

NMR SPECTRA OF FIVE SPIN SYSTEMS—I

The NMR Spectrum of Nitrobenzene

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ABSTRACT

The analysis of the NMR spectra of five nuclei each with spin $\frac{1}{2}$ has been undertaken. For such systems the nuclei may be arranged in groups of different symmetry. The proton magnetic resonance spectrum of nitrobenzene is an example of A_2B_2C type. From the analysis of this spectrum the values of various coupling constants and chemical shifts have been determined.

INTRODUCTION

FROM a high resolution NMR spectrum it is possible to determine the values of chemical shifts and coupling constants and thereby draw conclusions about the structure of the molecule. This procedure is relatively simple for molecules having only a few interacting nuclei or where nuclei can be divided into simple groups of two or three nuclei, not interacting with any of the nuclei of the other group. The analysis of the NMR spectra of the ABCD type (four non-equivalent nuclei with spin $\frac{1}{2}$) has been reported earlier by Dharmatti *et al.* (1962) and Govil *et al.* (1961). Among the five spin systems, spectra of three types have been observed and analysed. Mc Garvey and Slomp (1959) have reported the spectra of the A_2B_3 type. Spectra of the type ABX_3 were examined by Fessenden and Waugh (1959). The spectrum of pyridine an example of AB_2X_2 type was analysed by Schneider, Bernstein and Pople (1957) using the method of isotopic substitution. Lately spectra of the type A_2B_2X have been analysed by Kimura *et al.* (1960).

Here we present the analysis of the NMR spectrum of nitrobenzene (Fig. 1), an example of the A_2B_2C type without the use of isotopic substitution. The spectrum of this compound, at relatively lower resolution, was

first obtained by Corio and Dailey (1956). They did not rigorously analyse the spectrum but just estimated the values of the chemical shifts of the *ortho*, *meta* and *para* protons. They assumed the chemical shift of the *para* proton at the position of the peak with the highest intensity. This assumption was not reasonably correct and our detailed analysis shows that the chemical shift of *para* proton is at a lower field than that of the peak of maximum intensity.

THEORETICAL

Assuming the steady magnetic field in the negative Z-direction, the complete quantum mechanical Hamiltonian involving the scalar products of the spin vectors of all pairs of magnetic nuclei can be written as

$$H = \sum_i \nu_i I_z(i) + \sum_{i < j} J_{ij} \vec{I}_i \cdot \vec{I}_j$$

where \vec{I}_i is the spin vector of the nucleus i whose resonance frequency is ν_i , $I_z(i)$ is the z component of the spin and J_{ij} is the nuclear spin-spin interaction between the nuclei i and j .

The basic product functions can be written in the irreducible form after making use of the symmetry in the molecule. The diagonal and the off-diagonal matrix elements of the Hamiltonian with respect to these functions can be calculated by standard methods (Pople *et al.*, 1959). These are given in Table I. The secular equation for this system gets factorised into two 1×1 , two 2×2 , two 3×3 , two 4×4 and two 6×6 matrices.

Once these matrices are solved one gets the energy values and the stationary state wave functions. These quantities enable us to calculate the spectrum in terms of J_s and ν_s . The frequency corresponding to the transition $q \rightarrow q'$ is given by $E_q - E_{q'}$ and the intensity is proportional to $[q | \sum_i I_x(i) | q']^2$. The calculated spectrum is given in Table II in terms of E_s and the coefficient C_s of the various product functions in the stationary state function ϕ_q .

There are nine unknown parameters to be determined from the high resolution spectrum taken relative to a particular standard. These are the 3 chemical shifts and 6 coupling constants. There are 110 possible transitions out of which 24 belong to group A, 24 to B and 20 to C and the remaining are combination transitions. Out of these only nine transition frequencies are required to determine uniquely all these parameters. The

