal reference are compared with those of the external.

Now, these discrepancies of chemical shifts amounting about 0.8 to 1.0 ppm are seemed to be explained by the following factors⁴. About 0.5 ppm of these arises from anisotropy in the susceptibility of the solvent. It is well known that aromatic solvents tend to produce high field shifts in the solute. In the present case, methyl benzene solvents are seemed to shift the position of methylene chloride signal to high field by about 0.5 ppm in the internal reference case. And additional anisotropy in aromatic ring arising from formation of π -complexes of aromatics with reference substance, methylene chloride, is responsible for the remainder, about 0.5 ppm.

To detect the differences of chemical shifts caused by chemical factors, it is desirable to employ the internal reference, and it is more profitable to use the reference substance which has little solvent effects on spectra. Therefore, it was not so suitable to use methylene chlorid as the reference, because it has dipole moment and is affected easily the dielectric constant of the solvents. As the reference substance, relative inert and proper one is seemed to be cyclohexane,

C_6H_{12} , or cyclopentane, C_5H_{10} .

Returned to the results in Table II, except the case of mesitylene as solvents, the expected differences of chemical shifts which depend upon the concentrations of iodine are not able to be found. While, in the case of mesitylene (1,3,5-trimethylbenzene) as solvents, considerable differences of the chemical shifts which depend upon the concentrations of iodine, are found, as shown in Fig. 4, and are seemed probably to be significant, but in pseudocumene as solvents, it is rather surprising that the similar differences does not exist.

Now, more precise measurements employing cyclohexane as the internal reference substance and some theoretical considerations on the results are in progress.

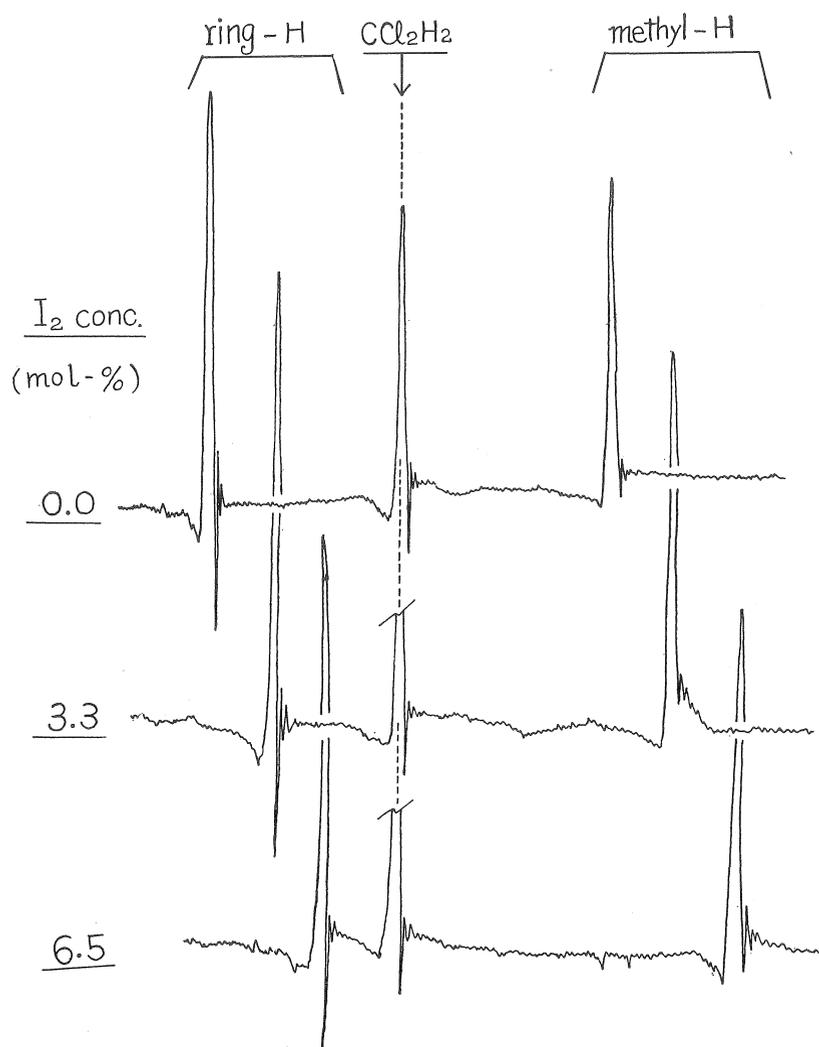


Fig. 4. I_2 -concentration-dependent proton chemical shifts of mesitylene.

Magnetic field increases from left to right.

Acknowledgments

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