HIGH RESOLUTION NMR SPECTRA OF SOME TRI-SUBSTITUTED BENZENES

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Abstract

This paper presents the analysis of the proton magnetic resonance spectra of 2:4 dinitro phenol, 1-chloro 2:4 dinitro benzene, 1-nitro, 2-methyl, 3-chloro benzene (2-chloro, 6-nitro toluene) and 5-sulpho, 3-nitro benzoic acid based on the exact solution obtained by Jha for the splitting of NMR lines of a three nuclei system of the ABC type.

Introduction

The analysis of the high resolution proton magnetic resonance spectra of the ABC type has aroused great interest during recent times. Fessenden and Waugh (1959) have given several rules which allow one to reduce the total number of independent parameters in such a system by inspection of the observed spectrum. Alexander (1960), Richards and co-worker (1960) and Sheppard *et al.* (1960) have analysed the spectra of styrene and vinyl compounds, all of which belong to the ABC type. However, in all such cases the 3×3 matrices involved in the analysis were not solved in terms of explicit expressions but numerical computations were made to diagonalise these matrices. Recently Jha (1961) has solved these matrices and obtained explicit expressions for the intensities and the frequencies arising out of the fifteen allowed transitions in such a system.

In the present paper we report the analysis of some tri-substituted benzenes based on these expressions. In all these cases a guess of different parameters was first made to the first order of approximation. A good fit between the observed and the calculated spectra was then obtained by a few trial and error calculations using Jha's expressions.

Experimental

(1) *NMR Measurements*

The spectra were recorded on a Varian High Resolution NMR Spectrometer operating at 60 Mc./s. The distances between the various peaks were

measured by the usual side band technique correct to $\pm$ 0·3 c./s. and have been expressed in frequencies relative to ν_0, the mean Larmor frequency for the three phenyl protons forming the ABC system. The intensities were measured in terms of amplitudes of the various peaks. It may be pointed out that this procedure of measuring intensities may create an error of about $\pm$ 15% which is rather large but inevitable in the absence of an elaborate integrating system; however, the procedure was satisfactory in most cases except when comparison was to be made between the observed and the calculated intensities of peaks which were not very well resolved. In such cases the observed intensities of the peaks which were in between two peaks were found to be always higher. The resolution under which these spectra were recorded was about 0·3 c./s. at the operating frequency of 60 Mc./s.

(2) *Chemicals*

(*a*) The sample of 2-chloro, 6-nitrotoluene was Eastman Kodak's and the spectrum was taken in solution in BDH 'Analar' grade carbon tetrachloride.

(*b*) α-dinitro phenol (2:4 dinitrophenol) was obtained from E. Merck and its soluton in E. Merck tetra hydro-furan was used for observing the spectrum.

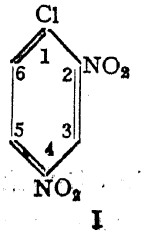
(*c*) 1-chloro, 2:4-dinitro benzene was prepared in the laboratory by nitration of chlorobenzene (Hoffman and Dame, 1919) and its solution in BDH 'Analar' grade carbon tetra chloride was used.

(*d*) The sodium hydrogen salt of 5-sulpho, 3-nitro benzoic acid was prepared by sulphonating benzoic acid followed by nitration according to the conditions given in the literature (Shah and Bhatt, 1933). The salt was then isolated by pouring the reaction mixture in saturated brine and was finally crystallised from water. The spectrum was taken in aqueous solution.

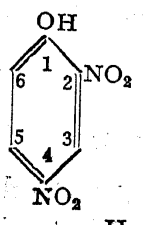
In all these cases sufficient nitrogen was bubbled through the solutions to remove any dissolved oxygen before recording the spectrum.

ANALYSIS OF THE SPECTRA

1, 2, 4 *Tri-substituted Benzenes.*—The compounds of this type which have been studied are 1-chloro, 2:4-dinitro benzene (I) and 2:4-dinitro phenol (II).