TABLE I
Basic functions and matrix elements of hamiltonian

TABLE - I BASIC FUNCTIONS AND MATRIX ELEMENTS OF HAMILTONIAN						
NO.	REPRESENTATION OF WAVE FUNCTION	WAVE FUNCTION	F_2	DIAGONAL MATRIX ELEMENTS	NON DIAGONAL ELEMENTS	
1	$5s_{3/2}$	$\alpha\alpha\alpha\alpha\alpha\alpha$	5/2	$1/2(2J_A + 2J_B + J_C) + 1/4(2J_1 + 2J_2 + 2J_3 + 2J_4 + J_5 + J_6)$		
2	$1s_{3/2}$	$\alpha\alpha\alpha\alpha\alpha\beta$	3/2	$1/2(2J_A + 2J_B - J_C) + 1/4(2J_1 + 2J_2 - 2J_3 - 2J_4 + J_5 + J_6)$	$H_{12} = 1/\sqrt{2} J_3$	
3	$2s_{3/2}$	$\frac{\alpha\beta + \beta\alpha}{\sqrt{2}} \alpha\alpha\alpha\alpha$		$1/2(2J_B + J_C) + 1/4(2J_4 + J_5 + J_6)$	$H_{13} = 1/\sqrt{2} J_4$	
4	$3s_{3/2}$	$\alpha\alpha\alpha \frac{\alpha\beta + \beta\alpha}{\sqrt{2}} \alpha$		$1/2(2J_A + J_C) + 1/4(2J_3 + J_5 + J_6)$	$H_{23} = 1/2(J_1 + J_2)$	
5	$1a_{3/2}$	$\frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \alpha\alpha\alpha\alpha$	3/2	$1/2(2J_B + J_C) + 1/4(2J_4 - 3J_5 + J_6)$	$H_{12} = 1/2(J_1 - J_2)$	
6	$2a_{3/2}$	$\alpha\alpha\alpha \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \alpha$		$1/2(2J_A + J_C) + 1/4(2J_3 + J_5 - 3J_6)$		
7	$1s_{1/2}$	$\alpha\alpha\alpha\beta\beta\alpha$	1/2	$1/2(2J_A - 2J_B + J_C) + 1/4(-2J_1 - 2J_2 + 2J_3 - 2J_4 + J_5 + J_6)$	$H_{12} = 0$ $H_{13} = 1/2(J_1 + J_2)$	
8	$2s_{1/2}$	$\beta\beta\alpha\alpha\alpha\alpha$		$1/2(-2J_A + 2J_B + J_C) + 1/4(-2J_1 - 2J_2 - 2J_3 + 2J_4 + J_5 + J_6)$	$H_{14} = 1/2(J_2 - J_1)$ $H_{15} = 0$ $H_{16} = 1/\sqrt{2} J_4$	
9	$3s_{1/2}$	$\frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \alpha$		$1/2 J_C + 1/4(J_5 + J_6)$	$H_{23} = 1/2(J_1 + J_2)$ $H_{24} = 1/2(J_2 - J_1)$ $H_{25} = 1/\sqrt{2} J_3$	
10	$4s_{1/2}$	$\frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \alpha$		$1/2 J_C + 1/4(-3J_5 - 3J_6)$	$H_{26} = 0$ $H_{34} = 1/2(J_1 - J_2)$ $H_{35} = 1/\sqrt{2} J_4$	
11	$5s_{1/2}$	$\frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \alpha\alpha\alpha\beta$		$1/2(2J_B - J_C) + 1/4(-2J_4 + J_5 + J_6)$	$H_{36} = 1/\sqrt{2} J_5$ $H_{45} = 0$ $H_{46} = 0$	
12	$6s_{1/2}$	$\alpha\alpha\alpha \frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \beta$		$1/2(2J_A - J_C) + 1/4(-2J_3 + J_5 + J_6)$	$H_{56} = 1/2(J_1 + J_2)$	
13	$1a_{1/2}$	$\frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \alpha$	1/2	$1/2 J_C + 1/4(J_5 - 3J_6)$	$H_{12} = 1/2(J_1 - J_2)$ $H_{13} = 0$	
14	$2a_{1/2}$	$\frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \alpha$		$1/2 J_C + 1/4(J_6 - 3J_5)$	$H_{14} = 1/\sqrt{2} J_3$ $H_{23} = 1/\sqrt{2} J_4$	
15	$3a_{1/2}$	$\frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \alpha\alpha\alpha\beta$		$1/2(2J_B - J_C) + 1/4(-2J_4 - 3J_5 + J_6)$	$H_{24} = 0$ $H_{34} = 1/2(J_1 - J_2)$	
