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# Electron Coupling of Nuclear Spins. I. Proton and Fluorine Magnetic Resonance Spectra of Some Substituted Benzenes<sup>1,2</sup>

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High resolution magnetic resonance spectra of the ring hydrogen and fluorine nuclei have been observed for a large number of substituted benzenes. These spectra have been analyzed in detail for the simpler cases and values have been obtained for the indirect coupling of the hydrogen and fluorine nuclei by the electrons. The coupling constants depend somewhat upon the substituents but the values are determined mainly by the atomic species themselves and by their relative positions in the benzene ring. The average numerical results for the H-H, H-F and F-F coupling constants for *ortho*, *meta* and *para* orientations, respectively, and the number of determinations are:  $A^{HH}$ , 7.9 (1), 2.1 (3) and 0.5 (3) c.p.s.;  $A^{HF}$ , 8.6 (12), 7.0 (8) and 2.2 (5) c.p.s.;  $A^{FF}$ , 20.5 (2), 3.1 (3) and 13.2 (2) c.p.s. A method is described for determining the relative signs of the coupling constants, which proves to be possible in certain cases. It is found that  $A_o^{HF}$  and  $A_m^{HF}$  are of like sign while  $A_o^{HF}$  and  $A_p^{HF}$  are of unlike sign.

## I. Introduction

Nuclear magnetic resonance multiplets<sup>3</sup> originate in the indirect coupling of nuclear spins<sup>4</sup> by their mutual interactions with the electrons in a molecule.<sup>5,6</sup> There are in general two main features to the study of the multiplets. The first is primarily phenomenological; it includes the assignment of the details of the absorption spectra to particular aspects of the molecular structure and geometry, and the determination of numerical values for the coupling constants. The second feature is the relation of the experimental coupling constants to the molecular electronic structures. A more complete understanding of both features is desirable for the effective use of high resolution n.m.r. spectra in structural determinations.

This article deals with the analysis of the simple to moderately complex proton and fluorine multiplets observed in a variety of substituted benzenes. The more complex spectra exhibited by several similar compounds will be discussed elsewhere<sup>7</sup> as will be the significance of the experimental values found for the F-F, H-F and H-H coupling constants and their dependence upon the relative positions of the atoms on the benzene ring.

The high resolution n.m.r. spectrum of a liquid is determined usually by the chemical shifts and the indirect spin-spin coupling, with due allowance for the effects of any dynamic processes.<sup>8</sup> The appropriate Hamiltonian for the nuclear spin system<sup>3-5,9</sup> may be written as

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} \\ = -\hbar \sum_i \gamma_i H_i I_{zi} + \hbar \sum_{i < j} A_{ij} I_i \cdot I_j \quad (1)$$

where  $\gamma_i$  is the nuclear magnetogyric ratio,  $H_i$  is the static magnetic field at nucleus  $i$  including any chemical shift and  $I_i$  is the nuclear spin opera-

tor. The coupling constant  $A_{ij}$  is in c.p.s. and the sign convention is chosen such that for a positive constant the more stable state is the state of anti-parallel magnetic moments.

The simplest type of spectrum is found when the nuclei occur in sets, a, b, . . . , which would have, in the absence of any coupling, resonance frequencies,  $\nu_a, \nu_b, \dots$ , satisfying the condition

$$\Delta = |\nu_a - \nu_b| \gg A_{ab} \quad (2)$$

Also, it is assumed that the coupling constant  $A_{ab}$  is identical for all pairs,  $a_i b_j$ , of unlike nuclei.<sup>10</sup> If equation 2 is satisfied, either by a large chemical shift or because the nuclei are of different species,  $\mathcal{H}^{(1)}$  may be treated as a first-order perturbation<sup>3</sup>

$$\mathcal{H}^{(1)} = \hbar A_{ab} F_{ra} F_{rb} + \\ \sum_{i < k} A^{aa} I_{ik} \cdot I_{ik} + \sum_{j < k} A^{bb} I_{jk} \cdot I_{jk} \quad (3)$$

The summations in equation 3 describe the coupling of the nuclear spins within each set of equivalent nuclei to form total spin states; these interactions do not give observable effects because transitions are forbidden between states of different total spin.

