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Strong Coupling in Nuclear Resonance Spectra. II. Field Dependence of Some Unsymmetrical Three-Spin Spectra*†

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Magnetic resonance spectra are calculated and compared with experiment for the vinyl group of styrene, 2,4-dichloroaniline, and 2,5-dichloroaniline at various magnetic field strengths. Some simple rules are presented which facilitate the determination of chemical shifts and coupling constants, including the signs of the latter. One of the spectra illustrates the occasional necessity for experiments at more than one field strength if the parameters are to be determined unambiguously. In each case the shielding and coupling constants are found to be field-independent within experimental accuracy.

INTRODUCTION

A GOOD deal of attention has recently been devoted to the analysis of high-resolution nuclear magnetic resonance spectra of molecules in which there are spin-spin interactions $J_{ij} = 2\pi A_{ij}$ comparable in magnitude to chemical shift differences $\gamma H_0(\delta_i - \delta_j)$.¹⁻⁵ With one notable exception⁶ the analysis has been performed by the traditional spectroscopic method of repeated solution of the appropriate eigenvalue problem until the input parameters give agreement with the experimental spectrum. The present work is in the same tradition and concerns itself with the totally unsymmetrical system of three spin- $\frac{1}{2}$ nuclei (ABC in the notation of Bernstein *et al.*)² The lack of symmetry characteristic of this system makes it very inconvenient (though not in principle impossible) to give formulas for the line positions and intensities in closed form, and for that reason we have solved all of the actual eigenvalue problems numerically.

The labor involved in each such process is not negligible; moreover, the problem contains six independent parameters which must be simultaneously adjusted (three coupling constants and three chemical shifts). For that reason we point out below some simple properties of the spectrum which in effect reduce the number of independent parameters and also provide good first approximations to their values. One of them,

in favorable cases, provides information about the relative signs of the coupling constants without necessitating the solution of the eigenvalue problem at all. The question of sign in proton spectra has been one of considerable recent interest.^{3,7-9}

It may also be noted that the field independence of J 's and δ 's, i.e., the sufficiency of the Hamiltonian (1) in the following, seems not to have been tested in the critical strong coupling region. Three-spin systems in this region are the simplest for which additional (though unexpected) "three-body" interactions, e.g., $\mathbf{I}_i \cdot \mathbf{I}_j \times \mathbf{I}_k$, are possible. We remark immediately that we have not found any cause for alarm in the field dependence studies reported in this paper.

METHODS OF ANALYSIS

We write the Hamiltonian for ABC in the form

$$\mathcal{H} = -h \left[\nu_0 \sum_{i=A}^C (1 - \delta_i) I_{zi} + \sum_{j>i} \sum A_{ij} \mathbf{I}_i \cdot \mathbf{I}_j \right] \quad (1)$$

to correspond to the notation in I .⁹ For actual computational purposes it is convenient to express \mathcal{H} in frequency units and to ignore the Zeeman energy operator $h\nu_0 \sum_i I_{zi}$, which in strong fields determines only the location of the spectrum and not its structure. Thus we will concern ourselves with

$$H = \nu_0 \sum_i \delta_i I_{zi} - \sum_{j>i} \sum A_{ij} \mathbf{I}_i \cdot \mathbf{I}_j \quad (2)$$

Previous workers^{1,2} have summarized the form of the matrix elements of (2) in the representation appropriate to uncoupled spins (m representation). We give them for the present case in Table I. The remaining problem is of course to diagonalize (2) for the proper set of A 's and δ 's. Absorption line frequencies are obtained from the eigenvalues using the selection rule $\Delta F_z = -1$ on the total magnetic quantum number. Since the experiments are actually done at constant

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§ Sloan Fellow.

¹ McConnell, McLean, and Reilly, *J. Chem. Phys.* **23**, 1152 (1955).

² Bernstein, Pople, and Schneider, *Can. J. Chem.* **35**, 65 (1957); **35**, 1060 (1957).

³ Gutowsky, Holm, Saika, and Williams, *J. Am. Chem. Soc.* **79**, 4596 (1957).

⁴ E. B. Wilson, Jr., *J. Chem. Phys.* **27**, 60 (1957).

⁵ R. E. Richards and T. Schaefer, *Mol. Phys.* **1**, 331 (1958).