16	$4a_{1/2}$	$\alpha\alpha\alpha \frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \beta$		$1/2(2J_A - J_C) + 1/4(-2J_3 + J_5 - 3J_6)$		
17	$1a_{-1/2}$	$\frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \beta$	-1/2	$-1/2 J_C + 1/4(J_5 - 3J_6)$	$H_{12} = 1/2(J_1 - J_2)$ $H_{13} = 0$	
18	$2a_{-1/2}$	$\frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \beta$		$-1/2 J_C + 1/4(-3J_5 + J_6)$	$H_{14} = 1/\sqrt{2} J_3$ $H_{23} = 1/\sqrt{2} J_4$	
19	$3a_{-1/2}$	$\frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \beta\beta\alpha\alpha$		$1/2(-2J_B + J_C) + 1/4(-2J_4 - 3J_5 + J_6)$	$H_{24} = 0$ $H_{34} = 1/2(J_1 - J_2)$	
20	$4a_{-1/2}$	$\beta\beta \frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \alpha$		$1/2(-2J_A + J_C) + 1/4(-2J_3 + J_5 - 3J_6)$		
21	$1s_{-1/2}$	$\alpha\alpha\alpha\beta\beta\beta$	-1/2	$1/2(2J_A - 2J_B - J_C) + 1/4(-2J_1 - 2J_2 - 2J_3 + 2J_4 + J_5 + J_6)$	$H_{12} = 0$ $H_{13} = 1/2(J_1 + J_2)$ $H_{14} = 1/2(J_2 - J_1)$	
22	$2s_{-1/2}$	$\beta\beta\alpha\alpha\alpha\beta$		$1/2(-2J_A + 2J_B - J_C) + 1/4(-2J_1 - 2J_2 + 2J_3 - 2J_4 + J_5 + J_6)$	$H_{15} = 1/\sqrt{2} J_3$ $H_{16} = 0$ $H_{23} = 1/2(J_1 + J_2)$	
23	$3s_{-1/2}$	$\frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \beta$		$-1/2 J_C + 1/4(J_5 + J_6)$	$H_{24} = 1/2(J_2 - J_1)$ $H_{25} = 0$ $H_{26} = 1/\sqrt{2} J_4$	
24	$4s_{-1/2}$	$\frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \beta$		$-1/2 J_C - 3/4(J_5 + J_6)$	$H_{34} = 1/2(J_1 - J_2)$ $H_{35} = 1/\sqrt{2} J_4$ $H_{36} = 1/\sqrt{2} J_5$	
25	$5s_{-1/2}$	$\frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \beta\beta\alpha\alpha$		$1/2(-2J_B + J_C) + 1/4(-2J_4 + J_5 + J_6)$	$H_{45} = 0$ $H_{46} = 0$ $H_{56} = 1/2(J_1 + J_2)$	
26	$6s_{-1/2}$	$\beta\beta \frac{(\alpha\beta + \beta\alpha)}{\sqrt{2}} \alpha$		$1/2(-2J_A + J_C) + 1/4(-2J_3 + J_5 + J_6)$		
27	$1a_{-3/2}$	$\frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \beta\beta\beta$	-3/2	$-1/2(2J_B + J_C) + 1/4(2J_4 - 3J_5 + J_6)$	$H_{12} = 1/2(J_1 - J_2)$	
28	$2a_{-3/2}$	$\beta\beta \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \beta$		$-1/2(2J_A + J_C) + 1/4(2J_3 + J_5 - 3J_6)$		
29	$1s_{-3/2}$	$\frac{\alpha\beta + \beta\alpha}{\sqrt{2}} \beta\beta\beta$	-3/2	$-1/2(2J_B + J_C) + 1/4(2J_4 + J_5 + J_6)$	$H_{12} = 1/2(J_1 + J_2)$	
30	$2s_{-3/2}$	$\beta\beta \frac{\alpha\beta + \beta\alpha}{\sqrt{2}} \beta$		$-1/2(2J_A + J_C) + 1/4(2J_3 + J_5 + J_6)$	$H_{13} = 1/\sqrt{2} J_3$	
31	$3s_{-3/2}$	$\beta\beta\beta\beta\alpha\alpha$		$-1/2(2J_A + 2J_B - J_C) + 1/4(2J_1 + 2J_2 - 2J_3 - 2J_4 + J_5 + J_6)$	$H_{23} = 1/\sqrt{2} J_4$	
32	$5 - s_{5/2}$	$\beta\beta\beta\beta\beta$	-5/2	$-1/2(2J_A + 2J_B + J_C) + 1/4(2J_1 + 2J_2 + 2J_3 + 2J_4 + J_5 + J_6)$		

