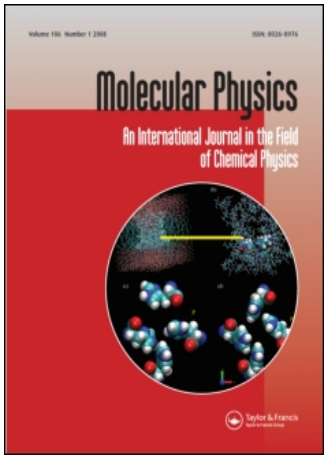

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S. Mohanty [a]; Putcha Venkateswarlu [a]
[a] Physics Department, Indian Institute of Technology, Kanpur, India

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Proton and fluorine N.M.R. spectra of fluorobenzene†

by S. MOHANTY and PUTCHA VENKATESWARLU
Physics Department, Indian Institute of Technology, Kanpur, India

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Proton and fluorine resonance spectra of fluorobenzene have been obtained under high resolution using a Varian spectrometer operating at 100 Mc/s and 94·1 Mc/s respectively. These have been analysed by treating the molecule as a six-spin system of the type AB_2C_2X with C_{2v} symmetry. The best parameters available were used to solve the secular equation using an IBM 1620 computer. Carbontetrachloride, chloroform, dioxan and benzene were used as solvents and spectra were obtained at different concentrations. Both ^1H and ^{19}F spectra show concentration dependence. Splittings of the spectra due to the natural abundance of ^{13}C were observed. The coupling constants $J_{^{13}C-H}$ and $J_{^{13}C-F}$ have the values $160·0 \pm 2·0$ c/s and $265·5 \pm 2·0$ c/s respectively.

1. INTRODUCTION

A partial analysis of the nuclear magnetic resonance spectra of fluorobenzene was reported earlier by Fujiwara and Shimizu [1]. Bak, Shoolery and Williams [2] investigated deuterated species of fluorobenzene and particularly analysed the fluorine spectrum of 4-D-fluorobenzene. Since the para H–F coupling is negligibly small, one expects identical fluorine spectra for fluorobenzene and 4-D-fluorobenzene. However Bak *et al.* obtained, at 30 Mc/s, a fluorine spectrum of fluorobenzene different from that of the 4-D-fluorobenzene and discussed it qualitatively. Fujiwara and Shimizu analysed the proton spectrum of fluorobenzene at 27·03 Mc/s. The present work was undertaken to perform a complete analysis of the spectra at a higher resolution with the hope of getting better parameters. We report here both the proton and fluorine spectra of fluorobenzene at 100 Mc/s and 94·1 Mc/s respectively. In addition to the analysis, solvent effects and ^{13}C splittings on both ^1H and ^{19}F resonances have been observed.

2. EXPERIMENTAL

The spectra were all obtained at room temperature (25°c) using a Varian HR–100 spectrometer. The separations of resonance peaks were measured in cycles per second using side band technique. Fluorobenzene was obtained from L. Light and Co. Ltd., England, and had the highest commercially available purity (99 per cent). Nitrogen gas was bubbled through all the samples (before sealing) to remove dissolved oxygen.

† A part of the work reported in this paper was presented at the 1966, Nuclear Physics and Solid State Physics Symposium, held at the Tata Institute of Fundamental Research, Bombay, 21–26 February.

3. Discussion

3.1. *Analysis of the spectra*

Fluorobenzene is a six-spin system of the type AB_2C_2X. It has C_{2v} symmetry. The spin Hamiltonian for the case where a static magnetic field H_0 is applied to the system in the z direction, is given by (in units of c/s):

$$\mathscr{H}=\frac{1}{2\pi}\sum_{i=A}^{x} r_iH_0(1-\sigma_i)I_z(i)+\frac{1}{2}\sum_{i,j=A}^{x} J_{ij}(1-\delta_{ij})\mathbf{I}_i \cdot \mathbf{I}_j,$$

where r, σ, I, J and δ are nuclear magnetogyric ratio, nuclear screening constant, nuclear spin, spin coupling constant and Kronecker delta function respectively. This system has sixty-four (2^6) basic symmetric functions. These symmetry functions are given by Fujiwara and Shimizu [1] and have been used here. The matrix elements of the Hamiltonian constitute a sixty-fourth order secular equation:

