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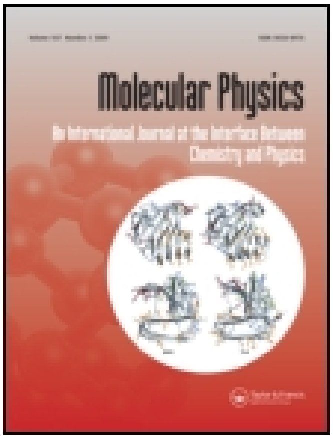

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^{1}H and ^{19}F nuclear magnetic resonance spectra of some para substituted fluorobenzenes†. II‡

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The ring proton and fluorine nuclear magnetic resonance spectra of *p*-fluoronitrobenzene, *p*-fluorobenzoyl chloride and *p*-fluorobenzene sulphonyl chloride have been studied as an A_2B_2X system at 40 and 56·445 Mc/sec. The involved spin coupling constants and chemical shifts are determined.

1. INTRODUCTION

In a recent communication [1] we have reported the analysis of the nuclear magnetic resonance spectra of *p*-fluoroacetophenone, *p*-fluoroethyl benzoate and *p*-fluorobenzonitrile as A_2B_2X system at 40 and 56·445 Mc/sec. Here we report the results of the analysis of the spectra of *p*-fluoronitrobenzene, *p*-fluorobenzoyl chloride and *p*-fluorobenzene sulphonyl chloride by the procedure given in reference [1] as well as by a modification of Anderson's method [2].

2. EXPERIMENTAL

2.1. *p-fluoronitrobenzene*

Prepared by the direct nitration of fluorobenzene by a mixture of concentrated sulphuric acid and fuming nitric acid at −10°C as described in the literature [3], the product was distilled twice in vacuum and the fraction boiling between 109–109·5°C/36 mm was used.

2.2. *p-fluorobenzoyl chloride*

The procedure described [4] for the preparation of *p*-nitrobenzoyl chloride was adopted with *p*-fluorobenzoic acid instead of *p*-nitrobenzoic acid. The final product was distilled (b.p. 104°C/38 mm) and used for N.M.R. measurements.

2.3. *p-fluorobenzene sulphonyl chloride*

Sodium *p*-fluorobenzene sulphonate was prepared [5] first and then it was treated with phosphorous pentachloride as described [6] for the preparation of benzene sulphonyl chloride.

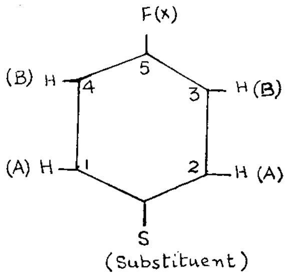
The spectra were recorded at 40 and 56·445 Mc/sec on a Varian V–4300B N.M.R. spectrometer. The separations of the resonance peaks were measured by the use of audio-frequency side bands. The proton chemical shifts in *p*-fluorobenzoyl chloride and *p*-fluorobenzene sulphonyl chloride were measured with respect to cyclohexane as internal standard at 56·445 Mc/sec and that of *p*-fluoronitrobenzene with respect to water as external standard at 40 Mc/sec.

† Our earlier paper [1] is referred to as I.

‡ Part of a thesis submitted by G. Aruldhas to Indian Institute of Technology, Kanpur, in partial fulfilment of the requirements for a Ph.D. degree.

3. Discussion

As in reference [1], the following labelling of nuclei and notation is used:



$$N = J_{23} + J_{24}$$
$$L = J_{23} - J_{24}$$
$$K = J_{12} + J_{34}$$
$$M = J_{12} - J_{34}$$

The fluorine resonance spectrum of each molecule shows nine lines. The spectrum is symmetrical about the central line and the intensity distribution of one half is 1:2:2:1:4 within experimental error. The proton resonance spectra of these molecules exhibit two groups of lines and the lines in the group on high field side are slightly broadened when compared with the lines on low field side. Assuming the signs of the coupling constants are the same the spectra have been analysed using the procedure described in reference [1]. The various parameters are listed in the table. In order to get the best fit between the experimental and theoretical spectra the quartic equations have been solved by the iteration method [7]. The agreement between the calculated and observed spectra is shown in figures 1, 2, 3 and 4. Only one fluorine spectrum is given as all are similar.

3.1. *Perturbation analysis of the system A_2B_2X*

In the total Hamiltonian

$$H = \sum_k \nu_k I_{zk} + \sum_{i<j} J_{ij} \ \mathbf{I}_i \cdot \mathbf{I}_j$$

the contribution due to the terms

$$H^0 = \sum_k \nu_k I_{zk} + J_{12} I_{z1} I_{z2} + J_{34} I_{z3} I_{z4} + \sum_{m=3,4} 2J_{2m} I_{z2} I_{zm} + \sum_{n=2,3} 2J_{n5} I_{zn} I_{z5}$$

has been chosen as the unperturbed Hamiltonian. The remaining terms

$$H' = J_{12}(I_{x1} I_{x2} + I_{y1} I_{y2}) + J_{34}(I_{x3} I_{x4} + I_{y3} I_{y4}) + \sum_{m=3,4} 2J_{2m}(I_{x2} I_{xm} + I_{y2} I_{ym}) + \sum_{n=2,3} 2J_{n5}(I_{xn} I_{x5} + I_{yn} I_{y5})$$

are treated as perturbation.