TABLE II
Theoretical spectrum for A_2B_2C system

TABLE II THEORETICAL SPECTRUM FOR A_2B_2C SYSTEM							
TRANSITION	NO. OF LINES	FREQUENCY	INTENSITY	GROUP			
				A	B	C	COMB.
$E_{iS_{3/2}} \rightarrow E_{iS_{1/2}}$ $l = 2, 3, 4$	3	$E_i - E_l$	$[(C_{11} + \sqrt{2} C_{12} + \sqrt{2} C_{13})]^2$	1 → 3	1 → 4	1 → 2	—
$E_{lS_{3/2}} \rightarrow E_{kS_{1/2}}$ $l = 2, 3, 4$ $k = 7, 8, 9, 10, 11, 12$	18	$E_l - E_k$	$[\sqrt{2} C_{11}(C_{k8} + C_{k6}) + C_{12}(\sqrt{2} C_{k2} + \sqrt{2} C_{k3} + C_{k5}) + C_{13}(\sqrt{2} C_{k1} + \sqrt{2} C_{k3} + C_{k6})]^2$	2 → 11 3 → 8 4 → 9 4 → 10	2 → 12 3 → 9 3 → 10 4 → 7	3 → 11 4 → 12	8
$E_{jS_{3/2}} \rightarrow E_{lS_{1/2}}$ $j = 5, 6$ $l = 13, 14, 15, 16$	8	$E_j - E_l$	$[C_{11}(\sqrt{2} C_{l2} + C_{l3}) + C_{12}(\sqrt{2} C_{l1} + C_{l4})]^2$	6 → 13 6 → 14	5 → 13 5 → 14	5 → 15 6 → 16	2
$E_{kS_{1/2}} \rightarrow E_{nS_{3/2}}$ $n = 21, 22, 23, 24, 25, 26$	36	$E_k - E_n$	$[C_{k1}(C_{n1} + \sqrt{2} C_{n3}) + C_{k2}(C_{n2} + \sqrt{2} C_{n4}) + C_{k3}(C_{n3} + \sqrt{2} C_{n5} + \sqrt{2} C_{n6}) + C_{k4} C_{n4} + \sqrt{2} C_{k5}(C_{n2} + C_{n3}) + \sqrt{2} C_{k6}(C_{n1} + C_{n3})]^2$	7 → 25 9 → 26 10 → 26 11 → 22 12 → 23 12 → 24	8 → 26 8 → 27 10 → 25 11 → 23 11 → 24 12 → 21	7 → 21 8 → 22 9 → 23 9 → 24 10 → 23 10 → 24	16
$E_{lS_{1/2}} \rightarrow E_{mS_{3/2}}$ $m = 17, 18, 19, 20$	8	$E_l - E_m$	$[C_{11}(C_{m1} + \sqrt{2} C_{m4}) + C_{12}(C_{m2} + \sqrt{2} C_{m3}) + \sqrt{2} C_{13} C_{m2} + \sqrt{2} C_{14} C_{m1}]^2$	13 → 20 14 → 20 16 → 17 16 → 18	13 → 19 14 → 19 15 → 17 15 → 18	13 → 17 15 → 16 14 → 17 14 → 18	4
$E_{nS_{1/2}} \rightarrow E_{pS_{3/2}}$ $p = 29, 30, 31$	18	$E_n - E_p$	$[\sqrt{2} C_{n1} C_{p1} + \sqrt{2} C_{n2} C_{p2} + \sqrt{2} C_{n3}(C_{p1} + C_{p2}) + C_{n6}(C_{p1} + \sqrt{2} C_{p3}) + C_{n5}(C_{p2} + \sqrt{2} C_{p3})]^2$	21 → 29 23 → 30 24 → 30 25 → 31	22 → 30 23 → 29 24 → 29 26 → 31	25 → 29 26 → 30	8
$E_{lS_{1/2}} \rightarrow E_{oS_{3/2}}$ $o = 27, 28$	8	$E_l - E_o$	$[\sqrt{2} C_{11} C_{o2} + \sqrt{2} C_{12} C_{o1} + C_{13} C_{o1} + C_{14} C_{o2}]^2$	17 → 28 18 → 28	17 → 27 18 → 27	19 → 27 20 → 28	2
$E_{pS_{1/2}} \rightarrow E_{32S_{3/2}}$	3	$E_p - E_{32}$	$[\sqrt{2} C_{p1} + \sqrt{2} C_{p2} + C_{p3}]^2$	29 → 32	30 → 32	31 → 32	—