I



II

Because of the low *para* coupling constant (J_{36}) which in general has been reported to be less than 0·5 c./s. (Pople, Bernstein, Schneider, 1959) the spectrum of this type is comparatively simple to analyse. For these compounds one expects a spectrum which generally consists of a doublet due to 3 position proton the separation of which will give J_{35} to the first order of approximation, a doublet due to 6 position proton the separation of which will give J_{56} to the first order and a quartet due to 5 position proton. Since the *ortho* and *meta* coupling constants (J_{56} and J_{35}) involved are widely different in magnitude (Pople, Bernstein, Schneider, 1959) one can analyse the spectrum without ambiguity.

The proton resonance spectra of the compounds (I) and (II) are shown in Figs. 1 and 2. It is seen from the spectrum that the coupling constant

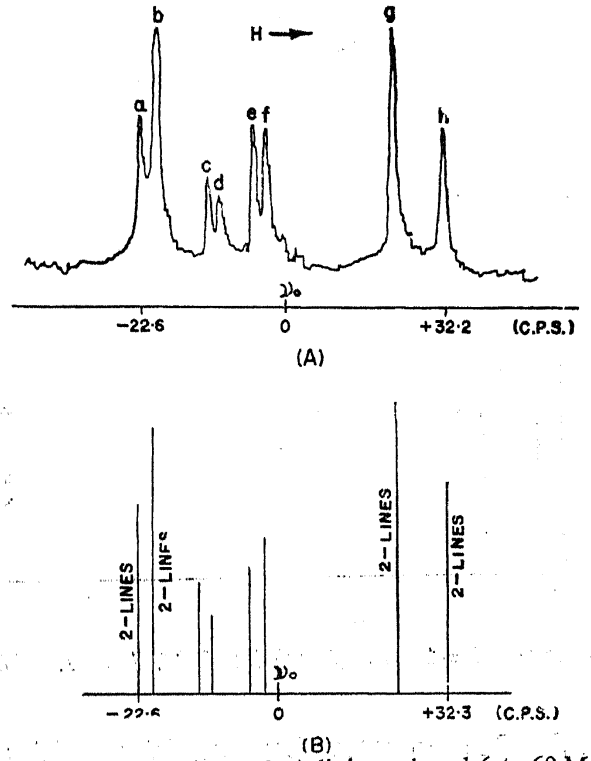


FIG. 1. NMR spectrum of 1-chloro, 2:4-dinitro phenol (at 60 Mc./s.). A. Observed; B. Calculated.

J_{36} must be less than 0·3 c./s. (the order of resolution in our experiment) since no further splitting of doublets for proton in 3 and 6 positions is observed. These considerations lead to an assignment to the various lines in the observed spectra of 1-chloro, 2:4-dinitro benzene and α-dinitro phenol. Thus lines (*a*) and (*b*) are due to proton in position (3) and (*g*) and (*h*) due to the proton in position 6. The proton in position (5) gives rise to a quartet represented