$$|\mathscr{H}_{mn}-\delta_{mn}\lambda_n|=0,$$

whose solutions are the energies. However, this reduces into four each 1×1, 2×2, 3×3, 4×4 and 6×6 dimensional sub-matrices if one considers the symmetry of the molecule and the fact that the z component of the total spin

$$F_z=\sum_i I_z(i)$$

and that of the fluorine spin commute with H. The eigenvalues and the eigenvectors cannot be written in explicit analytical form. One has to solve these higher order equations with the help of a computer. The system has a total of 416 transitions of which there are 40 each of A and X transitions and 48 each of B and C transitions and the rest are combination lines almost all of which are very weak in intensity.

The Hamiltonian H of the system is diagonalized by the computer to get its eigenvalues λ_n and eigenvectors $\varphi=U\chi$ where χ are the basic symmetry functions and U a unitary matrix which diagonalizes the total Hamiltonian. The intensity is proportional to the elements of the matrix I_n defined by:

$$(I_n)_{ij}=|\langle\varphi_i|I_x|\varphi_j\rangle|^2,$$

where I_x is the sum of x components of all the nuclear spins of the system. Using $\varphi=U\chi$:

$$(I_n)_{ij}=\left|\sum_{lk}U_{il}{}^*M_{lk}U_{jk}\right|^2=|(UMU^\dagger)_{ij}|^2,$$

where $M_{lk}=\langle\chi_l|I_x|\chi_k\rangle$, trace $M=0$ and $M_{lk}=M_{kl}$.

3.2. *Proton and fluorine resonance spectra*

The proton resonance spectrum (figure 1) spreads over 47 c/s approximately at 100 Mc/s resonance frequency. The zero position on the spectrum corresponds to the ortho protons. The spectrum is extremely complicated and involves a large number of transitions. Bak *et al.* [2] have observed meta protons at the lowest applied field in 4-D-fluorobenzene. Thus ortho protons occur at a higher applied field. The position of the para proton is found by adjusting the chemical shift parameters. Best fit between the experimental and theoretical lines (figure 2) shows that the chemical shift between ortho and para protons is zero. The

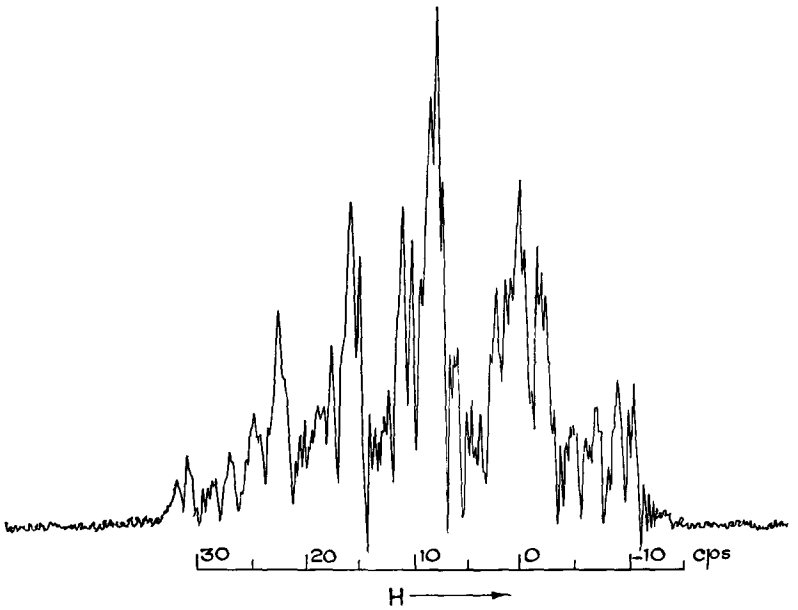

Figure 1. The proton resonance spectrum of fluorobenzene at 100 Mc/s.