HERE C_{rq} REPRESENTS THE COEFFICIENTS OF THE BASIC PRODUCT FUNCTION ϕ_q . THE LINEAR COMBINATIONS OF WHICH FORM THE STATIONARY STATE WAVE FUNCTION ψ_r CORRESPONDING TO EIGEN VALUE E_r ($r = i, j, k, l, m, n, o, p$)

frequencies and intensities of the remaining transitions then serve as checks on these values. In general, all the transitions may not be well resolved or may not have enough intensities to be recorded. However one may obtain sufficient number of well-resolved lines to carry out the analysis.

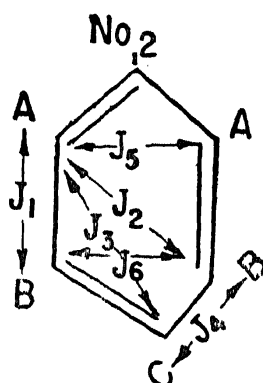


FIG. 1.

EXPERIMENTAL

The nuclear magnetic resonance spectrum of nitrobenzene (BDH-AR Grade) was taken on a Varian's high resolution spectrometer operating at

60 Mc./s. Sufficient nitrogen was bubbled through the sample prior to recording the spectrum to drive off the dissolved oxygen. The frequencies of various lines were determined relative to cyclohexane as external standard by usual side band technique correct to 2 cps. In a separate experiment the distances between the various peaks could also be measured with a much higher accuracy (± 0.2 cps.) with side-band technique.

RESULTS AND DISCUSSION

The NMR spectrum of nitrobenzene is shown in Fig. 2. Here the A band of the spectrum is well separated from the remaining lines and comes