Thus, the multiplets are described by the first term in equation 3, where  $F_z$  is the operator for the total z-component of the angular momentum for a given set of nuclei. The perturbation of the energies, produced by the coupling, is

$$E^{(1)} = \hbar A_{ab} M_a M_b \quad (4)$$

$M$  is the total nuclear magnetic quantum number for each set of nuclei. The net result is that the resonance of each set of nuclei is split into a symmetrical multiplet, with a splitting of  $A_{ab}$  c.p.s.,

(10) Internal molecular motions are often very important in establishing this condition. For example, in  $\text{CH}_2\text{CX}_2\text{F}$  the H-F coupling constant depends upon whether the particular hydrogen is *trans* or *gauche* to the fluorine atom. However, reorientations about the C-C bond are ordinarily fast enough to make the three protons exhibit the same coupling with the fluorine, an average of the different values which would have been found if the reorientations didn't occur. Molecules of low symmetry must be treated carefully because in some, various nuclei will remain non-equivalent in spite of fast internal rotations. This is the case in molecules of the type  $\text{CH}_2\text{X}-\text{CFYZ}$ . The chemical shifts of the two protons as well as their  $A_{HF}$  coupling constants are different functions of the internal rotation angle because of the asymmetry of the CFYZ group and its interaction with X. Such rotational non-equivalence was overlooked by J. J. Drysdale and W. D. Phillips in their interpretation of the proton and fluorine spectra of  $\text{CF}_2\text{X}-\text{CHXY}$  and  $\text{CF}_2\text{X}-\text{CFXY}$ ; see THIS JOURNAL, **79**, 319 (1957).

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(2) Taken in large part from the Ph.D. theses of C. H. Holm, September, 1955, and of G. A. Williams, September, 1956.

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and with a number of components and relative intensities given by the number and statistical weights of the  $M$ -values for the other set of nuclei.<sup>3</sup> If there are more than two sets of nuclei coupled together the effects are additive and the same arguments leading to equation 4 apply. A third set,  $c$ , of nuclei coupled with set  $a$  would add to equation 4 the term  $hA_{ac}M_aM_c$  as well as a similar term for any  $b$ - $c$  coupling. The net result on the resonance spectrum of set  $a$  is that each component produced by the  $a$ - $b$  coupling is split into a multiplet characteristic of the  $a$ - $c$  coupling.

If the two assumptions made in deriving equation 4 are not valid, the spectra and their analysis become more complex. One type of complexity<sup>4</sup> occurs when  $\Delta$ , the difference between the resonance frequencies of the sets of nuclei, becomes comparable to the coupling constant  $A_{ab}$ . The coupling then mixes the spin states of the two separate sets and the simple rules implicit in equation 4 break down. For example,<sup>4</sup> if a nucleus of spin  $1/2$  is in each set, there are still four lines in the spectrum as  $\Delta \rightarrow A_{ab}$ , but the outer two lines are weaker than the center two. The outer splitting (1-2 and 3-4) always equals  $A_{ab}$  but the separation between the two center lines (2-3) depends on the ratio  $\Delta/A_{ab}$ . As the ratio approaches zero, the center pair coalesces while the outer pair goes to zero intensity. General calculations of intensities and splittings have been made for several such systems with various numbers of nuclei in each set.<sup>11</sup> The proton spectra of ethanol and a few other molecules with similarly complex spectra have been studied in great detail, experimentally<sup>12</sup> as well as theoretically.<sup>13</sup>