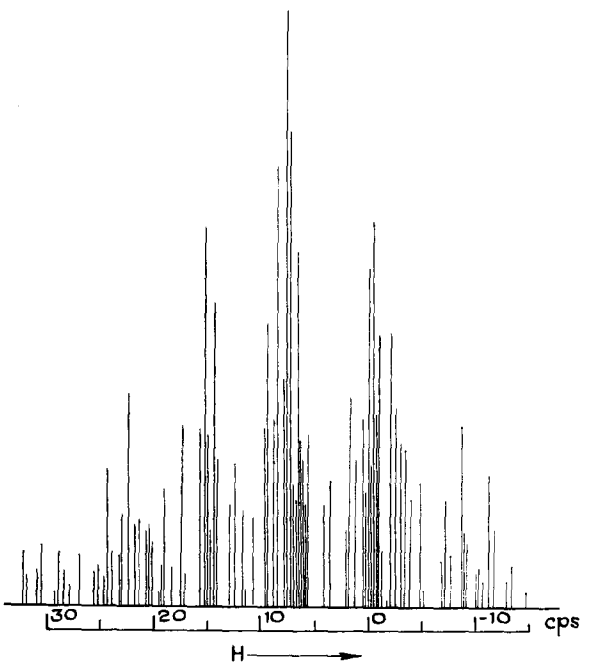

Figure 2. Calculated proton resonance spectrum of fluorobenzene at 100 Mc/s.

fluorine resonance spectrum spreads over 34 c/s approximately at 94·1 Mc/s resonance frequency. It shows very little similarity with that reported earlier by Bak *et al.* [2]. This may be due to the low resolution (30 Mc/s) at which they studied. The present spectrum clearly shows asymmetry about the centre

around ± 7 c/s and ± 14 c/s which arises from combination lines due to the presence of strong coupling between protons. The observed and the calculated spectra for fluorine are shown in figures 3 and 4 respectively.

3.3. *Signs of the coupling constants*

The sense of the asymmetry in the fluorine spectrum depends on the relative sign of the proton–proton and proton–fluorine couplings. The sense is reversed in the spectrum by changing the sign of J_0^{HH} and J_m^{HH} and no solution with J_m^{HH} having a sign opposite to J_0^{HH} fits the spectrum. A similar effect is found with J_m^{HF} and J_0^{HF} couplings. The H–F couplings are found to have the same sign as the H–H couplings. Attempts were also made to find out if the values for the para couplings ($J_p^{HH}=0=J_p^{HF}$) are different from zero. It was difficult to draw conclusions about these coupling constants from the agreement between the calculated lines with observed spectra since the spectra are complicated. The final results are given in table 1, for the best fit. These values agree well with the values obtained by earlier workers [1, 2].

$J_0^{HH}=8\cdot9$ c/s	$J_0^{HF}=9\cdot4$ c/s	Chemical shift between ortho and meta protons $=18\cdot0$ c/s
$J_m^{HH}=2\cdot2$ c/s	$J_m^{HF}=5\cdot8$ c/s	
$J_p^{HH}=0\cdot0$ c/s	$J_p^{HF}=0\cdot0$ c/s	Chemical shift between ortho and para protons $=0\cdot0$ c/s

Table 1. The coupling constants and chemical shifts of fluorobenzene.

4. Solvent effect

Carbontetrachloride, chloroform, benzene and dioxan have been used as solvents. The resonance spectra were obtained at different percentages of concentration (by volume). The separation of the ortho protons in the proton spectrum and the centre of gravity of the fluorine spectrum from the respective reference lines has been taken to be the chemical shift (δ). The zero position, which is approximately 8 c/s up-field from the highest peak in the proton resonance spectrum in figure 1, corresponds to the ortho protons. The proton shifts were measured relative to cyclohexane as an internal reference and the fluorine shifts were measured relative to difluoroacetic acid as an external reference. In both the cases, the reference signals appeared at higher fields. Figures 5 and 6 show the variation of chemical shift with dilution for proton and fluorine resonances respectively. In each case, the plot gives a straight line or a smooth curve which is extrapolated to give the chemical shift at infinite dilution. The results are given in table 2.

Contributions to nuclear screening can arise due to (i) bulk diamagnetic susceptibility of the medium (σ_b), (ii) anisotropy in the magnetic susceptibility of the solvent molecules (σ_a), (iii) distortion of the solute molecule by interaction with the solvent molecules through van der Waals type forces (σ_W), (iv) distortion of the solute molecule by an electric reaction field (polar effect, σ_E), (v) hydrogen bonding and (vi) other molecular association effects. The first four of these effects have been considered theoretically by Buckingham *et al.* [3]. The greatest

Solute	Solvent	Ortho-proton shift p.p.m. from cyclohexane	Fluorine shift p.p.m. from difluoroacetic acid
Fluorobenzene	Pure	−5·495	−15·445
	CCl_4	−5·755	−17·271
	$CHCl_3$	−5·760	−16·133
	C_6H_6	−5·365	−15·880
	$C_4H_8O_2$	−5·680	−15·115

Table 2. Proton and fluorine chemical shifts at infinite dilution (corrected for bulk susceptibility). Accuracy is within ±0·02 p.p.m. Negative sign indicates the signal occurs at lower field with respect to the reference line.