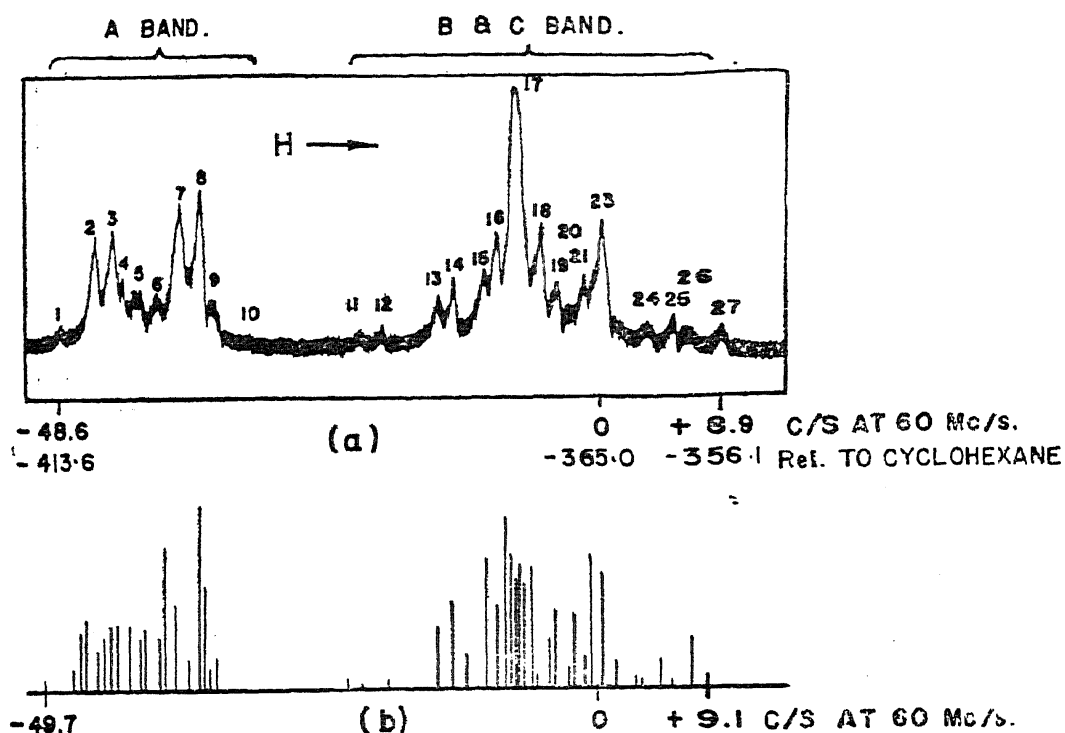


FIG. 2. NMR spectra of nitrobenzene. (a) Observed. (b) Calculated.

at the lowest frequency. This is because of the high electron withdrawing power of $-\text{NO}_2$ group. Among the B and C protons the former are expected to resonate at higher frequency because of the electron density being higher at this position as shown by chemical evidence (Hine, 1956).

The first-order values of the different parameters were reasonably guessed. These values were substituted in the matrices, and the spectrum was calculated by the help of Table II. The calculated spectrum was compared with the observed. This process of trial and error had to be repeated

till a good fit between the calculated and observed spectra was obtained. The following values were then obtained for the different parameters:

$$\nu_B - \nu_A = 38.1 \pm 0.3 \text{ cps.} = .635 \pm 0.005 \text{ p.p.m.}$$

$$\nu_C - \nu_A = 29.6 \pm 0.3 \text{ cps.} = .493 \pm 0.005 \text{ p.p.m.}$$

$$J_1 = 8.4 \text{ c./s.}; J_2 = 0.0 \text{ c./s.}; J_3 = 2.0 \text{ c./s.}; J_4 = 8.7 \text{ c./s.}; J_5 = 2.0 \text{ c./s.}; \\ J_6 = 2.0 \text{ c./s.}$$

The chemical shifts of the three protons relative to cyclohexane are as follows:

$$\nu_A = -404.9 \text{ c./s.} = -6.75 \text{ p.p.m.}; \quad \nu_B = -366.8 \text{ c./s.}$$

$$= -6.11 \text{ p.p.m.}; \quad \nu_C = -375.3 \text{ c./s.} = -6.26 \text{ p.p.m.}$$

The two internal chemical shift values can be compared with those obtained by Corio and Dailey (Table III).

TABLE III

Values of Corio and Dailey	Authors' Values
$\nu_B - \nu_A = 0.67 \text{ p.p.m.}$	$0.635 \pm .005 \text{ p.p.m.}$
$\nu_C - \nu_A = 0.55 \text{ p.p.m.}$	$0.493 \pm .005 \text{ p.p.m.}$

It can be seen that the values of chemical shifts obtained by Corio and Dailey differ from ours by about $\pm .05 \text{ p.p.m.}$ The values obtained by us after a complete analysis are correct within $\pm .005 \text{ p.p.m.}$ Thus we can study even extremely small changes in chemical shifts such as those caused by the substitution effects to an accuracy of $\pm 0.005 \text{ p.p.m.}$

The chemical shift of the *para* proton is -375.3 c./s. which is lower than the frequency of the peak with the maximum intensity (Peak No. 17 having a frequency of -372.6 c./s.). The assumption of Corio and Dailey regarding the chemical shift of this proton is therefore wrong.

The calculated spectrum of nitrobenzene with the above values of the parameters is compared with that obtained experimentally in Fig. 2 and Table IV. The agreement between the two spectra is extremely good.

