High Resolution Nuclear Magnetic Resonance Spectra of Ring Protons in Substituted Benzenes

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The electron distribution on the benzene ring has been considered to be a very interesting object by many organic chemists, especially with respect to the correlation with the reactivity of the molecule. An experiment of approach to this problem was carried out by Gutowsky and his coworkers[1]. They measured the fluorine nuclear magnetic resonance in a number of fluorobenzenes and investigated the effect of substituents on the fluorine resonance shift and found the correlations between the values of the Hammett σ constant and of the resonance shift. Recently, Bothner-By and Glick[2] and also Corio and Dailey[3] observed the proton resonance spectra of benzene derivatives and discussed the electron densities on the *o*-, *m*- and *p*- protons. The patterns of the proton resonance spectra obtained by them are simple and not adequate for the precise examination of the electron distribution in the benzene derivative molecules. Patterns simpler than the expected ones are mainly due to the fact that the resonance frequency of the experiments was as low as 30 Mc.

Hence, we planned to investigate the proton resonance spectra of the benzene ring protons of a variety of benzene derivatives at 56.4 Mc. This paper reports the results of the analysis of their spectra, and the spectra of disubstituted benzenes are discussed with correlation to the substituents.

Experimental

The Varian High Resolution NMR Spectrometer was operated at 56.4 Mc. The resolution of the apparatus was higher than 10^{-8} when the sample was spun.

The samples measured were of commercial guaranteed grade, and these were used without further purification. The spectra of the liquid samples were taken in pure liquid state. Most of the solid samples were dissolved in acetone to make saturated solutions, and the spectra were taken. The others were dissolved in ethanol or ether.

All of the NMR measurements were carried out at 20°C for the samples sealed in glass tubes with the outer diameter of 5 mm. The spectra were recorded by the Sanborn Recorder and the separations of the resonance peaks were measured on the recorded charts. The magnetic field was swept in both decreasing and increasing directions and the measurements were made by taking the average of the records of both directions of the sweep. The calibration of the sweep rate was made by recording the spectrum of the methylene group of ethanol and by reading the separation of the two highest peaks as 7.0 cps[4]. The sweep rate was about 1 cps/sec.

The chemical shift of the ring proton resonance referred to benzene ring proton was determined for several compounds by adding a small amount of benzene to the sample liquid as an internal standard. This method was found to be inadequate for the precise determination of the shift value, because it was noticed that an additive shift arose by the addition of benzene. Therefore the observed values of the shift referred to benzene, δ_B, include an error of about ± 0.05 p.p.m.

The experimental error over the entire measurements was about 3%. This arose mainly from the instability of the field sweeping of the spectrometer.

Analysis of the Spectra

The systems of the ring protons of benzene derivatives are represented as in Table I, according to the notation proposed by Bernstein et al.[5]. In these systems, the spectra with simple structure may be analyzed by solving the equations of the Hamiltonian of the nuclear spin system and the assignment of the spectral lines can be made. The ratio $J/\nu_0\delta$, where J and $\nu_0\delta$ are respectively the spin coupling constant and the chemical shift in cps between the two resonating nuclei, ranges from 0.2 to more than 1 in the case of benzene ring protons, and in some cases the chemical shift is very small compared with the values of the spin coupling constant. This should be noted when the analysis is made by any approximate method which neglects higher order perturbation terms or some coupling constants.

For each system of ring protons the appropriate approximation method was adopted to

1) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952).
2) A. A. Bothner-By and R. E. Glick, ibid., **78**, 1071 (1956).
3) P. L. Corio and B. P. Dailey, ibid., **78**, 3043 (1956).
4) Varian Assoc., "Technical Information Bulletin", No. II-2.
5) H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

TABLE I. PROTON GROUPINGS IN SUBSTITUTED BENZENES

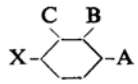
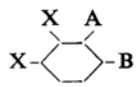
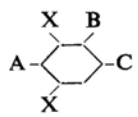
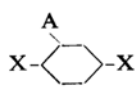
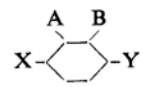
Mono-X benzene	AB_2C_2				
o-Di-X benzene	A_2B_2		*o*-XY benzene	ABCD	
m-Di-X benzene	AB_2C		*m*-XY benzene	ABCD	
p-Di-X benzene	A_4		*p*-XY benzene	A_2B_2	

TABLE II. SPREADING RANGE OF PROTON RESONANCE LINES OF MONO-SUBSTITUTED BENZENES (in cps at 56.4 Mc)