⁶ W. A. Anderson and H. M. McConnell, *J. Chem. Phys.* **26**, 1496 (1957).

⁷ G. A. Williams and H. S. Gutowsky, *J. Chem. Phys.* **25**, 1288 (1956).

⁸ S. Alexander, *J. Chem. Phys.* **28**, 358 (1958).

⁹ R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.* **30**, 994 (1959).

TABLE I. Definition of states and matrix elements of H in the m representation for the system ABC . $F_z = \sum m_i$.

n	$\psi_n(ABC)$	M	H_{nn}
1	$\beta\beta\beta$	$-\frac{3}{2}$	$-\nu_0/2(\delta_A + \delta_B + \delta_C) - \frac{1}{4}(A_{AB} + A_{AC} + A_{BC})$
2	$\alpha\beta\beta$	$-\frac{1}{2}$	$-\nu_0/2(-\delta_A + \delta_B + \delta_C) - \frac{1}{4}(-A_{AB} - A_{AC} + A_{BC})$
3	$\beta\alpha\beta$	$-\frac{1}{2}$	$-\nu_0/2(\delta_A - \delta_B + \delta_C) - \frac{1}{4}(-A_{AB} + A_{AC} - A_{BC})$
4	$\beta\beta\alpha$	$-\frac{1}{2}$	$-\nu_0/2(\delta_A + \delta_B - \delta_C) - \frac{1}{4}(A_{AB} - A_{AC} - A_{BC})$
5	$\alpha\alpha\beta$	$\frac{1}{2}$	$\nu_0/2(\delta_A + \delta_B - \delta_C) - \frac{1}{4}(A_{AB} - A_{AC} - A_{BC})$
6	$\alpha\beta\alpha$	$\frac{1}{2}$	$\nu_0/2(\delta_A - \delta_B + \delta_C) - \frac{1}{4}(-A_{AB} + A_{AC} - A_{BC})$
7	$\beta\alpha\alpha$	$\frac{1}{2}$	$\nu_0/2(-\delta_A + \delta_B + \delta_C) - \frac{1}{4}(-A_{AB} - A_{AC} + A_{BC})$
8	$\alpha\alpha\alpha$	$\frac{3}{2}$	$\nu_0/2(\delta_A + \delta_B + \delta_C) - \frac{1}{4}(A_{AB} + A_{AC} + A_{BC})$

$$H_{23} = H_{67} = -\frac{1}{2}A_{AB}$$

$$H_{24} = H_{57} = -\frac{1}{2}A_{AC}$$

$$H_{34} = H_{56} = -\frac{1}{2}A_{BC}$$

frequency and varying magnetic field the smallest transition frequency thus calculated corresponds to the line at *highest* field. In keeping with accepted practice we report experimental line positions in cps increasing *upfield*, although these require a sign inversion in order to be compared with the frequencies calculated directly from (2). The intensities follow from the eigenfunctions ϕ_k in the usual way, being proportional to $(\phi_k | I_{xA} + I_{xB} + I_{xC} | \phi_l)^2$.

Let us now examine some useful properties of (2). It will be helpful if we first investigate the behavior of the spectrum in the "first-order" or high-field limit, where all $\lambda_{ij} = A_{ij}/\nu_0(\delta_i - \delta_j) \rightarrow 0$. We can evidently do so by ignoring all the off-diagonal elements of (2), and the spectrum then consists of twelve lines of unit intensity. These fall into three quartets, each of which is assignable to one of the nuclei, as shown in Fig. 1. Such a spectrum has the well-known property that there are three spacings (equal numerically to the A 's) each of which is repeated four times. For example, from Table I, denoting the first-order transition frequencies at constant field by ν' ,

$$\nu_{78}' - \nu_{46}' \equiv H_{77} - H_{88} - H_{44} + H_{66} \equiv \nu_{68}' - \nu_{47}' = A_{AB}$$

$$= H_{33} - H_{55} - H_{11} + H_{22} \equiv \nu_{35}' - \nu_{12}' \text{ etc.}$$

