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Molecular Physics

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ANALYSIS OF THE $A_3(X_3)_3$ NUCLEAR SPIN SYSTEM AND π-ELECTRON COUPLED HYPERFINE SPLITTING CONSTANTS IN AROMATIC HYDROCARBONS

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ABSTRACT

The nuclear spin functions for the $A_3(X_3)_3$ system have been developed and used to analyze the NMR spectra of $(CH_3)_3C_6H_3$ and $(CF_3)_3C_6H_3$. The π-electron coupled hyperfine splitting constants, obtained from the Ramsey theory with simple Hückel M.O.'s for benzene and without the assumption of an average energy of excitation for the virtual processes which give rise to the coupling, are in agreement with the hyperfine constants observed between the methyl groups and the ring protons in the above compounds.

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1. INTRODUCTION

The π-electron coupled hyperfine interactions in hydrocarbons have recently received a great deal of attention from the experimental [1] and theoretical point of view [2,3]. McConnell [2] and Karplus [3] have used the Ramsey theory [4] to calculate the magnitude of the π-electron coupled constant J^{π}. It was found, however, that when an average energy of excitation for the virtual processes giving rise to the second order interaction was assumed, the theoretically predicted values in the M.O. approximation for aromatic hydrocarbons were smaller by an order of magnitude than the experimentally observed ones.

The long range coupling of the methyl groups to the aromatic protons in $(CH_3)_3C_6H_3$ and $(CF_3)_3C_6H_3$ can only arise from π-electron interactions which are as a rule very small. An exact analysis of NMR spectra of these compounds is, therefore, undertaken here in order to obtain accurate values for the observed J^{π}. In addition, the Ramsey theory is used to calculate the corresponding coupling constants without assuming an average energy of excitation for the virtual processes responsible for the mechanism. The agreement with the experimental results is within ten per cent for all the measured coupling constants, except for the coupling between the methyl groups.

2. ANALYSIS OF THE NMR SPECTRA

The NMR spectra are analyzed by making use of the full symmetry of the molecule which belongs to the operations of the point group $D_3 \times C_{3v} \times C_{3v} \times C_{3v}$ when free rotation of the methyl radicals is taken into account [5]. The parameters involved in the problem are shown in figure 1.

The spin functions are expressed in the group theoretical formalism developed by Wilson [6]; they are given by

$$\psi(\Gamma_i) = \eta \sum_P \chi^{\Gamma_i}(P) \cdot P\left[\psi^{\Gamma_0}(1,2,3) \times \psi^{\Gamma_1}(a,b,c)\right] \qquad (1)$$

where

$$\psi^{\Gamma}(i,j,k) = \sum_P \chi^{\Gamma}(P)\ P\left[\psi(m_i \times \psi(m_j) \times \psi(m_k)\right]$$

Here the $\psi(m_i)$ are the individual spin functions for the given z component of the angular momentum and the subscripts (1,2,3) and (a,b,c) refer to the ring protons and methyl groups respectively. The Γ_i are the reduced species of the product $\Gamma_0 \times \Gamma_1$ in the irreducible representation

$$\Gamma_0 \times \Gamma_1 = \sum_i \Gamma_i$$

The $\chi^{\Gamma_i}(P)$ are the characters corresponding to the permutation operators P and η is a normalization constant.

The complete character table for the problem is obtained now by forming the direct product of those for the subgroups which in this case are all isomorphic and given in table 1.

D_3	E	$2C_3$	$3C_2$	(molecule)
C_{3v}	E	$2C_3$	$3\sigma_v$	(methyl groups)
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	

Table 1. Character table for the subgroups D_3 and C_{3v}.

Since only the operations of the subgroup D_3 act on both types of nuclei, the species Γ_0 and Γ_1 can in equation (1) be expressed in these subgroups alone. Thus, according to the symmetry of the molecule, the corresponding decompositions in D_3 are given by

$$\begin{aligned} \Gamma_0 &= A_1 + E \\ \Gamma_1 &= A_1 + A_2 + 2E \end{aligned} \tag{2}$$

Here the degenerate species E is twofold when m_1 is different for all the three methyl groups, and in this case a new set of four orthogonal functions must be defined as follows:

$$\begin{aligned} E_{1g} &= 2^{-1/2}[E_1(abc) + E_1(acb)] \\ E_{2g} &= 2^{-1/2}[E_2(abc) + E_2(acb)] \\ E_{1u} &= 2^{-1/2}[E_2(abc) - E_2(acb)] \\ E_{2u} &= 2^{-1/2}[E_1(acb) - E_1(abc)] \end{aligned} \tag{3}$$

where

$$\begin{aligned} E_1(abc) &= 6^{-1/2}(2abc - cab - bca) \\ E_2(abc) &= 2^{-1/2}(cab - bca) \end{aligned}$$

The pairs of functions (E_{1g}, E_{2g}) and (E_{1u}, E_{2u}) transform now under the operations of the group within themselves. [5] Table 2 gives the decomposition of the product $\Gamma_0 \times \Gamma_1$.

Γ_0 \ Γ_1	A_1	A_2	E_g	E_u
A_1	A_1	A_2	E_g	E_u
E	E_g	E_u	$A_1+A_2+E_g$	$A_1+A_2+E_u$

Table 2. Decomposition of the product $\Gamma_0 \times \Gamma_1$ in the D_3 subgroup.

The nuclear spin Hamiltonian for the problem is given by

$$H = H^{(0)} + H^{(1)} + H^{(2)} \tag{6}$$

where

$$H^{(0)} = \sum_{i=0,1} \frac{\gamma_i}{2\pi} I_i^z H_i^E$$

$$H^{(1)} = 8J_{0/8} \sum_P P(I_1 \cdot I_2) + 27J_{1/8} \sum_P P(I_{1a} \cdot I_{1b})$$

$$+9J'_{1/8} \sum_P P(I_{1a} \cdot I_{2a})$$

$$H^{(2)} = \frac{10J}{8} \sum_P P(I_1 \cdot I_{1b}) + \frac{9J'}{8} \sum_P P(I_1 \cdot I_{1a}).$$

$H^{(0)}$ represents the Zeeman energy in the Paschen-Back high field case, $H^{(1)}$ and $H^{(2)}$ the interaction between equivalent and

and nonequivalent nuclei, respectively, and g is the dimension of the group [6].