Nitrobenzene	55	Bromobenzene	35
Benzaldehyde	40	Iodobenzene	50
Toluene	Single peak	Aniline	55
Chlorobenzene	22		

analyze the spectrum. In the system of *o*-di-X benzene, the result of the analysis of *o*-dichlorobenzene, obtained by solving the secular equation by Pople et al.[6] was adopted. In *m*-di-X benzene the calculation based on the second order perturbation theory could be adopted for molecules where the ratios $J/\nu_0\delta$ in the molecule are comparatively small. In *p*-XY benzene, the secular equation of the system was solved by neglecting the spin couplings between the protons in *m*-position and in *p*-position to each other[7]. In each case of analysis, the coupling constants between protons are assumed to have positive sign.

Results and Discussion

Monosubstituted Benzene. — The spectra of monosubstituted benzenes are generally very complicated ones and none of the spectral lines can be assigned completely by a simple glance of the structure of the spectra. The preliminary analysis of the spectrum of this system shows that the line groups of *o*-, *m*- and *p*-protons have many lines and each of these spreads over a wide range. In most cases, the *m*- and *p*-protons are overlapping each other as the result of the couplings of protons where the chemical shifts are very small. This chemical shift is, in certain cases, much smaller than the coupling constant between the protons concerned. In addition to this, the spreading range of the resonance lines of *p*-protons is generally wide compared to that of *m*-protons. This makes the assignment of the ring proton spectral lines of monosubstituted benzene very difficult

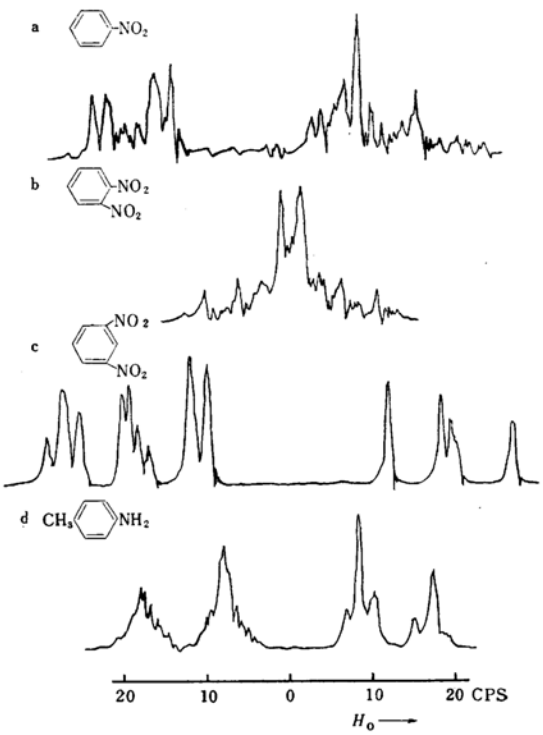


Fig. 1. NMR spectra of ring protons in mono- and di-substituted benzenes.

6) J. A. Pople, W. G. Schneider and H. J. Bernstein "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., New York (1959), pp. 145-149.
7) R. E. Richards and T. P. Schaefer, *J. Mol. Spectroscopy*, **2**, 1280 (1958).

compared with the other symmetrical systems. Though the spectra of the system reported by Corio and Dailey[3] are relatively simple, the simple spectra are due to the low resonance frequency of their experiment. It seems that the values of chemical shift reported by them may have errors as the result of the fact that the spectral patterns are not well resolved. An example of the spectrum of monosubstituted benzene is shown in Fig. 1a. The range of the spreading of the spectral lines is also shown in Table II. The spreading electron-range of the spectrum is wider as the releasing or withdrawing power of the substituent is stronger.

Disubstituted Benzene.—*o-Di-X Benzene.*—An example of the spectrum of the system is is shown in Fig. 1b. The spectrum spreads in a rather narrow range showing a symmetrical pattern. The magnitudes of the chemical shift and the spin coupling constants are listed in Table III. Generally, the chemical shift between A and B groups of protons is very small and this shows that the difference of the resultant electronic effects of the substituent on the protons of A and B groups is very small.

The chemical shift of the ring proton resonance referred to the benzene ring proton may be considered to arise from two origins. One is variation in the ring current and the other that in the electronic shielding of the protons affected by the substituent. The ring current variation might cause the shift of the whole spectrum in either direction according to whether the ring current density increases or decreases. On the other hand, electronic effects of the substituent would affect the protons at different positions separately by its inductive and resonance effects and the scectral figure would vary according to the difference in the effect on different protons.