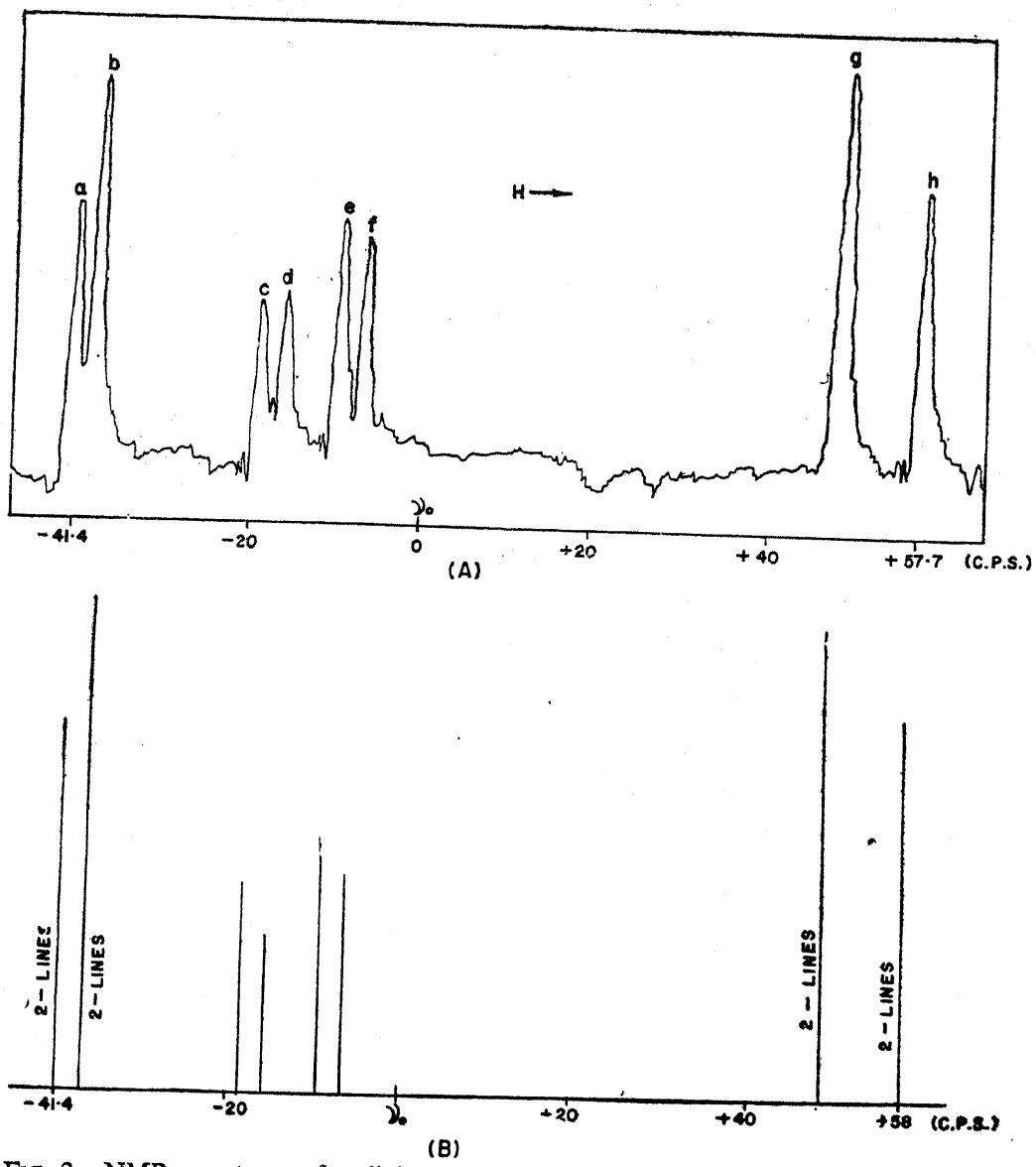


FIG. 2. NMR spectrum of α-dinitro phenol (at 60 Mc./s.). A. Observed; B. Calculated.

by lines *c*, *d*, *e* and *f*. The separation between (*a*) and (*b*) gives J_{35} and that between (*g*) and (*h*) gives J_{56} to the first orders of approximations.

Using Jha's expressions, the following values have been assigned to the various parameters:—

1-*chloro*, 2:4-*dinitrobenzene*

$$\nu_3 = -21{\cdot}3 \pm 0{\cdot}2 \text{ c./s.} = -0{\cdot}355 \pm 0{\cdot}003 \text{ p.p.m.}$$

$$\nu_5 = -6{\cdot}4 \pm 0{\cdot}2 \text{ c./s.} = -0{\cdot}107 \pm 0{\cdot}003 \text{ p.p.m.}$$

$\nu_6 = +27{\cdot}7 \pm 0{\cdot}2$ c./s. $= +0{\cdot}462 \pm 0{\cdot}003$ p.p.m.

$J_{35} = 2{\cdot}7 \pm 0{\cdot}2$ c./s.

$J_{56} = 8{\cdot}7 \pm 0{\cdot}2$ c./s.

$J_{36} < 0{\cdot}3$ c./s.

2: 4-*dinitro phenol*

$\nu_3 = -39{\cdot}9 \pm 0{\cdot}1$ c./s. $= -0{\cdot}665 \pm 0{\cdot}002$ p.p.m.