Since the necessary and sufficient condition for the NMR spectrum to be independent of the interaction between equivalent nuclei is that these couple equally to the rest of the system [7,8], the terms in J_1' do not have to be considered while those in J_0 and J_1 must be taken into account. Table 3 gives the exact spin product functions for the two sets of equivalent nuclei expressed in terms of the corresponding symmetry species.

The complete set of spin product functions in the irreducible representation are then obtained according to equation (1) as shown in table 4. These functions will interact via the coupling between nonequivalent nuclei, $H^{(2)}$. The nonzero matrix elements are given in table 4.

3. EXPERIMENTAL RESULTS

The nuclear resonance high resolution spectra for the two compounds are given respectively in figures 2 and 3. They were obtained with a Varian high resolution spectrometer operating at 60 Mcps for protons and 56.45 Mcps for fluorine (F^{19}) nuclei. The experimental results lead to the following approximations:

$$|\delta_0 - \delta_1| \gg \text{all } |J|$$
$$|J_0| > |J - J'| > |J'| > |J_1| \gtrsim 0 \qquad (6)$$

In this approximation the stationary state spin functions are given by

Table 3. Spin product functions for the equivalent sets of nuclei in the $A_3(X_3)_3$ system.

m_z	Spin function	$\langle H^{(1)} \rangle$	Multiplicity $\Gamma =$ A_1	A_2	E_g	E_u	Total
$\pm m_0$	$\Psi^{\Gamma_1}(a)$						
3/2	A_1	$\frac{3}{4} J_0$	1				
							1
1/2	A_1	$\frac{3}{4} J_0$	1				
	E	$-\frac{3}{4} J_0$			2		
							3
$\pm m_0$ $\pm m_1$ $\pm m_2$	$\Psi^{\Gamma_1}(b,c)$						
9/2 0 0	$A_1(a_1a_1a_1)$	$\frac{27}{4} J_1$	1				
							1
7/2 -2 0	$A_1(a_1'a_1a_1)$	$\frac{27}{4} J_1$	1				
	$E(a_1'a_1a_1)$	$\frac{9}{4} J_1$			2		
	$\Gamma(e'a_1a_1)$	$\frac{15}{4} J_1$	2		4		
							9
5/2 -4 0	$R_1 \times \begin{pmatrix} A_1(a_1''a_1a_1) \\ A_1(a_1a_1'a_1') \end{pmatrix}$	$\frac{27}{4} J_1$	1				
2 0		$-\frac{5}{4} J_1$	1				
	$R_2 \times \begin{pmatrix} E(a_1''a_1a_1) \\ E(a_1a_1'a_1') \end{pmatrix}$	$\frac{9}{4} J_1$			2		
		$-\frac{5}{4} J_1$			2		
	$R_3 \times \begin{pmatrix} \Gamma(e''a_1a_1) \\ \Gamma(a_1e'a_1') \end{pmatrix}$	$\frac{15}{4} J_1$	2		4		
		$\frac{1}{4} J_1$	2		4		
	$\Gamma(a_1a_1'e')$	$\frac{1}{4} J_1$		2		4	
	$\Gamma(a_1e'e')$	$\frac{7}{4} J_1$	3	1	6	2	
							36

$\pm m_0$	$\pm m_1$	$\pm m_2$	Spin function	$\langle H^{(1)} \rangle$	Multiplicity $\Gamma =$	A_1	A_2	E_g'	E_u	Total
3/2	-6	0	$A_1(\bar{a}_1 a_1 a_1)$	$\frac{27}{4} J_1$		1				
	0	0	$R_4 \times A_1(a_1' a_1' a_1')$	$-\frac{5}{4} J_1$		1				
	-3	-1	$A_1(a_1'' a_1' a_1')$	$-\frac{15}{4} J_1$		1				
			$E(\bar{a}_1 a_1 a_1)$	$\frac{9}{4} J_1$				2		
			$R_6 \times E_g(a_1'' a_1' a_1')$	$-\frac{5}{4} J_1$				2		
			$E_u(a_1'' a_1' a_1')$	$-\frac{15}{4} J_1$					2	
			$A_2(a_1 a_1' a_1'')$	$-\frac{15}{4} J_1$			1			
			$\Gamma(e' a_1' a_1')$	$\frac{15}{4} J_1$		2		4		
			$R_6 \times \Gamma(e' a_1'' a_1')$	$-\frac{1}{4} J_1$		2		4		
			$\Gamma(e'' a_1' a_1')$	$-\frac{9}{4} J_1$		2		4		
			$R_7 \times \Gamma(e'' a_1' a_1)$	$\frac{1}{4} J_1$			2		4	
			$\Gamma(e' a_1'' a_1)$	$-\frac{9}{4} J_1$			2		4	
			$R_8 \times \Gamma(a_1' e' e')$	$\frac{7}{4} J_1$		3	1	6	2	
			$\Gamma(a_1 e' e'')$	$-\frac{3}{4} J_1$		3	1	6	2	
			$\Gamma(a_1 e' e'')$	$-\frac{3}{4} J_1$		1	3	2	6	
			$\Gamma(e' e' e')$	$\frac{3}{4} J_1$		4		4		