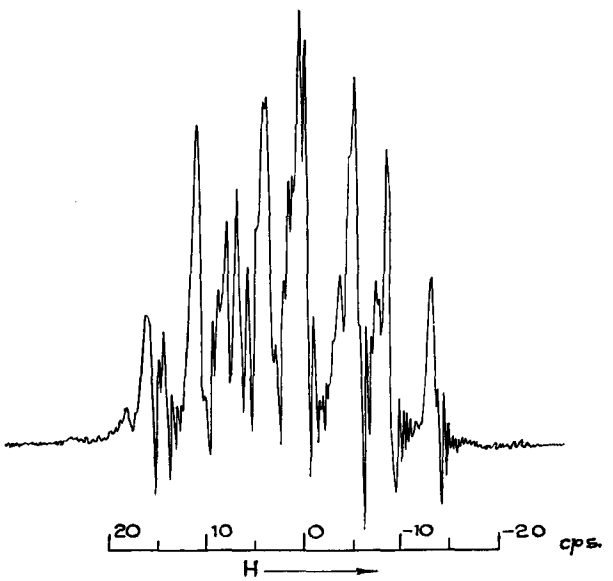

Figure 3. The fluorine resonance spectrum of fluorobenzene at 94·1 Mc/s.

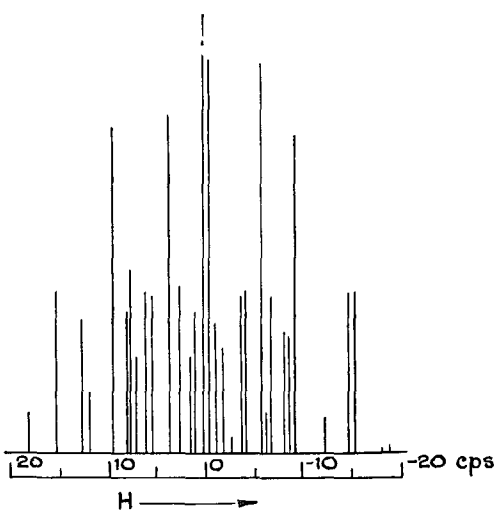

Figure 4. Calculated fluorine resonance spectrum of fluorobenzene at 94·1 Mc/s.