$\nu_5 = -13{\cdot}1 \pm 0{\cdot}1$ c./s. $= -0{\cdot}218 \pm 0{\cdot}002$ p.p.m.

$\nu_6 = +53{\cdot}1 \pm 0{\cdot}1$ c./s. $= +0{\cdot}885 \pm 0{\cdot}002$ p.p.m.

$J_{35} = 2{\cdot}9 \pm 0{\cdot}1$ c./s.

$J_{56} = 9{\cdot}2 \pm 0{\cdot}2$ c./s.

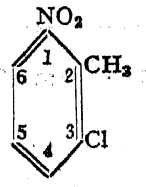
$J_{36} < 0{\cdot}3$ c./s.

The theoretical spectra constructed on the basis of these values have also been shown for each of the two compounds in Figs. 1 and 2 for comparison.

In both these compounds the proton in position 3 has the least resonance frequency. This result is expected in view of the presence of the two nitro-groups having electron withdrawing power and thus decreasing the electron density at the 3 position.

1, 2, 3 (1, 2, 6) *tri-substituted benzenes*

Among the various 1, 2, 3 tri-substituted benzenes only one compound, namely, 1-nitro, 2-methyl, 3-chloro benzene (III) was studied as an example of ABC system.



III

For this compound the spectrum should consist of four lines due to each of the protons 4, 5 and 6 and three lines due to their combinations according to the general theory. The spectra obtained for this compound at 60 Mc./s. as well as at 30 Mc./s. are shown in Fig. 3. The intensities and the line separations in the two spectra indicate a strong coupling of the ABC protons.

Of the three substituents present in the molecule, the NO_2 group has the greatest electron withdrawal power and hence ν_6 is expected to be the least, ν_5 the highest and ν_4 should have an intermediate value. From the spectrum obtained at 60 Mc./s. lines *a*, *b*, *d* and *e* were therefore attributed to the transitions corresponding to the proton in the 6 positions; the separations between

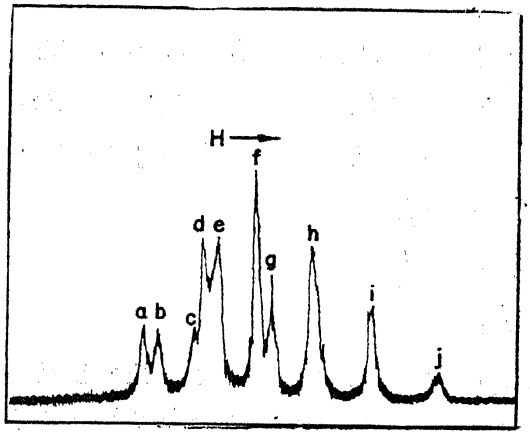


FIG. 3 A. NMR spectrum of 2-chloro, 6-nitro toluene (at 60 Mc./s.).

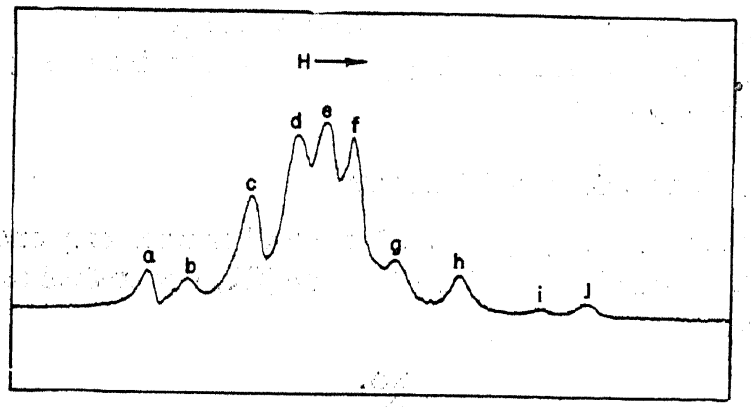


FIG. 3 B. NMR spectrum of 2-chloro, 6-nitro toluene (at 30 Mc./s.).

these lines give the first order values of J_{56} (*ortho*) and J_{46} (*meta*) in this compound. They are 8·4 c./s. and 2·9 c./s. respectively, in agreement with the generally expected values of these coupling constants. Similarly, lines *c*, *e*, *f* and *g* have been assigned to transitions corresponding to proton 4 and the lines *h*, *i*, *j* to those due to proton 5. The first order values of ν_4 and ν_5 and the various coupling constants thus obtained from the spectrum were then used in Jha's expressions for trial and error calculations. For a good agreement between the observed and the calculated spectra the following values had to be assigned to various parameters:

$\nu_6 = -0{\cdot}163 \pm 0{\cdot}003$ p.p.m.