Now in the strongly coupled case, $\lambda_{ij} \cong 1$, the off-diagonal elements of (2) become important as well. The transition to this case can thus be regarded simply as the performance of the unitary transformation, previously omitted, that diagonalizes (2). But the trace of (2), and thus also the traces of its four blocks of different total magnetic quantum number F_z individually, are unaffected by this transformation

$$H_{11} = E_1 = -(E_5 + E_6 + E_7) = -(H_{55} + H_{66} + H_{77})$$

$$H_{88} = E_8 = -(E_2 + E_3 + E_4) = -(H_{22} + H_{33} + H_{44}). \quad (3)$$

With this fact we now have for the correct transition frequencies ν

$$\nu_{78} - \nu_{46} \equiv E_7 - E_8 - E_4 + E_6 \equiv \nu_{68} - \nu_{47}$$

$$\equiv -E_8 - E_4 + (E_6 + E_7) = (E_2 + E_3 + E_4)$$

$$- E_4 - (E_1 + E_5)$$

$$= (E_3 - E_5) - (E_1 - E_2) \equiv \nu_{35} - \nu_{12}, \text{ etc.}$$

That is, the strongly coupled spectrum has the same properties of repeated spacings as exist in the first-order case. By examining any three-spin spectrum for repeated spacings, therefore, it is in general possible to make a grouping into three quartets. The spacings which appear, it should be noted, are no longer numerically equal to the coupling constants A_{ij} , but provide useful first approximations to them even in rather strongly coupled spectra.

There are altogether fifteen lines in a three-spin spectrum, ν_{27} , ν_{36} , and ν_{45} becoming allowed when the λ_{ij} are different from zero. These "combination transitions" may make the above grouping ambiguous in very strongly coupled cases, but cause no confusion

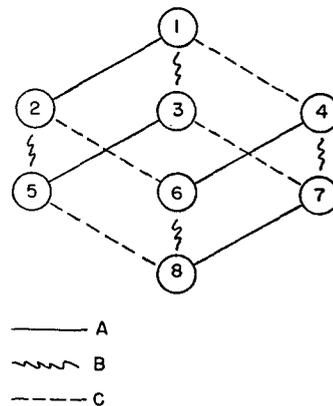


FIG. 1. First-order transitions for the system ABC . The states are numbered to correspond to Table I.

in any of the examples discussed here. This matter will be discussed more fully in a later paper.

The next fact to be noted is that, while the repeated spacings in a three-spin spectrum are not individually equal to the coupling constants, their *sum* is equal to $|A_{AB} + A_{AC} + A_{BC}|$. Since these quantities need not all have the same sign, it is important to take the relevant differences between transition frequencies in the proper order. Consider first the case in which all $A_{ij} > 0$. Then, by Table I, the lines lying at lowest field in each of the three groups are ν_{58} , ν_{68} , and ν_{78} . The sum of the positions of these lines is then

$$S_1 = \nu_{58} + \nu_{68} + \nu_{78} = -3E_8 + (E_5 + E_6 + E_7) = -3H_{88} - H_{11}.$$

Similarly, for the highest-field lines

$$S_2 = \nu_{12} + \nu_{13} + \nu_{14} = 3H_{11} + H_{88}.$$

Their difference, which no longer depends on the choice of origin, is then

$$S_2 - S_1 = (4H_{11} + H_{88}) = -2(A_{AB} + A_{AC} + A_{BC}). \quad (4)$$

Now if the sign of one of the A_{ij} is reversed, all pairs of lines "corresponding" to that coupling constant interchange their assignments. This is evident from Table I in the first-order case, and is also true when one or more $\lambda_{ij} = 1$, in view of the correspondence between the eigenvalues and the diagonal elements of (2). (The eigenvalues for a given F_z cannot cross as the off-diagonal elements of (2) are adiabatically applied.) The sum of the A 's is then obtained as above, after performing the indicated reversals. There are four such sets of assignments possible, corresponding to the four possibilities for the relative signs of three coupling constants. [The absolute signs of the coupling constants cannot be determined from nuclear magnetic resonance experiments and the sign of the second term of (2) is arbitrary.] Thus for a given assumption about the signs of the A 's, one variable can immediately be eliminated from the spin interaction problem.