For all *o*-di-X benzenes observed, the spectral lines spread almost in similar magnitude while the variety in δ_B is rather remarkable. This result would lead to the conclusion that the ring current is considerably affected by the substituent. The same consideration will be held for the other proton systems.

m-Di-X Benzene.—The spectrum of this system is characterized by its three-group pattern as illustrated in Fig. 1c. The last column in Table IV shows the arrangement of spectral line groups in increasing field direction. The order of arrangement of these groups in the spectrum is understood mainly in terms of the electron-releasing and withdrawing power of the substituent X. The resonance position of the A proton is greatly influenced by the electronic nature of the substituent because the position of the proton is between two X's,

TABLE III. CHEMICAL SHIFT AND COUPLING CONSTANT IN *o*-di-X BENZENES
(in cps at 56.4 Mc)

Compound	Solvent	$\nu_0\delta_{AB}$	J_{AB}	$J_{AB'}$	$J_{BB'}$	δ_B (in p.p.m.)
o-Dinitrobenzene	Acetone	7.1	8.4	0.9	3.1	−0.74
Phthalic acid	Acetone	9.3	7.8	0.5	4.1	−0.35
o-Xylene	—	0.0				
o-Dichlorobenzene	—	13.8	8.4	1.9	6.9	+0.24
Catechol	Acetone	11.2	8.1	1.3	5.0	+0.43

TABLE IV. CHEMICAL SHIFT AND COUPLING CONSTANT IN *m*-di-X BENZENES
(in cps at 56.4 Mc)

Compound	Solvent	$\nu_0\delta_{AB}$	$\nu_0\delta_{BC}$	J_{BC}	J_{AB}	J_{AC}	Spectrum
m-Dinitrobenzene	Acetone	12.6	33.0	7.6	2.0	0.5	A-B-C
Isophthalic acid	$(CH_3)_2SO$	23.4	30.2	8.0	1.6	1.0	A-B-C
m-Xylene	—						C-A-B
m-Dichlorobenzene	—						C-A-B
Resorcinol	Acetone		36	8.5	2	1	C-A-B
m-Phenylenediamine	Acetone	4.8	45.2	8.4	2	1	C-B-A

TABLE V. CHEMICAL SHIFT IN *p*-di-X BENZENES

Compound	Solvent	δ_B (in p.p.m.)
p-Dinitrobenzene	Acetone	−1.17
Terephthalaldehyde	Acetone	−0.77
p-Xylene	—	+0.29
p-Dichlorobenzene	Acetone	−0.05
p-Dibromobenzene	Acetone	+0.30
p-Phenylenediamine	Acetone	+0.85

TABLE VI. CHEMICAL SHIFT AND COUPLING CONSTANT IN *p*-XY BENZENES (in cps at 56.4 Mc)

Compound	Solvent	$\nu_0\delta_{AB}$	J_{AB}	δ_B (in p.p.m.)
p-Nitrobenzaldehyde	Acetone	12.3	9.3	−0.87
p-Nitrobenzoic acid	Acetone	23.1	8.4	
p-Nitrotoluene	—	38.1	9.5	−0.32
p-Nitrochlorobenzene	Acetone	31.7	9.0	−0.53
p-Nitrobromobenzene	Acetone	22.1	9.8	−0.71
p-Nitrophenol	Acetone	68.0	9.5	−0.23
p-Nitroaniline	Acetone	64.7	8.9	−0.05
p-Hydroxybenzaldehyde	Ethanol	46.7	9.5	
p-Aminobenzaldehyde	Acetone	45.8	8.2	+0.02
p-Toluic acid	Acetone	37.0	8.1	
p-Chlorotoluene	—	12.1	8.3	+0.27
p-Bromotoluene	—	22.9	8.2	+0.22
p-Cresol	—	0.0		
p-Toluidine	Ether	23.7	9.0	+0.69
p-Bromochlorobenzene	Acetone	11.6	8.8	
p-Chlorophenol	—	14.1		
p-Chloroaniline	Acetone	26.1	9.0	+0.51
p-Bromophenol	Ether	31.4	9.7	
p-Iodoaniline	Acetone	48.4	8.8	+0.41

while the C proton is not so much influenced.

