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NOTE

Quantum Mechanical Analysis of High Resolution NMR-Spectra of Some Tri-Substituted Benzenes

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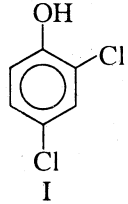
High Resolution NMR-Spectra (recorded at 90 MHz and 270 MHz) of some three spin aromatic systems (ABC type), *viz.*, 2,4-dichlorophenol and 3,4-dimethylphenol have been analysed quantum mechanically with the help of second-order perturbation theory.

In both cases, δ_{ij}/J_{ij} suggests the failure of first order rule. The analysis of complex spectra was carried out with the help of successive iterations and convergence of the J_{ij}'s and δ_{ij}'s. With these converged values, intersities of several spectral transitions were calculated and then used to draw the theoretical stick-spectrum to compare them with experimental ones.

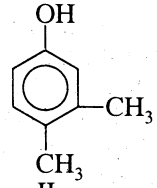
Key Words: Spectral analysis, NMR, Substituted benzene.

During recent past NMR has been a dominating structural and analytical tool in structural and physicochemical investigation[1]. Due to this successful experimental progress in NMR-techniques, it became a subject of interest for both theoretical and experimental chemists, for the structural analysis of molecules. The two phenomenological parameters[2–4] (δ_{ij} and J_{ij}) are of great importance.

Our present work is related to a symmetrical tri-substituted (three spin or three protons aromatic systems) *viz.*, 2,4-dichlorophenol **(I)** and 3,4-dimethylphenol **(II).**



I



II

The high resolution measurements (90 MHz and 270 MHz) were done at C.D.R.I., Lucknow and R.S.I.C. at I.I.Sc., Bangalore. The spectra of the samples (Sisco-Chem and Hi-Media make) was recorded at 90 MHz on Perkin-Elmer R-32 spectrometer in solution in $CDCl_3$. 270 MHz ^{1}H-spectrum was recorded with single channel (memory size 16a spinning rate 20 Hz) using acetonitrile as solvent. In all the cases TMS was used as an internal reference compound.

High resolution NMR-techniques are used where multiplet structure don't obey first order rule[5,6] and so the analysis is carried out with second order perturbation method[7].

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TABLE-1
FIRST ORDER VALUES OF SPECTRAL PARAMETERS OF INVESTIGATED COMPOUNDS AT 90 MHz AND 270 MHz

Parameters	Compound investigated			
	2,4-dichlorophenol		3,4-dimethylphenol	
	90 MHz	270 MHz	90 MHz	270 MHz
$J_{AB}(1)$	13.882	42.949	12.07	8.450
$J_{AC}(1)$	1.132	2.206	7.81	2.238
$J_{BC}(1)$	15.964	46.260	10.46	11.631
$\nu_A(1)$	652.337	1981.479	615.92	1878.226
$\nu_B(1)$	626.272	1880.446	581.14	1784.404
$\nu_C(1)$	634.141	1903.548	583.16	1778.817
$\delta_{AB}(1)$	26.065	101.033	36.78	93.822
$\delta_{AC}(1)$	18.198	77.931	34.76	99.409
$\delta_{BC}(1)$	–7.869	–23.102	–2.02	5.587

TABLE-2
CONVERGED VALUES OF SPECTRAL PARAMETERS FOR INVESTIGATED COMPOUNDS AT DIFFERENT FIELDS

Parameters	Compound investigated			
	2,4-dichlorophenol		3,4-dimethylphenol	
	90 MHz	270 MHz	90 MHz	270 MHz
M_+	7.269	3.243	–3.915	2.914
N_1	0.019	0.191	1.997	0.013
O_+	2.300	9.809	0.112	0.199
M_-	–3.575	4.591	2.463	4.706
N_-	0.017	0.194	1.674	0.012
O_-	1.382	7.326	0.130	0.180
δ_{AB}	19.692	68.116	31.544	50.460
δ_{AC}	15.103	46.409	27.375	97.905
δ_{BC}	4.589	–21.707	4.169	–7.445
J_{AB}	17.574	56.473	10.170	10.241
J_{AC}	3.460	–15.241	9.419	0.427
J_{BC}	16.884	50.083	11.751	11.651
ΣJ_{ij}	37.918	91.315	30.340	22.319

The starting phenomenological spectral parameters, chemical shifts (δ_{ij}'s) and coupling constants (J_{ij}'s) are measured from experimental spectra with the help of "Rule of equal spacings" and "Internsity Sum Rule"[8]. From $\nu_i(1)$ and $J_{ij}(1)$ values and perturbation terms ($M_\pm$, $N_\pm$, $O_\pm$) eigen values have been deduced to

draw their corresponding supporting energy level diagrams[9]. Energy of each eigen state was calculated by Ionic method[8]. After a number of successive interactions (to bring the Hamiltonians into diagnose form by similarity transformation method) both δ_{ij}'s and J_{ij}'s appeared to converge but in higher fields we observed a "Slow-Convergence". With these converged[11] values of δ_{ij}'s and J_{ij}'s (Table-3) the intensities of various transitions were evaluated by using co-factor method[2] to draw the "Stick-spectrum" to compare these with experimental ones.

TABLE-3

Sum of Intensities	Compounds investigated			
	2,4-dichlorophenol		3,4-dichlorophenol	
	90 MHz	270 MHz	90 MHz	270 MHz
ΣI_A	5.753	3.200	4.713	2.766
ΣI_B	2.068	3.564	4.805	2.891
ΣI_C	5.267	3.179	3.964	2.978
$\frac{1}{2}[I_2 + I_3 + \ldots + I_{15}]$	3.588	2.716	4.447	2.166
$[I_1 + I_5 + I_{11}]$	3.631	2.324	3.166	2.270
$[I_4 + I_8 + I_{14}]$	3.607	3.065	3.889	2.154

Finally, we verified the results obtained by the "Intensity Sum Rule" (Table-3) which were in a good agreement with the theoretical ones.

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