$\pm m_0$	$\pm m_1$	$\pm m_2$	Spin function	$\langle H^{(1)} \rangle$	Multiplicity Γ = A_1	A_2	E_g	E_u	Total
1/2	-5	-1	$A_1(\bar{a}_1 a_1' a_1)$	$\frac{27}{4} J_1$	1				
	-2	0	$R_9 \times A_1(\bar{a}_1'' a_1' a_1')$	$-\frac{5}{4} J_1$	1				
	4	0	$A_1(a_1 a_1'' a_1'')$	$-\frac{13}{4} J_1$	1				
			$A_2(\bar{a}_1 a_1' a_1)$	$-\frac{15}{4}$		1			
			$E_g(\bar{a}_1 a_1' a_1)$	$\frac{9}{4} J_1$			2		
			$R_{10} \times E_u(\bar{a}_1 a_1' a_1')$	$-\frac{5}{4} J_1$				2	
			$E(a_1'' a_1' a_1')$	$-\frac{15}{4} J_1$			2		
			$E(a_1 a_1'' a_1'')$	$-\frac{21}{4} J_1$			2		
			$\Gamma(e' \bar{a}_1 a_1)$	$\frac{15}{4} J_1$	2		4		
			$R_{11} \times \Gamma(e'' a_1' a_1')$	$\frac{1}{4} J_1$	2		4		
			$\Gamma(e' a_1'' a_1')$	$-\frac{9}{4} J_1$	2		4		
			$\Gamma(e'' a'' a_1)$	$-\frac{15}{4} J_1$	2		4		
			$\Gamma(e' \bar{a}_1 a_1)$	$\frac{1}{4} J_1$		2		4	
			$R_{12} \times \Gamma(e' a_1'' a_1)$	$-\frac{9}{4} J_1$		2		4	
			$\Gamma(e'' a'' a_1)$	$-\frac{15}{4} J_1$		2		4	
			$\Gamma(a_1' e' e'')$	$\frac{7}{4} J_1$	3	1	6	2	
			$R_{13} \times \Gamma(a_1'' e' e')$	$-\frac{3}{4} J_1$	3	1	6	2	
			$\Gamma(a_1 e'' e'')$	$-\frac{9}{4} J_1$	3	1	6	2	
			$\Gamma(a_1 e' e'')$	$-\frac{3}{4} J_1$	1	3	2	6	
			$\Gamma(e' e' e'')$	$\frac{3}{4} J_1$	2		4		
			$\Gamma(e' e' e'')$	$\frac{1}{4} J_1$		2		4	
			$R_{14} \times \Gamma(e' e' e'')$	$\frac{3}{4} J_1$	2		4		
			$\Gamma(e'' e' e')$	$-\frac{3}{4} J_1$	2		4		

(a) Since the subgroups D_3 and C_3 are isomorphic, capital letters are used to designate the species of the former and small ones for the latter which, for the methyl group, are given by

$$\Gamma(cx_3) = a_1 + e$$

(b) The value of m_1 for the methyl group is indicated by the superscript on the spin function, i.e.

$$\begin{array}{ll}
m_1 = 3/2 & a_1 = \alpha\alpha\alpha \\
\quad\;\; 1/2 & a_1' = 3^{-1/2}(\beta\alpha\alpha + \alpha\beta\alpha + \alpha\alpha\beta) \\
 & e_1' = 6^{-1/2}(2\beta\alpha\alpha - \alpha\beta\alpha - \alpha\alpha\beta) \\
 & e_2' = 2^{-1/2}(\alpha\beta\alpha - \alpha\alpha\beta) \\
\quad -1/2 & a_1'' = 3^{-1/2}(\alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha) \\
 & e_1'' = 6^{-1/2}(2\alpha\beta\beta - \beta\alpha\beta - \beta\beta\alpha) \\
 & e_2'' = 2^{-1/2}(\beta\alpha\beta - \beta\beta\alpha) \\
\quad -3/2 & \bar{a}_1 = \beta\beta\beta
\end{array}$$

$$m_1 = m_a + m_b + m_c$$
$$m_1 = 2m_a - m_b - m_c$$
$$m_2 = m_b - m_c$$

(c) The rotations R_i which give the eigenfunctions of J_1 are given by

$$R_1 = \frac{1}{2}\begin{pmatrix} 1 & \sqrt{3} \\ -\sqrt{3} & +1 \end{pmatrix} \qquad R_2 = \frac{1}{\sqrt{7}}\begin{pmatrix} 2 & -\sqrt{3} \\ \sqrt{3} & 2 \end{pmatrix} \qquad R_3 = \frac{1}{\sqrt{7}}\begin{pmatrix} 1 & -\sqrt{6} \\ \sqrt{6} & 1 \end{pmatrix}$$

$$R_4 = \begin{pmatrix} \frac{1}{\sqrt{28}} & \frac{3}{\sqrt{28}} & \frac{5\sqrt{2}}{\sqrt{28}} \\ +\frac{3}{2\sqrt{5}} & -\frac{3}{2\sqrt{5}} & +\frac{1}{\sqrt{10}} \\ \frac{6}{\sqrt{70}} & \frac{4}{\sqrt{70}} & -\frac{3}{\sqrt{35}} \end{pmatrix} \qquad R_5 = \begin{pmatrix} 5\sqrt{\frac{2}{126}} & \frac{9}{\sqrt{126}} & \frac{3\sqrt{6}}{\sqrt{126}} \\ \frac{9}{\sqrt{315}} & \frac{3\sqrt{2}}{\sqrt{315}} & -\frac{5\sqrt{6}}{\sqrt{315}} \\ \frac{6}{\sqrt{60}} & -\frac{3}{\sqrt{30}} & +\frac{1}{\sqrt{10}} \end{pmatrix}$$

$$R_6 = \begin{pmatrix} \frac{9}{17} & \frac{3\sqrt{6}}{17} & -\frac{3\sqrt{6}}{17} \\ \sqrt{\frac{8}{35}} & \frac{2}{\sqrt{35}} & \frac{3}{\sqrt{35}} \\ \frac{2}{\sqrt{10}} & -\sqrt{\frac{3}{5}} & 0 \end{pmatrix} \qquad R_7 = \frac{1}{\sqrt{5}}\begin{pmatrix} -2 & 1 \\ 1 & 2 \end{pmatrix} \qquad R_8 = \frac{1}{\sqrt{5}}\begin{pmatrix} \sqrt{3} & -\sqrt{2} \\ \sqrt{2} & \sqrt{3} \end{pmatrix}$$

$$R_9 = \begin{pmatrix} \frac{\sqrt{2}}{\sqrt{14}} & \frac{3}{\sqrt{14}} & \sqrt{\frac{3}{14}} \\ 3\sqrt{\frac{1}{15}} & -\frac{3}{\sqrt{30}} & \sqrt{\frac{3}{30}} \\ \frac{3}{\sqrt{23}} & \sqrt{\frac{2}{23}} & -2\sqrt{\frac{6}{23}} \end{pmatrix}, \qquad R_{10} = \begin{pmatrix} \frac{5}{4}\sqrt{\frac{6}{26}} & -\frac{5}{4}\sqrt{\frac{2}{26}} & \frac{5}{2}\sqrt{\frac{5}{26}} & -\frac{3}{\sqrt{26}} \\ +2\sqrt{\frac{3}{35}} & 3\sqrt{\frac{1}{35}} & \sqrt{\frac{3}{70}} & \frac{5}{\sqrt{70}} \\ -\sqrt{\frac{3}{10}} & +\frac{1}{\sqrt{10}} & \sqrt{\frac{3}{5}} & 0 \\ 0 & \frac{3}{\sqrt{15}} & -\frac{1}{\sqrt{10}} & -\frac{3}{\sqrt{30}} \end{pmatrix}$$