There is a similar relation for the sum of the chemical shifts,

$$S_2 + S_1 = 2(H_{11} - H_{88}) = -\nu_0(\delta_A + \delta_B + \delta_C), \quad (5)$$

but in practice it does not accomplish any simplification since the sum depends on the origin chosen. Thus of the six δ 's and A 's characterizing the spin problem, we are left with five independent parameters describing the spectrum. The adjustment of two of them (the reference point from which δ 's are measured and a scale factor for the whole spectrum) is trivial.

The ambiguity arising from the existence of four possibilities for the relative signs of the A_{ij} can be resolved in many cases by a useful relation among the intensities. The allowed transitions $\Delta F_z = -1$ (including combination transitions) fall into three groups

$$F_z: \frac{3}{2} \leftrightarrow \frac{1}{2}, \quad \frac{1}{2} \leftrightarrow -\frac{1}{2}, \quad \text{and} \quad -\frac{1}{2} \leftrightarrow -\frac{3}{2}.$$

Taking as an example the last of these, which involves the lines ν_{12} , ν_{13} , and ν_{14} , and denoting the correct eigenfunctions by ϕ_m we have for the sum of the intensities in this group

$$g(1/2, 3, 4) = \sum_{m=2}^4 (\phi_m | I_x | \phi_1)^2 = \sum_{n=2}^4 \left\{ \sum_{m=2}^4 u_{mn} (\psi_n | I_x | \psi_1) \right\}^2$$

where u_{mn} is the transformation that diagonalizes \mathcal{H} . Thus

$$\begin{aligned} g(1/2, 3, 4) &= \sum_{n,p} (\psi_n | I_x | \psi_1) (\psi_p | I_x | \psi_1) \sum_m u_{mn} u_{mp} \\ &= \sum_{n,p} (\psi_n | I_x | \psi_1) (\psi_p | I_x | \psi_1) \delta_{np}, \end{aligned}$$

making use of the unitary property of u_{mn} . If we then normalize the intensities of lines in the first-order case so that

$$(\psi(F_z) | I_x | \psi(F_z')) = \delta_{F_z, F_z' \pm 1}$$

for single spin flips, we have

$$g(1/2, 3, 4) = \sum_{n=2}^4 (\psi_n | I_x | \psi_1)^2 = 3. \quad (6a)$$

That is, the total intensity of this group is unaffected by the introduction of strong spin coupling. Similarly we have

$$g(8/5, 6, 7) = 3; \quad g(2, 3, 4/5, 6, 7) = 6. \quad (6b)$$

If all the coupling constants have the same sign, the preceding sums are over (a) the lowest field lines of the three groups; (b) the highest field lines; and (c) all the rest, including combination transitions. Reversal of sign of one of the A 's however reverses the assignment of inner and outer lines in two of the quartets, as we have seen. Thus the lines of the experimental spectrum over which the above sums are to be made are different, and this fact often makes it possible to select the proper assignment in advance.

EXPERIMENTAL DETAILS

Styrene (Eastman Kodak White Label) was vacuum-distilled to remove the polymerization inhibitor and atmospheric oxygen and investigated as a pure liquid. 2,5-Dichloroaniline was studied as a saturated solution (about 3M) in CCl_4 and 2,4-dichloroaniline was dissolved in a mixture of 80% CCl_4 and 20% acetone by volume. No reference standards, either internal or external, were employed since no "absolute" chemical shifts were measured in this work. It was noted that the 2,4-dichloroaniline spectrum grew by about 3 cps in total length when the sample was dissolved in pure CCl_4 instead of the above mixture. Because of the possibility of effects of this sort, care should be used in interpreting the chemical shift differences reported below.

The apparatus and the methods of recording and calibrating spectra were the same as those described

in I.⁹ Because of field instabilities caused by a sick stabilizer, intensities of lines were taken as proportional to the heights and not the areas of lines. This procedure is valid when all line widths are determined by field inhomogeneity. Where two or more lines of differing intensities fall close together the height of each one is affected by the tail of its neighbors. Accordingly, an arbitrary curved base line was drawn in some cases before the intensities were measured. In view of the difficulty of making accurate intensity measurements no attempt was made to find a more objective procedure.