According to the set of basic functions given in part I, the difference between some of the energy levels is of the same order as the corresponding off-diagonal elements. For example, $H_{9,10}/(H_{99} - H_{10,10})$ is of the order of unity and a perturbation calculation is inappropriate. A different set of basic functions, similar to the one given by Richards and Schaefer [8], is, therefore, selected. The diagonal and off-diagonal matrix elements have been obtained without the simplifying assumptions of Richards and Schaefer [8], i.e. without setting the para H–H coupling constants to zero and the two meta H–H coupling constants equal.

Compound	Spectra at Mc/sec	Method of analysis	J_0^{HH}	J_m^{HH}	J_p^{HH}	J_0^{HF}	J_m^{HF}	$(\nu_A - \nu_B)$†	$\nu - \nu_{\text{cyclohexane}}$	$\nu - \nu_{\text{fluorobenzene}}$
p-$FC_6H_4NO_2$	40·000	Reference [1]	9·14	2·85	0·33	8·09	4·86	39·5 ± 0·3		415·8 ± 3·5
	56·445	,,	9·09	2·79	0·30	8·14	4·82	39·4 ± 0·2		
	40·000	Perturbation	9·08	2·93	0·40	8·17	4·78	39·3 ± 0·3		
p-FC_6H_4COCl	40·000	Reference [1]	8·64	2·53	0·35	8·33	5·20	36·6 ± 0·3		474·2 ± 3·0
	56·445	,,	8·73	2·55	0·25	8·26	5·28	36·8 ± 0·3	371·0 ± 3·0	
	40·000	Perturbation	8·59	2·64	0·40	8·25	5·22	36·5 ± 0·3		
p-$FC_6H_4SO_2Cl$	40·000	Reference [1]	8·85	2·52	0·33	8·14	4·97	30·4 ± 0·4		522·4 ± 4·0
	56·445	,,	9·00	2·57	0·27	8·22	4·96	30·6 ± 0·3	380·3 ± 3·0	
	40·000	Perturbation	8·82	2·59	0·36	8·14	4·98	30·3 ± 0·4		

Spin–spin coupling constants‡ and chemical shifts (in c.p.s.).

† The $(\nu_A - \nu_B)$ values at 56·445 Mc/sec are multiplied by (40/56·445) to compare with the values at 40 Mc/sec.

‡ The error involved in any of the spin–spin coupling constants is about ± 0·15 c.p.s.

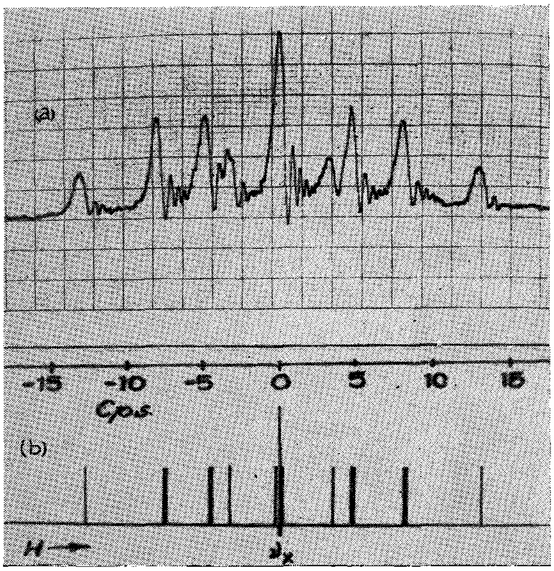


Figure 1. ^{19}F N.M.R. spectrum of para fluoro nitrobenzene at 40 Mc/sec. (*a*) Experimental. (*b*) Calculated.