$$R_{11} = \begin{pmatrix} \frac{2}{\sqrt{70}} & -\frac{3\sqrt{2}}{\sqrt{70}} & \frac{6}{\sqrt{70}} & -\frac{2\sqrt{3}}{\sqrt{70}} \\ \frac{3}{\sqrt{210}} & \frac{6}{\sqrt{105}} & \frac{9}{\sqrt{210}} & \frac{4}{\sqrt{70}} \\ +\frac{3}{\sqrt{15}} & -\sqrt{\frac{2}{15}} & -\frac{1}{\sqrt{15}} & -\sqrt{\frac{3}{15}} \\ \frac{3}{\sqrt{30}} & -\frac{2}{\sqrt{15}} & -\frac{1}{\sqrt{30}} & \frac{2}{\sqrt{10}} \end{pmatrix} \qquad R_{12} = \begin{pmatrix} \sqrt{\frac{3}{5}} & \sqrt{\frac{1}{5}} & \sqrt{\frac{1}{5}} \\ \sqrt{\frac{2}{5}} & -\sqrt{\frac{3}{10}} & -\sqrt{\frac{3}{10}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

$$R_{13} = \begin{pmatrix} \frac{6}{\sqrt{60}} & -\frac{3}{\sqrt{30}} & -\frac{1}{\sqrt{10}} \\ \frac{1}{\sqrt{15}} & 2\sqrt{\frac{2}{15}} & -\sqrt{\frac{2}{5}} \\ \frac{2}{\sqrt{12}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \end{pmatrix} \qquad R_{14} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & \sqrt{2} \\ -\sqrt{2} & 1 \end{pmatrix}$$

Table 4. Complete set of product functions for the $A_3(X_3)_3$ system and matrix elements for the interaction between nonequivalent nuclei.

Symmetry	Spin function	$\langle \psi_i \lvert H^{(2)} \rvert \psi_i \rangle$ (a)
$\Gamma = A_1, A_2, E_g, E_u$	$\psi_1 = A_1 \times \Gamma(m_1)$	$1/3m_0m_1(2J + J')$
A_1	$\psi_2 = A_1 \times A_1$	$1/3m_0m_1(2J + J')$
A_1	$\psi_3 = 2^{-1/2}[E_1E_{1g} + E_2E_{2g}]$	$1/3m_0m_1(2J + J') + \Delta_1$
A_1	$\psi_4 = 2^{-1/2}[E_1E_{1u} + E_2E_{2u}]$	$1/3m_0m_1(2J + J') - \Delta_1$
A_2	$\psi_5 = A_1 \times A_2$	$1/3m_0m_1(2J + J')$
A_2	$\psi_6 = 2^{-1/2}[E_2E_{1u} - E_1E_{2u}]$	$1/3m_0m_1(2J + J') + \Delta_1$
A_2	$\psi_7 = 2^{-1/2}[E_2E_{1g} - E_1E_{2g}]$	$1/3m_0m_1(2J + J') - \Delta_1$
E_g	$\psi_8 = A_1 \times E_g$	$1/3m_0m_1(2J + J')$
E_g	$\psi_9 = E \times A_1$	$1/3m_0m_1(2J + J')$
E_g	$\psi_{10}(E_1) = 2^{-1/2}[E_2E_{2g} - E_1E_{1g}]$	$1/3m_0m_1(2J + J')$
E_g	$\psi_{10}(E_2) = 2^{-1/2}[E_2E_{1g} + E_1E_{2g}]$	$1/3m_0m_1(2J + J')$
E_u	$\psi_{11} = A_1 \times E_u$	$1/3m_0m_1(2J + J')$
E_u	$\psi_{12} = E \times A_2$	$1/3m_0m_1(2J + J')$
E_u	$\psi_{13}(E_1) = 2^{-1/2}[E_2E_{2u} - E_1E_{1u}]$	$1/3m_0m_1(2J + J')$
E_u	$\psi_{13}(E_2) = 2^{-1/2}[E_2E_{1u} + E_1E_{2u}]$	$1/3m_0m_1(2J + J')$

Table 4. (con't)

Nonzero off diagonal matrix elements

(ψ_i, ψ_j)	$\langle \psi_i \lvert H^{(2)} \rvert \psi_j \rangle$
(2,3) and (5,6)	$\sqrt{2}\ \Delta_1$
(2,4) and (5,7)	$-\sqrt{2}\ \Delta_2$
(3,4) and (6,7)	Δ_2
(8,9), (11,12), (11,13) and (12,13)	Δ_1
(8,10) and (9, 10)	$-\Delta_1$
(8,12), (10,12) and (9,13)	Δ_2
(8,13), (9,11) and (10,11)	$-\Delta_2$

where

$$\Delta_1 = 1/3 m_0 m_1 \ (J - J')$$

$$\Delta_2 = \frac{1}{\sqrt{3}} m_0 m_2 \ (J - J')$$

(a) The values of $\langle H^{(2)} \rangle$ are obtained by using the symmetry of the molecule [6]

$$\langle \psi_i | H^{(2)} | \psi_j \rangle = g/d \sum_{n=1}^{d} \langle \psi_i^n | H_{11}^{(2)} | \psi_j^n \rangle$$

where d is the degeneracy of the species and

$$H_{11}^{(2)} = 2(I_1 \cdot I_{1b})J + (I_1 \cdot I_{1a})J' .$$

Here the value of $\langle H^{(2)} \rangle$ is independent of the symmetry species for the methyl group.