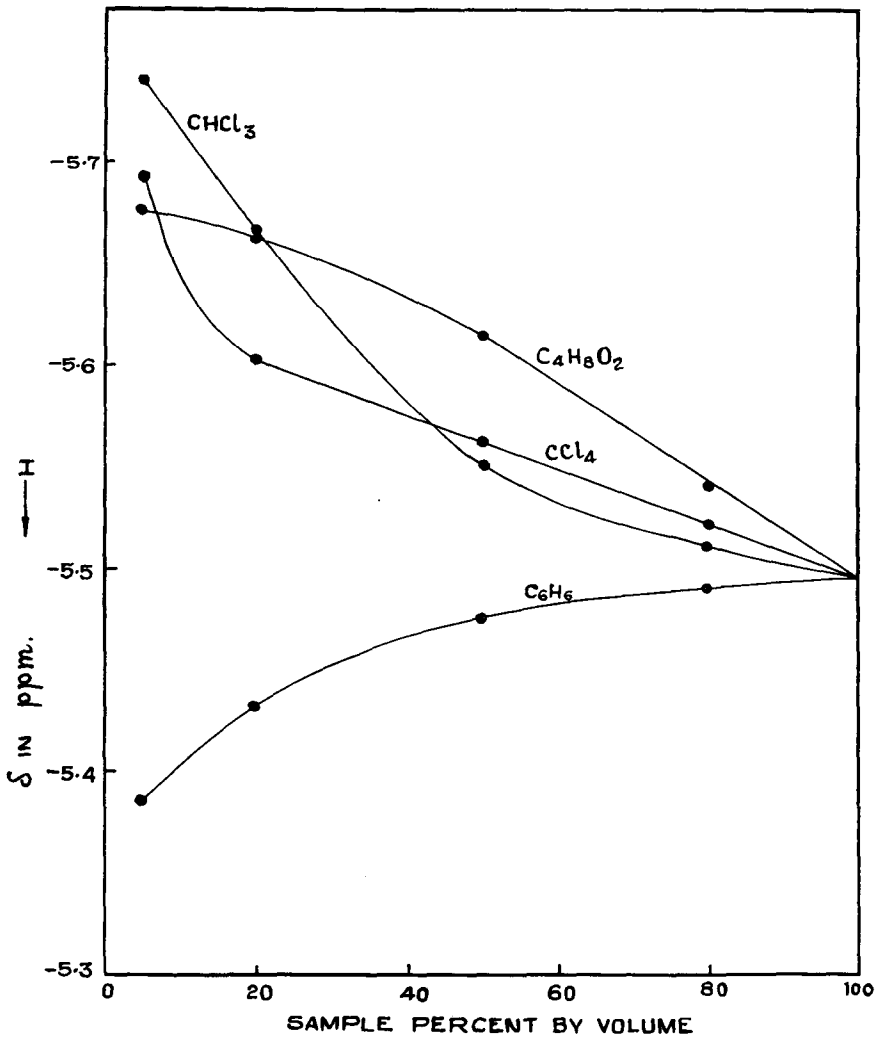

Figure 5. Solvent-dilution shift of the proton resonance signal of fluorobenzene. Chemical shifts δ are referred to cyclohexane as an internal reference at 100 Mc/s.

single uncertainty in the chemical shifts comes from the bulk susceptibility correction. Change in chemical shift due to this, is:

$$\Delta\delta = \frac{2\pi}{3}(\chi_{v,\,\mathrm{ref}} - \chi_v) = \frac{2\pi}{3}\Delta\chi_v$$

(for cylindrical samples), where $\Delta\chi_v =$ difference in bulk susceptibility of reference and pure liquid. For solutions of varying concentrations, measured with respect to an external reference, the bulk susceptibility required is weighted according to the volume fractions [4] given by:

$$\chi_{v,\,\mathrm{mixture}} = \phi_1\chi_{v1} + \phi_2\chi_{v2},$$

where ϕ_1 and ϕ_2 are the volume fractions of the components and χ_{v1} and χ_{v2} are their volume susceptibilities.