If the coupling constant  $A_{ij}^{ab}$  is not identical for all pairs  $a_i b_j$  of unlike nuclei, the other type of complexity occurs.<sup>14</sup> In  $\text{CF}_2\text{F}=\text{CH}_2$  it was found<sup>9</sup> that although the two protons are structurally equivalent, as are the two fluorines, they are not equivalent in terms of their couplings, that is  $A_{11}^{\text{HF}} \neq A_{12}^{\text{HF}}$ . In consequence, the fluorine and proton resonances are not simple triplets as predicted by equation 4; instead, each resonance has at least eight components. The unequal coupling serves to mix the total spin states of each set of nuclei, and transitions are allowed which otherwise are forbidden. Cases of this sort, as well as the still more complex ones in which one also finds  $\Delta \cong A_{ab}$ , can be handled by standard group theoretical methods first applied to the problem by McConnell, *et al.*<sup>9</sup> Zero-order wave functions having the symmetry of the molecule are constructed from the spin functions ( $\alpha, \beta$  for  $I = 1/2$ ) of the individual nuclei. This factors the secular equation and usually simplifies the problem very greatly. The remaining, lower order, secular equations can then either be solved exactly or approximated by perturbation theory.

Preliminary observations of the proton and fluorine spectra were reported earlier<sup>14</sup> for the

mono-,  $p$ -di-, 1,3,5-tri-, and 1,2,4,5-tetrafluorobenzenes. The results suggested that the indirect spin-spin coupling constants might be obtained for proton and fluorine nuclei on different relative positions in the benzene ring. Also, observations of proton and fluorine spectra in substituted benzenes have been reported by Baker.<sup>15</sup> Since then, the spectra of the fluorobenzenes have been re-examined under higher resolution and considerable additional fine structure obtained. Also, the spectra of a number of substituted fluorobenzenes have been observed. Some of the spectra, particularly those of 1,3,5-trifluorobenzene, proved to be very complex and the methods mentioned above were essential in order to obtain numerical values for the coupling constants. In the course of the work it became apparent that in certain cases the relative signs could be obtained<sup>16</sup> for different coupling constants within the same molecule. Inasmuch as the signs can be useful in the theoretical interpretation<sup>17</sup> of the observed constants a special effort was made to obtain spectra suitable for sign determinations.

## II. Experimental Details

Unless otherwise specified the spectra were observed with an improved version<sup>8</sup> of a high resolution spectrometer<sup>18</sup> using a permanent magnet with a field of 4165 gauss. In a few instances, usually only when the spectra at the lower field suggested the desirability, observations were made at 6300 gauss with another permanent magnet. The spectra were recorded, with a Sanborn Model 127 Recorder, at a fixed radiofrequency (17.735 and 16.685 Mc. for  $\text{H}^1$  and  $\text{F}^{19}$ ) by sweeping the magnetic field. However, the abscissa in the figures has been converted to c.p.s. by the Larmor equation,  $\nu = \gamma H/2\pi$ . The magnetic field decreases from left to right.

The spectra were obtained under a variety of experimental conditions. Those in a given figure have been reduced to a common frequency scale to facilitate comparison. The origin of the frequency scale is taken as the center of the symmetrical multiplets and is located arbitrarily for the others unless a particular choice is suggested by the equations used in analyzing the spectrum. Fluorine chemical shifts with respect to fluorobenzene have been reported<sup>19</sup> for many of the compounds; the shifts in the others are not given inasmuch as they usually do not deviate significantly from values estimated from those for the monosubstituted fluorobenzenes, assuming additivity<sup>19</sup> of the substituent effects. Chemical shifts of the non-equivalent protons in the substituted benzenes have not been reported previously; some values are included here insofar as they arise in analysis of the spectra.

The numerical values obtained for the coupling constants fall between 0.4 and 20 c.p.s. Some of these are known more accurately than others, mainly because of differences in apparent line widths. The values given are the averages, usually from about five recordings. Effects of systematic errors are not included explicitly in the probable errors because random effects are by far the most important. The recordings of the spectra were usually calibrated by running 1,2,4,5-tetrafluorobenzene as a reference. This compound has sharp and intense components with a splitting of  $8.65 \pm 0.15$  c.p.s., a convenient value for calibrating the spectra of other fluorobenzenes; this splitting was measured using the sideband resonances produced by audiomodulation of the magnetic field.<sup>20</sup> The audiofrequency was checked with a frequency counter.