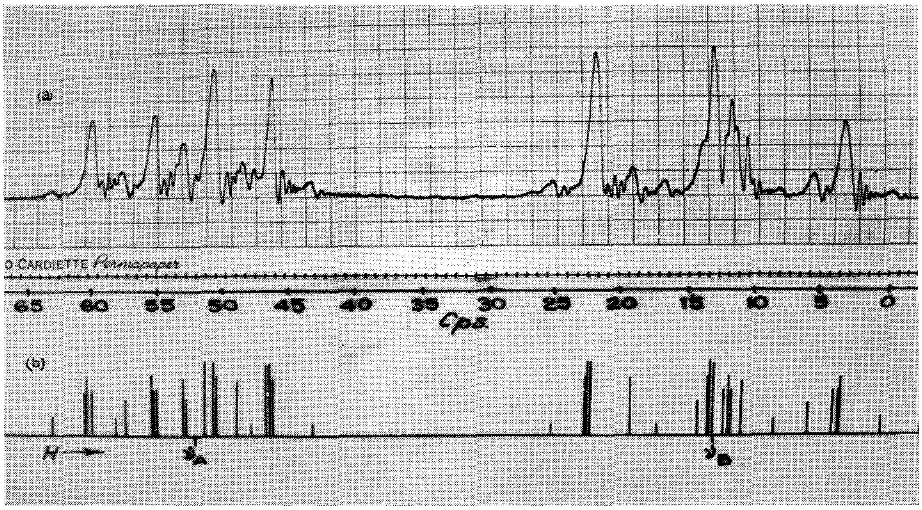


Figure 2. ^{1}H N.M.R. spectrum of para fluoro nitrobenzene at 40 Mc/sec. (*a*) Experimental. (*b*) Calculated.

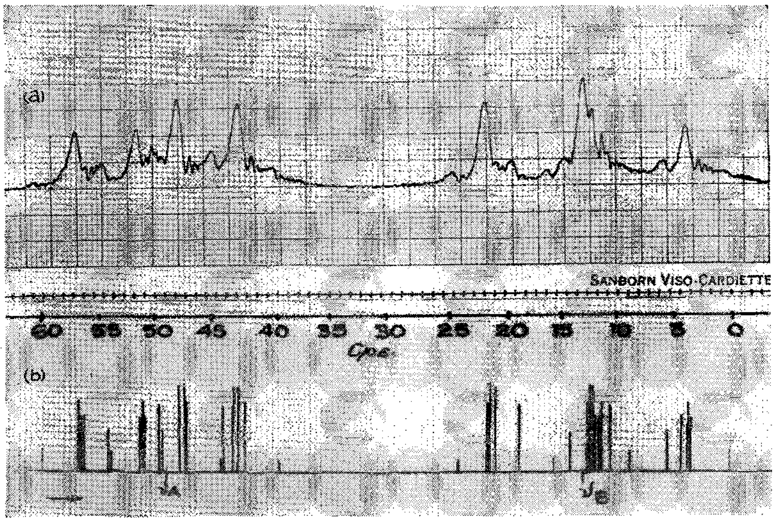


Figure 3. ^{1}H N.M.R. spectrum of para fluoro benzoyl chloride at 40 Mc/sec. (*a*) Experimental. (*b*) Calculated.

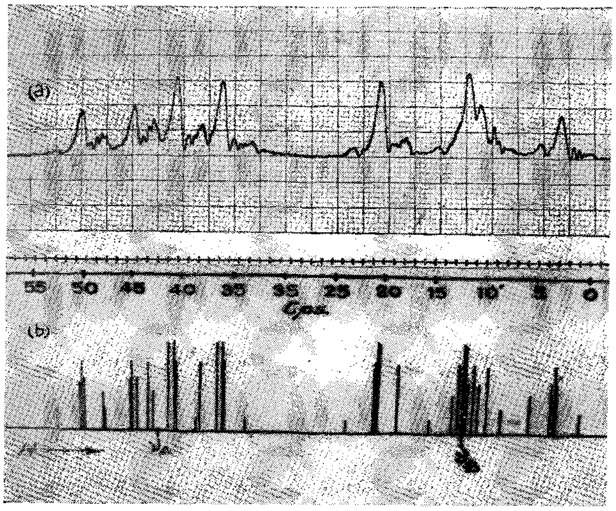


Figure 4. ^{1}H N.M.R. spectrum of para fluoro benzene sulphonyl chloride at 40 Mc/sec. (*a*) Experimental. (*b*) Calculated.

The first-order correction to the energy levels is the diagonal matrix element of the perturbation and it is zero as the z-component of the spin–spin interaction is included in the unperturbed part. The second-order perturbation correction [9] for the various levels has been calculated and the spectra have been analysed to determine all the parameters (table).

It has been found from the analyses that $M=0$, i.e. the two meta H–H coupling constants are equal unlike the compounds studied in reference [1]. The values of the parameters obtained at 56·445 Mc/sec are in agreement with those at 40 Mc/sec. The values of the corresponding coupling constants obtained here, including those in reference [1], do not differ appreciably from one compound to another. Further, it does not deviate much from the corresponding values for monofluorobenzene [10], 4d-fluorobenzene [11] and other substituted benzenes [8, 12, 13], showing that they are not very sensitive to substitution. But the dependence of chemical shifts on the substituent appears to be considerable.

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The spectra at 40 Mc/sec are taken with the high resolution N.M.R. spectrometer at the Muslim University, Aligarh, and those at 56·445 Mc/sec with the spectrometer at the Tata Institute of Fundamental Research, Bombay. The authors wish to express their thanks to the authorities of both the institutions. Thanks are due to Dr. S. S. Dharmatti for the cordiality shown to one of us (G. A.) during his stay in Tata Institute.

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