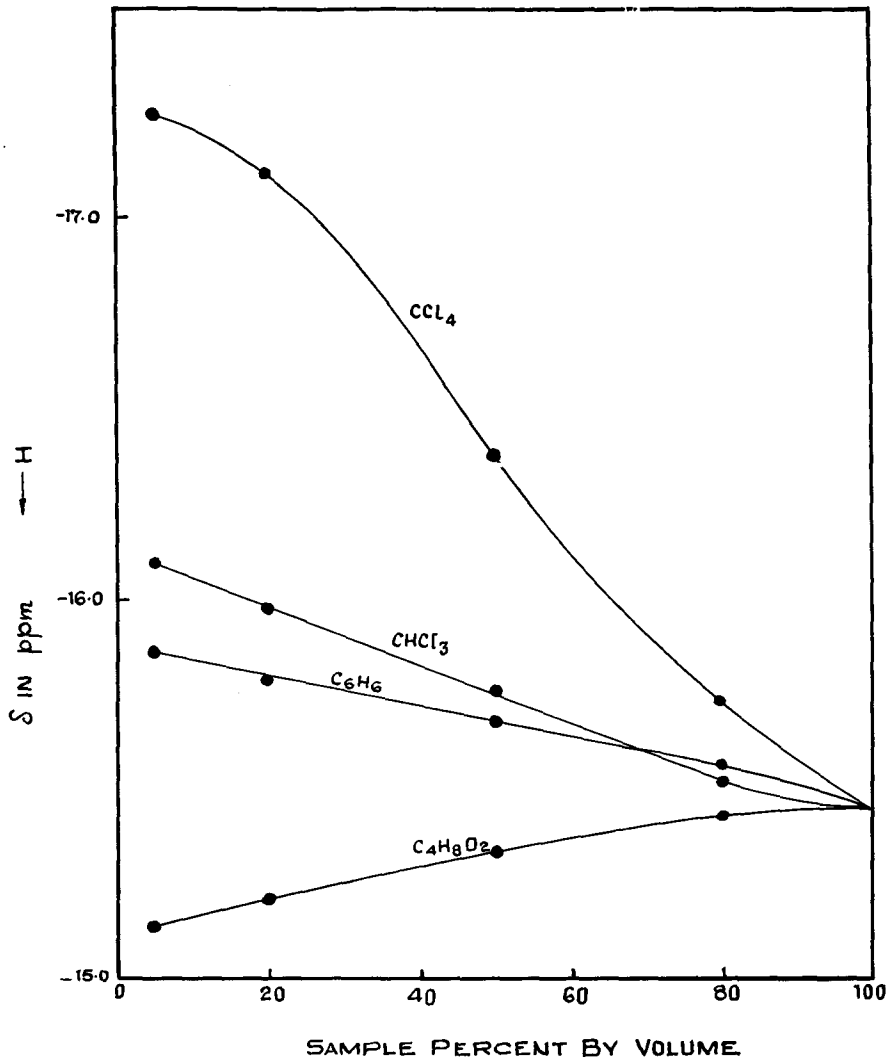

Figure 6. Solvent-dilution shift of the fluorine resonance signal of fluorobenzene. The chemical shifts δ (corrected for bulk susceptibility) are relative to difluoro-acetic acid as an external reference at 94·1 Mc/s.

Volume susceptibility of CF_2HCOOH is not available in the literature. We have determined it experimentally by the Quincke method [5] using an Alpha Scientific Laboratories, Inc., Berkeley, magnet Model AL 7500 with a Varian Model F-8A nuclear fluxmeter. The value is found to be $-0{\cdot}535\times10^{-6}$ as against $-0{\cdot}464\times10^{-6}$ determined by Pascal's constants. The experimental value is used in this paper for bulk susceptibility corrections. Bulk susceptibility correction is zero for proton shifts since cyclohexane is used as an internal reference here. The values for proton and fluorine shifts after these corrections are given in table 2.

Usually contributions to nuclear screening due to σ_b and σ_W are negative and σ_E and σ_a can be either positive or negative [3]. Thus the major contribution to the screening is negative and hence resonance occurs at lower applied fields

with dilution. But the proton resonance shifts to the higher field with respect to pure sample with dilution when benzene is solvent (figure 5). This can be explained by the fact that σ_a is positive for disc shaped solvents like benzene [3] and environment of aromatic molecules tends to lead to an increased solute screening constant in aromatic solvents like benzene [3, 4]. Similarly fluorine resonance shifts to the higher field with dioxan as solvent (figure 6); this is possibly due to positive σ_E.

Fluorine resonance shows larger solvent effects. This is probably because distortion due to polarization (and other intermolecular interactions) will have greater effects on the fluorine than on the proton screening constants since more electrons are involved in the former. Also the largest shifts appear with solvents containing heavy halogen atoms as in the case of CCl_4 and $CHCl_3$ (figure 6). Glick and Ehrenson [6] have also made similar observations in other compounds. These could be approximately correlated with the molecular polarizability of the solvent molecules.

5. ^{13}C–H AND ^{13}C–F COUPLING CONSTANTS

Splittings of the ^{1}H and ^{19}F resonance spectra due to ^{13}C–H and ^{13}C–F spin–spin coupling constants are observed due to the natural abundance of ^{13}C (1·108 per cent). These signals are weak due to low abundance and are observed with r.f. fields considerably higher than usual. The values of the coupling constants are found to be $J_{^{13}C\text{-}H} = 160{\cdot}0 \pm 2{\cdot}0$ c/s and $J_{^{13}C\text{-}F} = 265{\cdot}5 \pm 2{\cdot}0$ c/s. These splittings are due to coupling between ^{13}C with ^{1}H and ^{19}F in the nearest position. Muller and Pritchard [7] using a semi-empirical formula for ^{13}C–H coupling which is given by:

$$J_{^{13}C\text{-}H} = J_0 a^2 b^2,$$

have found the $J_{^{13}C\text{-}H}$ constants for aromatic bonds lie in the range 154·0 to 160·0 c/s. The present result agrees well with this theory.

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