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TABLE I: SPIN-SPIN INDIRECT COUPLING CONSTANTS, IN C.P.S., FROM ANALYSES OF PROTON AND FLUORINE HIGH RESOLUTION N.M.R. SPECTRA OF SUBSTITUTED BENZENES<sup>a</sup>

Compound	$A_{oHF}$	$A_{mHF}$	$A_{pHF}$	$A_{oHF}$	$A_{mHF}$	$A_{pHF}$	$A_{oHF}$	$A_{mHF}$	$A_{pHF}$
I. 2,3,5,6-Tetrachlorofluorobenzene				8.4 ± 0.3			2.1 ± 0.1		
II. 2-Nitro-3-fluoro-5,6-dichloro-benzotrifluoride									
III. 2,6-Dinitro-3,5-dichlorobenzene									
IV. 2,4-Dimethyl-6-nitroaniline	1.2 ± 0.3								
V. 2,4-Difluoromesitylene									
VI. 2-Fluoromesitylene									
VII. 2,6-Dichloro-3,5-difluorobenzotrifluoride				7.8 ± .3					
VIII. 1,3,5-Trifluoro-2,6-dichlorobenzene				8.6 ± .2			2.2 ± .2		1.9 ± 0.2
IX. 2,4-Dinitro-6-chlorophenol									
X. 2,6-Dibromophenol	7.9 ± 0.2								
XI. 1,4-Difluoro-2,3,5-trichlorobenzene				+8.4 ± .2			+6.3 ± .2		12.0 ± 0.2
XII. 2-Fluoro-4,6-dichlorophenol				+9.6 ± .3 <sup>b</sup>			-2.1 ± .2 <sup>b</sup>		
XIII. 2-Amino-3,5-difluoro-4-chloro-nitrobenzene				+9.4 ± .3 <sup>b</sup>			-2.2 ± .3 <sup>b</sup>		3.1 ± .1
XIV. 2-Fluoro-4,5-dichlorophenol			0.4 ± 0.2	+10.1 ± .2 <sup>b</sup>			+8.3 ± .2 <sup>b</sup>		
XV. 2,6-Dichloro-3-fluorobenzotrifluoride				≥ +6.2 ± .2 <sup>b</sup>			≤ +6.2 ± .2 <sup>b</sup>		
XVI. 2,3-Difluoro-5,6-dibromonitrobenzene				8.7 ± .3			6.8 ± .3		20.2 ± 0.3
XVII. 2,4-Dichloro-3,5-difluoronitrobenzene				8.0 ± .1 <sup>b</sup>			2.3 ± .1 <sup>b</sup>		4.2 ± .2
XVIII. 2,4-Dichloro-3,6-difluoronitrobenzene				8.2 ± .4 <sup>b</sup>			6.3 ± .4 <sup>b</sup>		14.4 ± .4
XIX. 2-Chloro-4,5-difluoronitrobenzene			<1.0	9.5 ± .2			7.1 ± .2		20.8 ± .3

<sup>a</sup> The signs given for some of the constants indicate relative signs only; absolute signs were not determined for any of the constants. <sup>b</sup> The assignment of the numerical values to particular coupling constants is based on relative magnitudes found unambiguously in other compounds.

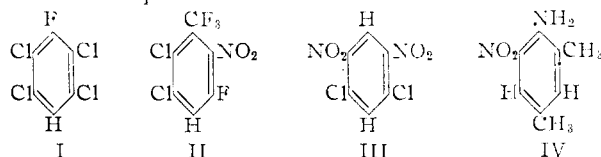
The spectra were observed with the sample in the pure liquid state; samples which are solid at room temperature were heated above their melting points. The sample tubes were usually 2.5 mm. i.d., with an effective sample height of about 5 mm. Sample spinning was ordinarily used to improve resolution. The various fluorobenzene samples were supplied by Dr. G. C. Finger and R. E. Oesterling of the Fluorine Chemistry Division of the Illinois State Geological Survey. We are greatly indebted to them for their interest and very generous assistance which made this study possible. The other samples were in main the white label grade supplied by Eastman Kodak Co.