$$\Psi^{\Gamma}(\pm 3/2, m_1) = A_1(\pm 3/2) \times \Gamma(m)$$

$$\begin{pmatrix} \Psi_2^{\Gamma}(\pm 1/2, m_1) \\ \Psi_3^{\Gamma}(\pm 1/2, m_1) \\ - - - - - - \\ - - - - - - \end{pmatrix} = R \times \begin{pmatrix} \Psi_2'(\pm 1/2, m_1) \\ \Psi_3'(\pm 1/2, m_1) \\ - - - - - - \\ - - - - - - \end{pmatrix}_{\Gamma}$$

Under the assumption that $J_1 \cong 0$, R is a 3 x 3 rotation for all the species and the secular equation obtained from table 4 reduces to

$$\begin{vmatrix} W & \sqrt{2}\,\Delta_1 & -\sqrt{2}\,\Delta_2 \\ \sqrt{2}\,\Delta_1 & (W - 3/2J_0) + \Delta_1 & \Delta_2 \\ -\sqrt{2}\,\Delta_2 & \Delta_2 & (W - 3/2J_0) - \Delta_1 \end{vmatrix} = 0 \qquad (8)$$

where

$$W = E^0 + 3/4J_0 + 1/3m_0m_1(2J + J') - E$$

and

$$\begin{pmatrix} \psi_2' \\ \psi_3' \\ \psi_4' \end{pmatrix}_{\Gamma} = \begin{pmatrix} \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}_{A_1}, \begin{pmatrix} \psi_5 \\ \psi_6 \\ \psi_7 \end{pmatrix}_{A_2}, \text{ and } \begin{pmatrix} \frac{1}{\sqrt{2}}(\psi_8 \pm \psi_{11}) \\ \frac{1}{2}[(\psi_9 \pm \psi_{12}) + (\psi_{10} \pm \psi_{13})] \\ \frac{1}{2}[(\psi_9 \pm \psi_{12}) - (\psi_{10} \pm \psi_{13})] \end{pmatrix}_E$$

In this particular case, $J_1 = 0$ the secular equation is the same for all the species and it is a direct consequence of the fact that $H^{(2)}$ belongs to the operations of the point group D_6.

Equation (8) can be solved exactly except for the two cases when $m_2 \neq 0$. For $m_2 = 0$ the energy levels and the corresponding

$R_{(\theta)}$ are given by

$$E_1 = E^0 + 1/3 m_0 m_1 (2J + J')$$

$$E_{2,3} = E^0 + 1/3 m_0 m_1 (2J + J') + 1/2\, \Delta_1 \mp C$$

$$E_4 = E^0 - 3/4 J_0 + 1/3 m_0 m_1 (2J + J') - \Delta_1 \qquad (9)$$

$$R_\theta = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

where

$$C \cos 2\theta = 3/4 J_0 - \Delta_1$$

$$C \sin 2\theta = 2\, \Delta_1$$

The value of $2J + J'$ is obtained directly from the spectra by noting that under the first of assumptions (6) when $m_0 = \pm 3/2$ the transitions $\Delta m_1 = \pm 1$ obtained from equation (8) are given by

$$\nu_{\pm} = \frac{\gamma_1 H_1}{2\pi} \pm 1/2 (2J + J')$$

since the transition moment is nonzero only between eigenstates with the same eigenvalue of $H^{(1)}$. These transitions are indicated in figures 2 and 3, respectively. The ratios J/J' for the two compounds are different and were obtained by fitting the calculated spectra according to equation (9) to the transitions $\Delta m_0 = \pm 1$ as shown in figures 2 and 3. Table 5 gives the observed parameters for the spectra.

	$(CH_3)_3C_6H_3$	$(CF_3)_3C_6H_3$	C_6H_6 [8]
δ_0	-8.63 ppm from TMS	-8.07 ppm from TMS	-7.50 ppm from TMS
δ_1	-2.23 ppm from TMS		
$2J_1+J_1'$	$\pm$ (2.24 $\pm$ .05 cps)	$\pm$ (2.07 $\pm$ .05 cps)	
J_0	$\pm$ (2.2 $\pm$ .1 cps)	$\pm$ (1.9 $\pm$ .1 cps)	
J_1	~ 0	~ 0	

Table 5. Parameters measured directly from the NMR spectra

4. COUPLING CONSTANTS

The electron coupled indirect interaction between two nuclear spins, N,N', correct to second order in the Ramsey theory [4] is given by

$$J_{NN'} = -\frac{2}{3h} \sum_n \frac{\langle {}^1\Psi_0 | H_N | {}^3\Psi_n \rangle \langle {}^3\Psi_n | H_{N'} | {}^3\Psi_n \rangle}{E_n - E_0} \qquad (10)$$

where

$$H_N = \delta_0 \sum_k I_N \cdot S_k \, \delta(r_{Nk}), \quad (\delta_0 = \frac{8\pi}{3} g_e g_N \beta_e \beta_N)$$

Here the electron-nuclear spin hyperfine interaction gives rise to the coupling between nuclear spins through the virtual processes which excite the electron system of the molecule from the ground state singlet ${}^1\Psi_0$ to the triplet ${}^3\Psi_n$.

The long range hyperfine interactions in aromatic molecules have been attributed to π-electron couplings [1] where the σ-π

interaction which gives rise to a nonzero spin density at the in-plane protons in aromatic free radicals is the principal mechanism [9,10]. If the σ-π electron systems are assumed to be separable to a first order approximation and mix only via the exchange integral $H^{\sigma-\pi}$ [11], then the expression for the ground state and the excited triplet states is given by

$$
\begin{aligned}
{}^1\Psi_0 &= {}^1\Sigma_0 \times {}^1\Pi_0 - \sum_{i,n} \frac{\langle H^{\sigma-\pi} \rangle_{i,n}}{\Delta\epsilon_{in}} \, {}^1({}^3\Sigma_i \times {}^3\Pi_n) + \cdots \\
{}^3\Psi_n &= {}^3({}^1\Sigma_0 \times {}^3\Pi_n) - \sum_{i,n} \frac{\langle H^{\sigma-\pi} \rangle_{i,n}}{\Delta\epsilon'_{in}} \, {}^3({}^3\Sigma_i \times {}^1\Pi_0) + \cdots
\end{aligned}
\tag{11}
$$