$\nu_4 = -0{\cdot}047 \pm 0{\cdot}003$ p.p.m.

$\nu_5 = +0{\cdot}217 \pm 0{\cdot}003$ p.p.m.

$J_{46} = 2{\cdot}3 \pm 0{\cdot}2$ c./s.

$J_{45} = 8{\cdot}0 \pm 0{\cdot}2$ c./s.

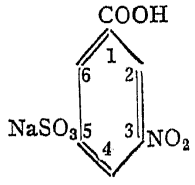
$J_{56} = 8{\cdot}0 \pm 0{\cdot}2$ c./s.

The spectrum (Fig. 3 B) at 30 Mc./s. obtained incidentally in an earlier experiment also gave assignments in good agreement with the above values. Table I shows at a glance the general agreement between the calculated and the observed values of the frequencies and the intensities of the allowed transitions in this compound at 60 Mc./s. as well as at 30 Mc./s.

1, 3, 5 *Tri-substituted Benzenes*

The proton resonance spectra of 1, 3, 5 tri-substituted benzenes are in general more difficult to analyse than the previous cases. All the coupling constants for such compounds are of the same order $J_{meta} \approx 1$ to 3 c./s. and thus the two middle lines in each group A, B, C will in general not be resolved and, therefore, the spectrum will consist of nine lines. One can get the values of the three coupling constants and the two chemical shifts from the analysis but the assignment of these values to the three protons in the system has to be properly reasoned out.

As an example of 1, 3, 5 tri-substituted benzenes, we have studied the proton resonance in a saturated aqueous solution of sodium hydrogen salt of 5-sulpho, 3-nitro benzoic acid (IV).



IV

The total spectrum (Fig. 4) of the ABC type protons covers a narrow range of 11·5 c./s. in this case. Using Jha's expressions, it was found that the following parameters gave the best agreement between the theoretical and the observed spectra.

$\nu_A = -3{\cdot}8 \pm 0{\cdot}2$ c./s. $= -0{\cdot}063 \pm 0{\cdot}003$ p.p.m.

$\nu_B = -0{\cdot}5 \pm 0{\cdot}2$ c./s. $= -0{\cdot}008 \pm 0{\cdot}003$ p.p.m.

$\nu_C = +4{\cdot}2 \pm 0{\cdot}2$ c./s. $= +0{\cdot}070 \pm 0{\cdot}003$ p.p.m.

$J_{AB} = 2{\cdot}2 \pm 0{\cdot}2$ c./s.

$J_{AC} = 1{\cdot}4 \pm 0{\cdot}2$ c./s.

$J_{BC} = 1{\cdot}5 \pm 0{\cdot}2$ c./s.