STYRENE

The 40-Mc spectrum shown at the top of Fig. 2 provides a case that is strongly coupled enough so that

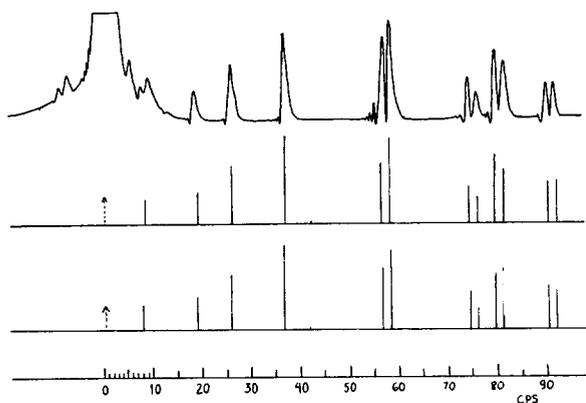


FIG. 2. Proton spectrum of the vinyl group of styrene at 40 Mc. The two calculated spectra correspond to different choices of relative signs of the coupling constants (see text). The line at about 37 cps is visible at higher gain settings.

the above rules are helpful in assigning parameters and determining signs of coupling constants, but which still resembles a first order case closely enough that the correspondence is visible even. We shall ignore the

TABLE II. Experimental and calculated spectrum of styrene at 40 Mc. Line positions are in cps measured from the center of the aromatic proton absorption. Intensities are normalized to a total of 12.00. Lines are listed in order of increasing applied field, and those of intensity less than 0.01 are omitted. Assignment of transitions corresponds to the choice of all $A > 0$.

Transition	Origin	Position		Intensity	
		Obs	Calc	Obs	Calc
78	A	2.60	3.00	0.28*	0.51
35	A	13.50	13.74	0.53	0.64
46	A	20.78	20.74	0.94	1.12
12	A	31.78	31.47	1.60	1.70
36	comb.	36.87	36.67	0.02	0.02
68	B	51.23	51.07	1.51	1.19
25	B	53.05	52.87	1.86	1.65
47	B	68.68	68.81	0.75	0.70
13	B	70.60	70.60	0.48	0.48
58	C	74.15	74.00	1.28	1.30
26	C	75.96	75.80	1.10	1.05
37	C	84.41	84.74	0.78	0.81
14	C	86.05	86.52	0.86	0.82
Standard deviations:		0.06 cps		0.03	

* Overlapping the tail of the aromatic absorption.

$A > 0$, and involves through (4) and (6) only the lowest-field and highest-field lines of the three multiplets. Assignment II refers to the spectrum obtained by interchanging all pairs of lines separated by the smallest of the reported spacings and then proceeding as in I. Assignments III and IV refer to the situations where, instead, the intermediate-sized or the largest repeated spacings are used as points of interchange. It is evident from Table III that the most satisfactory agreement is obtained for Assignment I, but that IV is also worthy of consideration.

By successive adjustment of the parameters that are still free, we have determined the best sets of parameters which correspond to assignments I and IV, the consequences being shown in Fig. 2. Although I appears to be the most satisfactory, IV is probably also

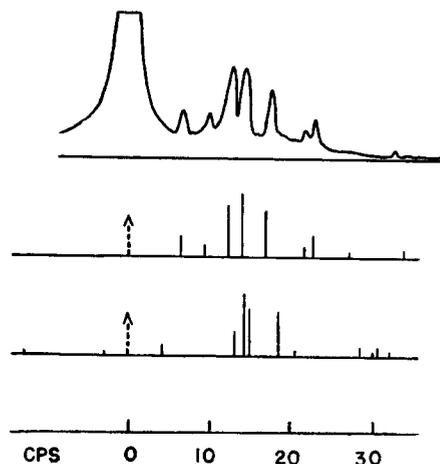


FIG. 3. Proton spectrum of the vinyl group of styrene at 10 Mc. The calculated spectra correspond to the two assignments of Fig. 2.