where

$$
\begin{aligned}
{}^1\Sigma_0 &= \mathcal{A}[\sigma_1(1)\,\bar{\sigma}_1(2) \cdots \sigma_1(k-1)\,\bar{\sigma}_1(k)] \\
{}^1\Pi_0 &= \mathcal{A}[\pi_1(k+1)\,\bar{\pi}_1(k+2) \cdots \pi_n(\ell-1)\,\bar{\pi}_n(\ell)] \\
{}^3\Sigma_i &= \mathcal{A}[\sigma_1(1)\,\bar{\sigma}_1(2) \cdots \chi_\sigma(k,k') \cdots] \\
{}^3\Pi_n &= \mathcal{A}[\pi_1(k+1)\,\bar{\pi}_1(k+2) \cdots \chi_\pi(\ell,\ell') \cdots]
\end{aligned}
$$

$$
\chi(i,j) = \mathcal{A}_{ij} \begin{pmatrix} \sigma_i\sigma'_i \\ \text{or} \\ \pi_n\pi'_n \end{pmatrix} \times \begin{Bmatrix} \alpha_i\alpha_j & \text{for } m = 1 \\ 2^{-1/2}(\alpha_i\beta_j + \beta_i\alpha_j) & \text{for } m = 0 \\ \beta_i\beta_j & \text{for } m = -1 \end{Bmatrix}
$$

$\mathcal{A}$ is the antisymmetrization operator and the σ_i and π_n are the LCAO M.O.s given by [12].

$$\sigma_i = \sum_k a_k^i \phi_k, \text{ with energy } \epsilon_i$$

$$\pi_n = \sum_\ell a_\ell^n \phi_\ell, \text{ with energy } \epsilon_n$$

and if only orbital-excitation energies are involved

$$\Delta\epsilon_{in} = [(\epsilon_i' - \epsilon_i) + (\epsilon_n' - \epsilon_n)] = \Delta\sigma_i + \Delta\pi_n$$

$$\Delta\epsilon_{in}' = [(\epsilon_i' - \epsilon_i) - (\epsilon_n' - \epsilon_n)] = \Delta\sigma_i - \Delta\pi_n$$

Assuming the σ-orbitals to be localized for the C-X fragment ($X = N, N'$) and since the exchange interaction occurs only between nearest neighbors, it is given by

$$\langle H_{in}^{\sigma-\pi} \rangle = a_x^n a_x^{n'} J_{ix} \tag{12}$$

where a_x^n, $a_x^{n'}$ are the coefficients of the $2p\pi$ atomic orbital for the carbon bonded to the X group and,

$$J_{ix} = \int \sigma_{ix}(1)\, \pi_x(2) \frac{e}{r_{12}} \sigma_{ix}(2)\, \pi_x(1)\, d\tau_1 d\tau_2$$

The expression for the π-electron coupled hyperfine interaction is then given by

$$J_{N,N'}^{\pi} = -\frac{2}{3h} \sum_n \frac{(a_N a_{N'})^n (a_N a_{N'})^{n'}}{\Delta\pi} \frac{J_{iN} J_{iN'}}{\Delta_{i\ell n}} \langle {}^1\Sigma_0 | H_N | {}^3\Sigma_i \rangle \langle {}^3\Sigma_\ell | H_N | {}^1\Sigma_0 \rangle \tag{13}$$

where

$$(\Delta_{i\ell n})^{-1} = 4\left[\Delta\sigma_i \Delta\sigma_\ell (1 - \Delta_{ni}^2)(1 - \Delta_{n\ell}^2)\right]^{-1}, \quad \Delta_{nk} = \frac{\Delta\pi_n}{\Delta\sigma_k}$$

The integrals in equation (13) have been evaluated semiempirically for protons and methyl groups from the hyperfine splitting observed in the ESR spectra of aromatic free radicals by McConnell [10] and McLachlan [13]. They lead to a value of J_{H-CH_3} in aromatic hydrocarbons of

$$J^{\pi}_{H-CH_3} = -\frac{2}{3h} Q_H Q_{CH_3} \sum_{n,n'} 4 \frac{(a_H a_{CH_3})^n (a_H a_{CH_3})^{n'}}{\Delta\pi_n (1 - \Delta^2_{1n})(1 - \Delta^2_{1n})} \tag{14}$$

where

$$Q_H \cong -63 \text{ Mcps}$$

$$Q_{CH_3} \cong +75 \text{ Mcps}.$$

For alternate hydrocarbons, equation (14) reduces to the expression obtained by McConnell [1]

$$J^{\pi}_{H-CH_3} = \frac{2}{3h} \frac{Q_H Q_{CH_3} A_{H-CH_3}}{\bar{\Delta}_{\pi}} \tag{15}$$

where an average value of $\Delta\pi_n$ is assumed.

The values of J, J', and J_1 were calculated using simple Huckel M.O.'s for benzene and equation (14) with the spectroscopic value for the resonance integral in benzene, $\beta = 2.86$ ev and $\Delta\sigma = 12$ ev [14]. These are given together with the experimental results in Table 6 along with the results obtained by McConnell [1] using a valence bond calculation. The values of J^{π} calculated from equation (14) agree with the experimental results within the accuracy of the measurement for the hydrocarbon except for J^{π}_1. In this case one may assume that there exists another coupling mechanism which

	Experimental Results		M.O. (this work)	V.B. [1]
	$(CH_3)_3C_6H_3$	$(CF_3)_3C_6H_3$		
J	$\pm$ .89 cps	$\pm$ .91 (.97)[a]	- .87 cps	- .60 cps
J'	$\pm$ .45	$\pm$ .22 (.23)	- .37	- .24
$2J+J'$	$\pm$ 2.24 $\pm$ .05	$\pm$ 2.09 $\pm$ .10	-2.27	-1.24
J_1	0	0	- .32	- .29

Table 6. Calculated values of J^{π} from M.O. theory according to equation (14).

(a) The values in parentheses are corrected here for the difference in nuclear moments between F^{19} and H^1. Here no empirical evaluation for Q_{CF_3} has been measured but from the value obtained by Gutowsky et al [15] for Q_F the value of Q_{CF_3} can be predicted to be close to Q_{CH_3}.

cancels out the π-electron contribution. In the case of the $(CF_3)_3C_6H_3$ the observed difference for the ratio $\frac{J}{J'}$ from the parent hydrocarbon indicates that most likely there exist other coupling mechanisms between the $-CF_3$ groups and the ring protons.