The analyzed results are tabulated in Table IV. The perturbation treatment of the second order could be applied to two compounds (*m*-dinitrobenzene and *m*-dichlorobenzene) well, but not to the others where the resonance positions of A and B protons are closely located. For these compounds, the analysis of the spectrum should be accomplished with the higher order approximation.

p-Di-X Benzene.—The spectra are single line as expected from the symmetry consideration of this system. The chemical shift referred to benzene is shown in Table V.

p-XY Benzene.—This system has two different substituents and the different electronic effect is given on the proton neighboring to each of them. In addition to this, the spectrum of this system is comparatively simple and can be analyzed easily Therefore, the investigation of the spectrum of this system is interesting to show the overlapping extent of the effects of both substituents on the ring. An example of the spectrum of this system is shown in Fig. 1d. This consists of two groups A and B, which correspond to the protons A and B in the molecule.

This system has been analyzed for several compounds with appropriate approximation by Richards and Schaefer[7]. The present spectra were analyzed according to their method. The values of the chemical shift and the coupling constant obtained are listed in Table VI, where the J_{AB} is the coupling constant between A and B protons when the $J_{AB'}$ (coupling constant between A and B′ protons which one *p*-position to each other) is neglected.

Qualitatively, the shift between the two groups A and B is large when the electronic effects of the two substituents X and Y upon the ring protons are greatly different and vice versa. For example, δ_{AB} of *p*-nitroaniline is very large where the electronic nature of NO_2 and NH_2 group are greatly different to each other as is well known by the evidence of their effect on the substitution reaction of ring protons, whereas the one of bromochloro-benzene is very small as is expected.

Other Systems.—The spectral figures of the other systems are generally more complicated than the systems described above. *o*-XY- and *m*-XY-benzenes are of this sort. These systems have no symmetry, therefore their analyses are of course very cumbersome. These systems will not be dealt with further in this paper.

The values of the coupling constant between two protons on the benzene ring are approximately definite with respect to their mutual *o*-, *m*- or *p*-positions. The values deduced from the results of the analyses may be summarized as follows;

J between two protons located at

o-position mutually	7∼9 cps
m-position mutually	1∼3 cps
p-position mutually	0∼1 cps

The values indicated that the coupling is attenuated in proportion to the exponent of about −5 to the direct bond length between the two protons concerned. The values listed above

coincide well with the description which appeared in the book of Pople et al.[8]

The resonance position of a benzene ring proton is closely related to the relative location of the proton to the substituent on the benzene ring. The same evidence was discussed by Gutowsky et al.[1] with the fluorobenzene derivatives. They showed also that the shift values for the ring fluorine of polysubstituted fluorobenzenes may be calculated from the shift values of monosubstituted fluorobenzenes with the assumption of an additive law of shift. Their calculated results with this law coincide with the experimental values with deviations less than 10%. We applied the law to the samples investigated. The values for the disubstituted benzenes were calculated with the shift values of the monosubstituted benzenes reported by Corio and Dailey[3]. The results of the calculation showed that the shift values do not necessarily coincide well, but showed a close relation with the experimental values. The explanation of the shift values with the additive law may of course be oversimplified by neglecting to take into account all the interactions in the molecule, and further consideration of the results will be postponed until more experimental data with monosubstituted benzenes become available.

The resonance lines for the protons just adjacent to the methyl group on the ring generally show fine structure. This splitting is illustrated in Fig. 1d for the ring proton resonance of *p*-toluidine. Hoffman[9] reported that the ring proton resonance line of mesitylene showed broadening, and he assumed that this broadening arose from the coupling between the ring proton and the methyl protons by hyperconjugation mechanism. Although the observed fine structure reported here may be a similar one to the case of mesitylene, further experimental verification seems necessary for deciding the true origin of the splitting.

The present work is carried out with saturated acetone solutions in almost all cases, however; the solvent effect on the shift between ring protons appears to be noticeable. Thus the shift values may differ from one another among solutions with different concentrations. This intramolecular shift may be assumed to arise from the selective interaction between the proton located at the specific position on the ring and the solvent molecule. The nature of this interaction is at present unexplained.

8) Ref. 6, p 193, Table 8-1.
9) R. A. Hoffman, *Mol. Phys.*, 1, 326 (1958).

Summary

High resolution proton magnetic resonance spectra of a variety of mono- and di-substituted benzenes were observed at 56.4 Mc. The spectra of molecules with higher symmetry were analyzed, and the values of chemical shifts among the ring protons and those referred to benzene were obtained as well as spin coupling constants. The spectra were discussed with correlation to the substituents.

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