The final set of parameters is found to be

$$\delta_B - \delta_A = 0.98 \pm 0.01 \text{ ppm,}$$

$$\delta_C - \delta_A = 1.50 \pm 0.01 \text{ ppm,}$$

$$A_{AB} = 17.8 \pm 0.5 \text{ cps,}$$

$$A_{AC} = 11.3 \pm 0.5 \text{ cps,}$$

$$A_{BC} = 1.2 \pm 0.5 \text{ cps.}$$

In order to determine the positions of *A*, *B*, and *C* in the vinyl group we have examined the spectra of α -methylstyrene and *trans*- β -methylstyrene,⁹ on the assumption that the chemical shifts and coupling constants for the remaining vinyl protons would resemble those in styrene closely enough to permit a decision. The shifts in the former compound at 40 Mc, relative to the ring protons, are 72 and 86 cps, suggesting that the lowest-field proton in styrene is to be assigned to the α position. The coupling between the olefinic protons in the second model compound is 15.6 cps,⁹ suggesting that proton *B* in styrene is the one *trans* to *A*. These conclusions are also consistent with other workers' studies of the vinyl group.¹⁰

For the sake of completeness we have calculated the best sets of parameters corresponding to assignments II and III in the foregoing, and find that the calculated line intensities are in wild disagreement with experiment. Calculated spectra, using the correct *A*'s and δ 's, are shown over the whole range of λ in Fig. 4, from which one can easily see the manner in which the spectrum at very high fields is correlated with the actual experimental situations and the limiting case of very small field ($\delta \rightarrow 0$). We have made other measurements in various parts of this range [at 30 Mc (using a spectrum kindly provided by Dr. W. D. Phillips), at

22.55 Mc, and at 6.6 Mc]. We do not reproduce the spectra here since they add nothing essential to the argument.

2,4-DICHLOROANILINE

The division of the spectrum at the top of Fig. 5 into three quartets is not immediately obvious, but can easily be made once one is aware of the possibility. The first four lines from the left belong to multiplet *A*, the next four to *B*, and the last four to *C*. The best set of parameters is found to be

$$\delta_B - \delta_A = 0.230 \pm 0.007 \text{ ppm,}$$

$$\delta_C - \delta_A = 0.570 \pm 0.007 \text{ ppm,}$$

$$A_{AB} = 2.4 \pm 0.4 \text{ cps,}$$

$$A_{AC} = 0.4 \pm 0.3 \text{ cps,}$$

$$A_{BC} = 8.8 \pm 0.4 \text{ cps.}$$

The spectrum expected at 22.55 Mc for the same set of parameters has been calculated, and is compared with experiment at the bottom of Fig. 4.

Choice of $A_{AC} = 0$, which would make the small splittings in groups *A* and *C* go to zero in the first-order case, does not do so in the presence of strong spin coupling but leaves a residual splitting of about 0.4 cps. A series of trial calculations lead to the value and error quoted above.

The three aromatic protons can be tentatively identified with the various positions on the ring by making use of the tabulations of aromatic proton-proton coupl-

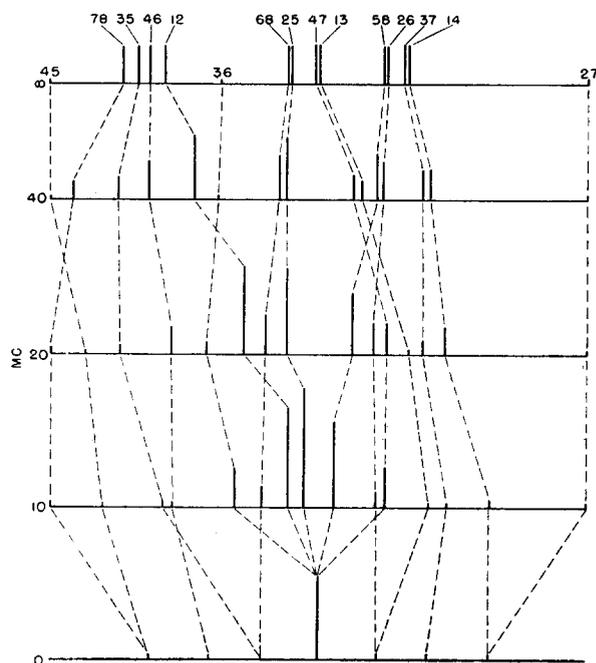


FIG. 4. Field-variation of the styrene spectrum. The topmost spectrum, for extremely high fields, is drawn schematically. The numbering of the transitions corresponds with Tables I and II.