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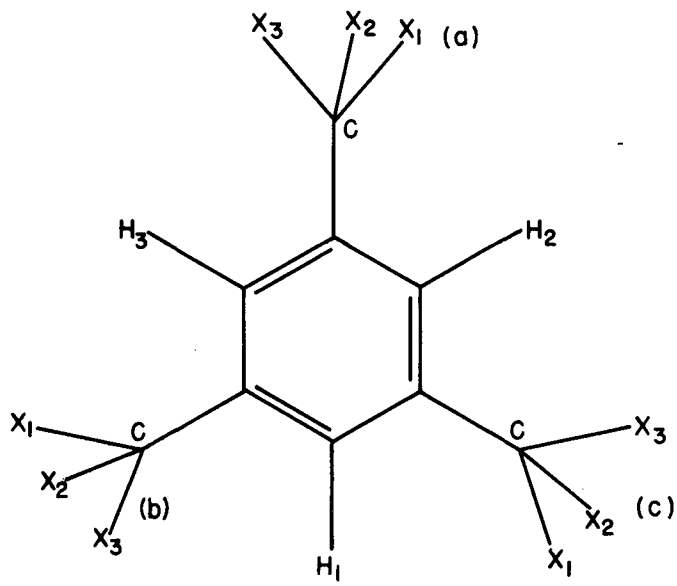

Chemical shifts

$\delta_0 = \delta(H_1) \ldots$

$\delta_1 = \delta(X_a) \ldots, X = F, H$

Coupling constants

$J_0 = J(H_1 - H_2), \ldots$ $\quad J' = J(H_1 - X_a), \ldots$

$J_1 = J(X_a - X_b), \ldots$ $\quad J = J(H_1 - X_b), \ldots$

$J_1' = J(X_{ia} - X_{ja}), \ldots$

MU-23417

Fig. 1. NMR spectrum parameters for the $A_3(X_3)_3$ system.

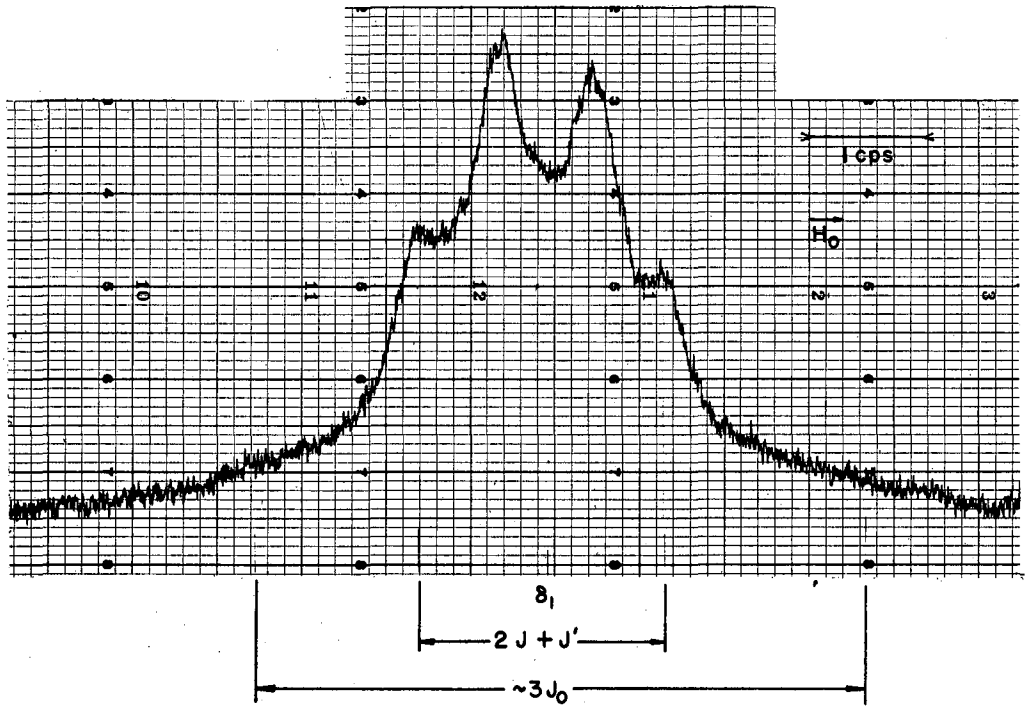

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Fig. 2a. NMR spectrum of $(CH_3)_3\ C_6H_3$: the (CH_3) groups.