In the particular case of nitrobenzene eight trial and error calculations had to be done. This involved a lot of calculations but the work was considerably reduced by the use of our computer.

TABLE IV

Calculated and observed spectrum of nitrobenzene (A_2B_2C System)(The frequency of the line No. 23 relative to cyclohexane is -365.0 c./s.)

No.	Group	Frequency		Intensity	
		Calculated cps.	Observed cps.	Calculated	Observed
1	A	-49.7	-48.6	0.24	0.33
	Comb	-48.9		0.10	
2	A	-46.7	-45.4	0.50	3.13
	A	-46.1		1.48	
	A	-45.6		0.38	
	A	-45.6		1.48	
3	A	-44.2	-43.8	1.00	3.13
	A	-43.6		1.32	
	A	-43.4		1.64	
4	A	-42.9	-42.0	1.65	1.65
	A	-41.8		0.88	
5	A	-41.7	-41.0	0.85	1.65
	A	-40.8		1.30	
6	A	-40.1	-39.5	1.54	1.66
	A	-38.7		1.29	
7	A	-38.3	-37.4	1.95	3.96
	Comb	-38.3		0.17	
	A	-38.2		1.48	
	A	-37.6		2.09	
	A	-36.2		0.83	
8	A	-35.3	-35.1	0.81	4.30
	A	-35.2		2.62	
	A	-35.2		1.34	
	A	-34.7		2.66	
9	A	-34.0	-33.8	0.47	1.31
	A	-33.2		0.75	
10	Comb	-29.9	-30.7	0.30	0.33

TABLE IV—(Contd).

No.	Group	Frequency		Intensity	
		Calculated cps.	Observed cps.	Calculated	Observed
11	C	-23.8	-21.4	0.00	0.33
	C	-21.7		0.00	
	C	-21.6		0.11	
	C	-21.5		0.13	
	Comb	-21.4		0.31	
12	C	-20.4	-19.5	0.11	0.33
	C	-18.4		0.26	
13	C	-15.5	-14.7	0.02	1.31
	C	-15.5		0.04	
	C	-14.3		0.01	
	C	-13.7		0.71	
	C	-13.7		0.88	
14	C	-12.4	-13.3	1.15	1.81
	C	-12.3		1.16	
15	B	-11.1	-10.8	0.88	1.62
16	C	-9.2	-9.7	3.40	2.98
17	B	-8.4	-7.6	1.38	6.8
	C	-8.2		0.85	
	B	-7.6		4.53	
	B	-7.0		3.43	
	C	-6.6		2.67	
	C	-6.3		0.56	
	C	-6.3		2.68	
18	B	-6.0	-5.5	2.80	3.30
	C	-5.9		0.19	
	B	-5.1		3.24	
19	B	-4.6	-4.1	0.36	1.65
	B	-3.6		1.35	
20	C	-3.2	-3.0	2.01	1.31
21	B	-1.9	-1.8	0.51	1.82
22	B	-1.5	-1.2	2.0	1.82
	B	-0.6		0.82	

TABLE IV—(Contd.)

No.	Group	Frequency		Intensity	
		Calculated cps.	Observed cps.	Calculated	Observed
23	B	- 0.4	- 0.0	1.49	3.48
	B	+ 0.2		3.47	
	B	+ 1.0		2.21	
	B	+ 1.7		0.0	
24	B	+ 4.5	+ 3.7	0.30	0.85
	B	+ 4.1		0.09	
	B	+ 3.6		0.26	
	B	+ 2.0		0.65	
25	B	+ 5.7	+ 5.6	0.73	0.83
26	B	+ 6.8	+ 7.0	0.24	0.49
27	B	+ 9.1	+ 8.9	0.33	0.55

Other combination lines of very weak intensities (calculated) are as follows:

Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
-57.3	0.01	-33.8	0.06	+ 8.5	0.02
-54.5	0.03	-32.9	0.05	+ 9.2	0.02
-53.4	0.03	-23.5	0.03	+15.0	0.02
-52.2	0.03	-23.3	0.04		

The observed intensities are not in very good agreement with those calculated because of overlapping of lines and inaccuracies in their measurements.

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