TABLE I

Calculated and observed spectra of 2-chloro, 6-nitro toluene

No.	30 Mc./s. spectrum				No.	60 Mc./s. spectrum			
	Frequencies		Relative intensities			Frequencies		Relative intensities	
	Obs. c./s.	Cal. c./s.	Obs.	Cal.		Obs. c./s.	Cal. c./s.	Obs.	Cal.
1	..	−18·4	0	0·00	1	..	−35·2	0	0·00
2	−11·3	−11·7	0·16	0·12	2	−22·2	−22·2	0·33	0·25
3	..	− 8·5	..	0·02	3	−19·3	−19·3	0·33	0·49
4	− 7·4	− 7·9	0·13	0·13	4	−15·7	−15·6	0·20	0·31
5	Unresolved	− 5·5	0·40	0·10	5	−15·1	−15·1	0·60	0·31
6	− 5·4	− 4·7		0·24	6	−12·7	−12·7	0·83	0·61
7	− 1·8	− 1·7	0·90	0·76	7	−12·1	−12·2	0·79	0·82
8	0·4	− 0·2	1·00	1·00	8	− 7·4	− 7·4	1·00	1·00
9	2·1	1·9	0·95	0·78	9	− 4·3	− 5·0	0·46	0·31
10	Unresolved	3·6	..	0·13	10	..	0·2	..	0·23
11	4·0	4·9	0·20	0·15	11	0·7	0·7	0·74	0·87
12	8·2	7·1	0·17	0·16	12	7·5	7·3	0·46	0·41
13	11·0	10·3	0·05	0·05	13	..	8·4	..	0·04
14	13·0	13·5	0·04	0·03	14	16·9	16·9	0·18	0·16
15	15·6	16·4	0·07	0·06	15	..	15·0	0	0·01

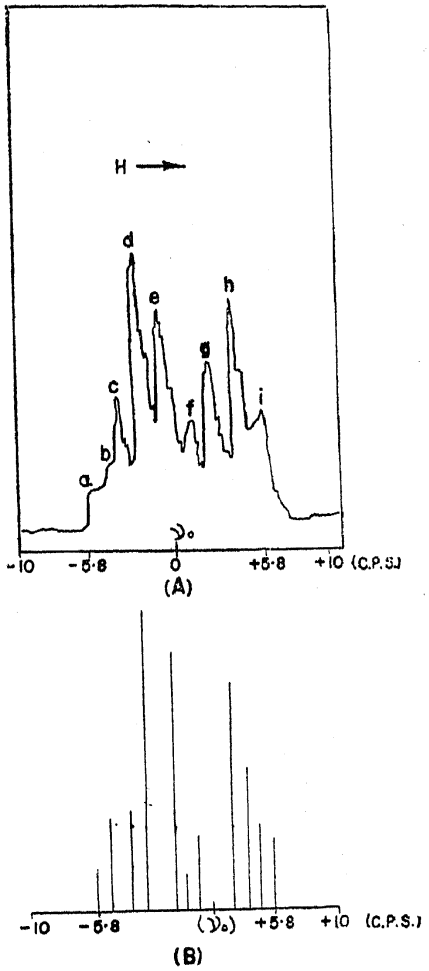


FIG. 4. NMR spectrum of sodium hydrogen salt of 5-sulpho, 3-nitro benzoic acid (at 60 Mc./s.). (A) Observed; (B) Calculated.

But the real difficulty in this case lies in determining which one of these shifts belongs to which proton. It seems reasonably right to presume that the shift ν_C is due to proton in position 6 because the $-NO_2$ group is the most electron withdrawing as compared with $-NaSO_3$ and $-COOH$ groups and consequently the protons in 2 and 4 positions are expected to resonate at lower fields compared to this proton. It is difficult, however, to assign the frequency ν_B or ν_A to a particular proton in the remaining two, unless isotopic substitution method is employed.

From the values of the spin coupling constants derived from the analysis of the four compounds studied in this investigation, the following general observations can be made:

(1) The order of the magnitude of coupling constants is:

$$J_{ortho} > J_{meta} > J_{para}$$

(2) The values of the *ortho* coupling constants are in the range 8–9 c./s. the *meta* coupling constants vary from 1·0 to 3·0 c./s. and the *para* coupling constants are less than 0·3 c./s. These are the ranges so far observed for substituted benzenes (Pople *et al.*, 1959).

(3) Two of the *meta* coupling constants (J_{AC} and J_{BC}) in 5-sulpho, 3-nitro benzoic acid are very much lower than the normal values (Pople, Bernstein and Schneider, 1959). It appears that these low values are due to steric effects of the groups —COOH and —$NaSO_3$ from the work that is in progress in our laboratory, the details of which will be published elsewhere.

(4) All the observed coupling constants in this work have the same sign.

SUMMARY

It is thus found that the explicit expressions for the exact solution of the splitting up of NMR lines for the three nuclei of the type ABC are extremely useful for the analysis of the NMR spectra of the three spin systems.

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