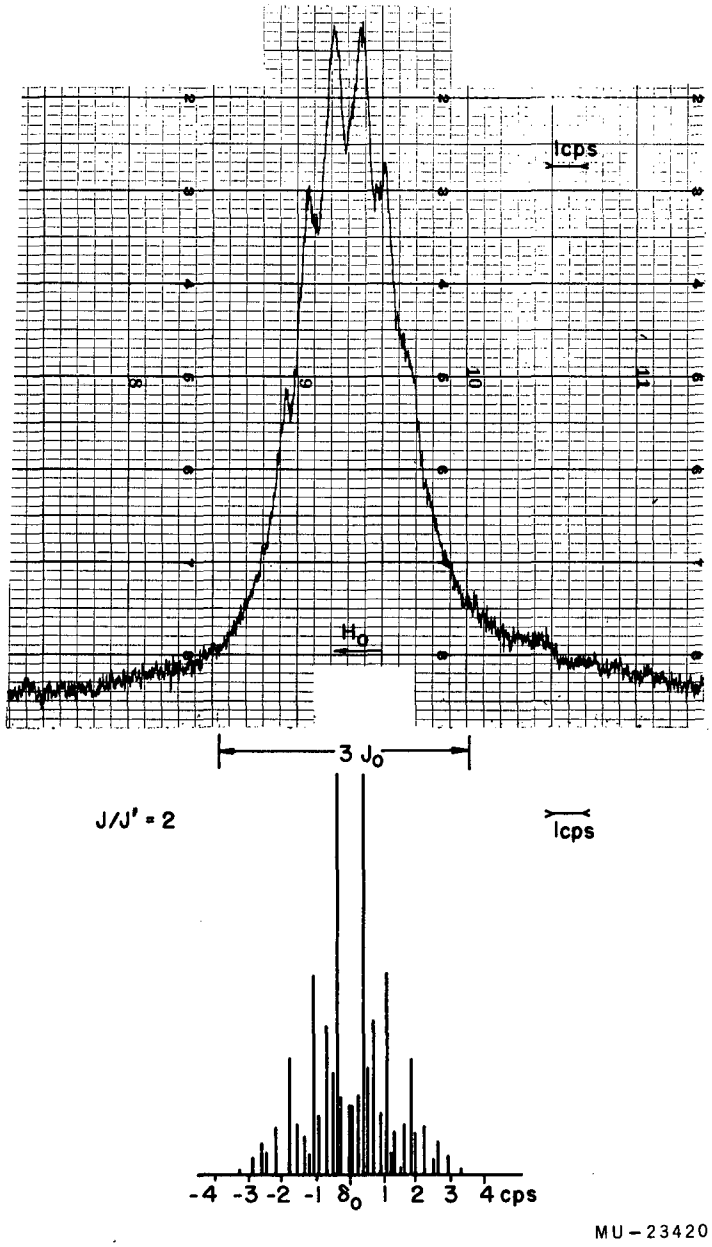

Fig. 2b. NMR spectrum of $(CH_3)_3\ C_6H_3$: the ring protons.

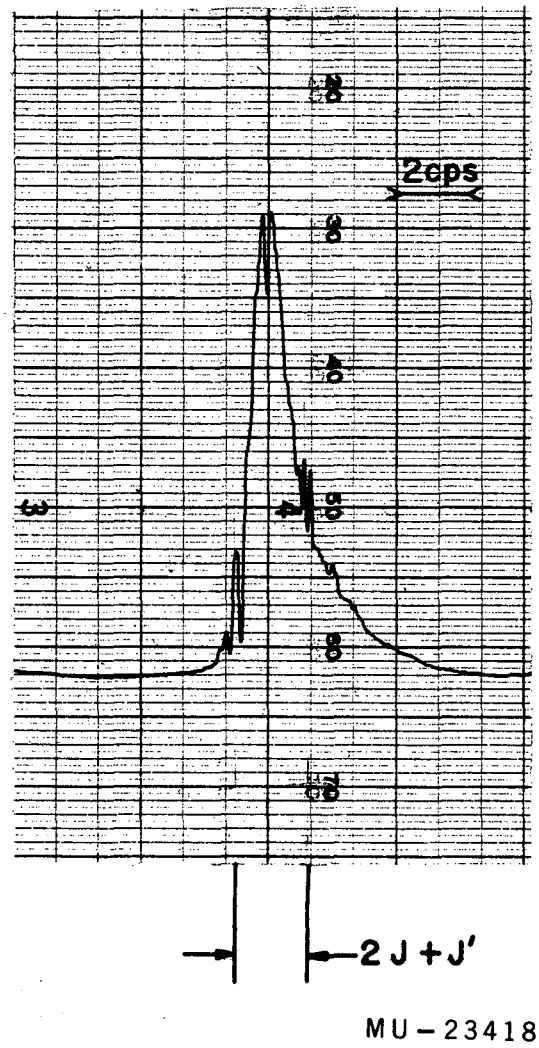

Fig. 3a. NMR spectrum of $(CF_3)_3 C_6H_3$: the (CF_3) groups.

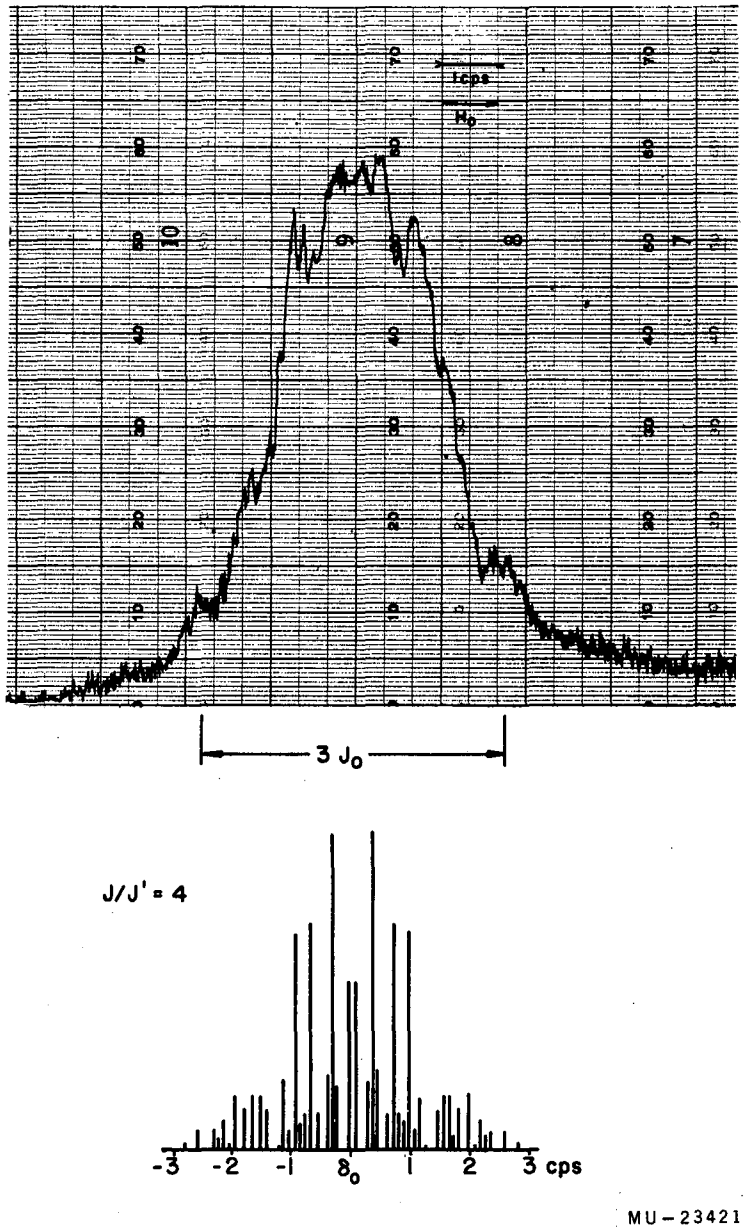

Fig. 3b. NMR spectrum of $(CF_3)_3\ C_6H_3$: the ring protons