¹⁰ W. A. Anderson and H. S. Gutowsky (private communications).

ing constants given by Gutowsky *et al.*³ One concludes that *A*, *B*, and *C* correspond to the 3, 5, and 6 positions, respectively. The relatively large positive shift of *C* is doubtless connected with the location of this proton *ortho* to the strongly electron-donating amino group. A corresponding shift of the center of gravity of the aniline spectrum has been observed,¹¹ although it is not possible in that case to estimate the individual chemical shifts of the *o*, *m*, and *p* protons.

2,5-DICHLOROANILINE

The spectrum shown in Fig. 6 is somewhat more difficult to attack than the previous two, since not all of the lines theoretically present in first order are resolved. By analogy with 2,4-dichloroaniline and other aromatic compounds, however, we are led to expect a situation with all coupling constants positive and having a sum in the neighborhood of 11–12 cps. Thus with a little experimentation we are led to the grouping indicated in the figure. Adjustment of the parameters then leads to the final values

$$\delta_B - \delta_A = 0.478 \pm 0.007 \text{ ppm,}$$

$$\delta_C - \delta_A = 0.490 \pm 0.007 \text{ ppm,}$$

$$A_{AB} = 8.6 \pm 0.4 \text{ cps,}$$

$$A_{AC} = 0.6 \pm 0.5 \text{ cps,}$$

$$A_{BC} = 2.6 \pm 0.4 \text{ cps.}$$

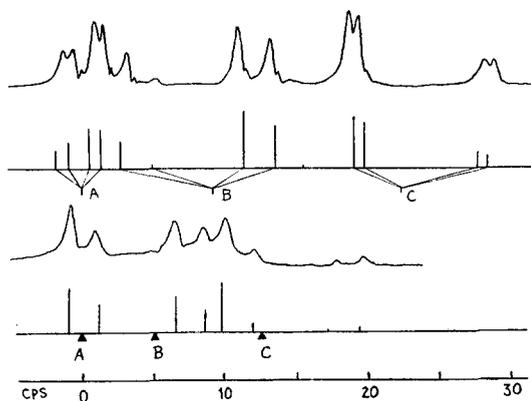


FIG. 5. Proton spectra of 2,4-dichloroaniline at 40.00 and 22.55 Mc.

¹¹ P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.* **78**, 3043 (1956).

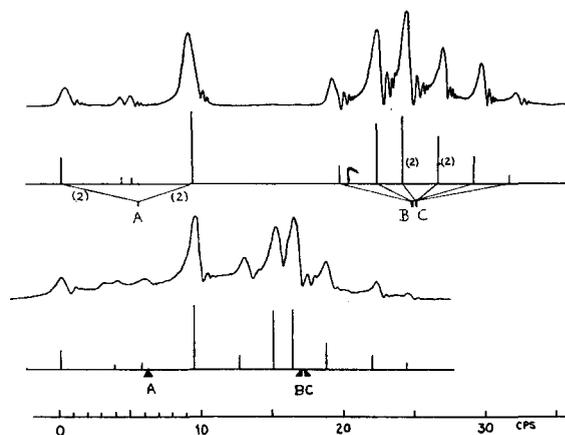


FIG. 6. Proton spectra of 2,5-dichloroaniline at 40.00 and 22.55 Mc.

The same parameters successfully reproduce the observed spectrum at 22.55 Mc. By the same arguments used above we conclude tentatively that *A*, *B*, and *C* correspond to the 3, 4, and 6 positions, respectively, on the aromatic ring.

Taking $A_{AC}=0$ results in a residual splitting "corresponding" to this coupling to about 0.4 cps, much as in the case of the 2,4-isomer. The value of 0.6 cps in the foregoing is that necessary to make this splitting vanish, as observed.

This spectrum provides a clear illustration of the fact that two nuclei may be magnetically nonequivalent even though they have the same chemical shift. Were *B* and *C* equivalent, they would in first order be split into a simple doublet by *A* and into a pattern still strongly resembling that even when the off-diagonal elements of coupling are taken into account. The right-hand portion of the spectrum is actually very much different, the nonequivalence of *B* and *C* arising from their greatly different couplings to *A* (and not from their very small difference in chemical shift). *A* uncouples *B* and *C* from the singlet and triplet states which would describe them if they were indeed equivalent.

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