## *Chemical Shifts of Proton Resonance and Mesomeric Effects in Substituted Benzene*

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(Received December, 8, 1958)

In regard to the chemical shift phenomena of nuclear magnetic resonance, efforts have been made to correlate the observed values with the bond characters of the compounds including the resonating nuclei, and successful results have been obtained with the fluorine resonances in binary systems[1]. Further study for the dependence of the chemical shifts on the substituents in polyatomic molecules were made by Gutowsky et al. and showed that *mata* and *para* substituents in substituted fluorobenzenes produced fluorine shifts proportional, respectively, to the inductive and the resonance effects of the substituents as is inferred from chemical reactivities. They showed also that the substituent effects in polysubstituted fluorobenzenes are reasonably additive[2]. Since these results offer most valuable informations for the investigations of the reactions of simple organic molecules, further study of the problem has been made by Corio and Dailey for the proton shifts in monosubstituted benzenes[3], but the results are rather complicated and have been interpreted in terms of the polarization effects in aromatic substitution reactions.

As the last results are complicated by the electron coupling of the proton spins, we have planned here to make measurements of proton resonance in substituted benzenes at a moderate resolution, where the ring protons will give a sharp line, and to investigate the proton shifts in relation with the characters of the substituent groups. The apparatus used is the one constructed in this laboratory, being operated at 27.030 Mc and using a permanent magnet.

In the actual experiments of the measurements, each sample was mixed with cyclohexane at the ratio of 1 : 1 by volume and the shift was measured as the average of the separations between the sample and cyclohexane in several records. Then, as shown in Table I, the shift values were

TABLE I

CHEMICAL SHIFT OF PROTON MAGNETIC RESONANCE IN SUBSTITUTED BENZENES

| Substance | Chemical shifts (ref. benzene) |
|---|---|
| $C_6H_5$-$NO_2$ | +14.5±0.5 cps |
| -COCl | +14.5 〃 |
| -$CH_3$ | − 2.5 〃 |
| -F | − 8.0 〃 |
| -Cl | − 4.0 〃 |
| -Br | − 3.5 〃 |
| -I | − 0.5 〃 |
| -OH | − 9.5 〃 |
| -$NH_2$ | −19.5 〃 |
| resonance frequency: | 27.030 Mc. |

1) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).

2) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952).

3) P. L. Corio and B. P. Dailey, ibid., **78**, 3043 (1956).

4) C. K. Ingold, "Strurcture and Mechanism in Organic Chemistry", G. Bell & Sons Ltd. (1953).

calculated taking benzene as the reference.

It is noted in Table I that there are observed very small but definite shifts for both bromo and chlorobenzene from benzene and, furthermore, our results in the table show a fine proportionality with the ability of each group to cause mesomeric effect[4].

Authors are very grateful to Professor Osamu Simamura of the University of Tokyo for valuable discussions. Our thanks are also due to Miss M. Nakahara who has made the purification of some of the samples.

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