### III. Results and Discussion

The values for the various coupling constants and the relative signs determined in this study are compiled in Table I. The nuclear species are designated by the superscripts of the coupling constant while the orientation of the atoms with respect to one another on the benzene ring is given by the subscripts *o*, *m* and *p*, for *ortho*, *meta* and *para*. The simpler cases are analyzed first because a knowledge of the approximate range for a particular type of coupling can help in the more complex spectra. Practically all of the compounds investigated are substituted fluorobenzenes. However, the spectra of a few non-fluorine containing substituted benzenes were observed to obtain values for the H-H coupling constants. In all cases considered below only fluorine nuclei and/or protons are involved. Therefore, the analyses and discussion assume nuclear spins of  $1/2$ ; extensions can, of course, be made to nuclei with  $I > 1/2$ .

#### Simple Cases Obeying Equation 4

**Only Two Interacting Nuclei.**—2,3,5,6-Tetrachlorofluorobenzene (I) and 2-nitro-3-fluoro-5,6-dichlorobenzotrifluoride (II) have only one F and one H atom attached directly to the benzene ring. The spectra of these nuclei are simple doublets and the splitting is the coupling constant. In I, the splitting of the proton resonance is  $2.0 \pm 0.3$  c.p.s. and of the fluorine,  $2.1 \pm 0.3$  c.p.s.; this gives  $A_{pHF} = 2.1 \pm 0.1$  c.p.s. In II, the splittings are  $8.6 \pm 0.8$  and  $8.0 \pm 1.7$  c.p.s.; this gives  $A_{oHF} = 8.4 \pm 0.3$  c.p.s.

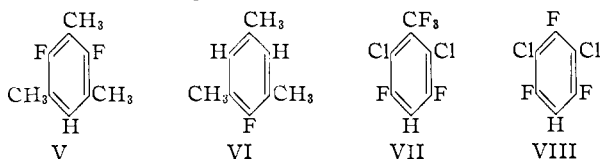


In 2,6-dinitro-3,5-dichlorobenzene (III) and 2,4-dimethyl-6-nitroaniline (IV) the magnetic nuclei in question are two structurally non-equivalent ring protons. In III the protons are *para* while in IV they are *meta*. The proton spectrum of III consists of two components of equal intensity, separated by  $14.8$  c.p.s. This is a chemical shift because if it were a multiplet there would have to be two doublets.<sup>21</sup> The multiplet splitting must, therefore, be less than the widths of the two lines observed. The resolution was better than 1 c.p.s. so we conclude that  $A_{pHH} < 1$  c.p.s. The spectrum of IV is very much like that of III, a pair of lines separated by  $12.2$  c.p.s. However, each line is a partially resolved doublet with a splitting of  $1.2 \pm 0.3$  c.p.s., which is the value of  $A_{mHH}$ .

(21) If  $A_{pHH} \gg \Delta$ , the spectrum of the two protons would consist of a single line; see reference 1.

**Three-spin Systems with Two Planes of Symmetry.**—Unless the number of nuclei coupled together is small, structural equivalence is no guarantee that the nuclei have equivalent indirect spin-spin coupling. A three-spin system is the largest for which structural equivalence always implies equivalent coupling. If a magnetic nucleus of species a lies on one plane of symmetry and two nuclei of species b on a perpendicular plane of symmetry, the spectra follow equation 4; the a-b coupling does not mix the total spin states of the b nuclei and the splitting is  $A_{ab}$ .

Compounds of this type are 2,4-difluoromesitylene (V), 2-fluoromesitylene (VI) and 2,6-dichloro-3,5-difluorobenzotrifluoride (VII). The proton spectra of V and VII are triplets and of VI, a doublet, with fluorine spectra the reverse. The spectra of V and VII were observed at 6300 gauss. The resonance components for all three compounds were broader than field inhomogeneities, probably because of unresolved structure from coupling with the  $\text{CH}_3$  and  $\text{CF}_3$  groups. The proton and fluorine splittings are, respectively, V  $7.6 \pm 0.5$  and  $7.8 \pm 0.5$  c.p.s.; VI  $7.0 \pm 0.4$  c.p.s., protons only; and VII  $8.2 \pm 0.3$  and  $7.4 \pm 0.3$  c.p.s. The final values are  $7.7 \pm 0.3$  and  $7.0 \pm 0.4$  c.p.s. for  $A_m^{\text{HF}}$  and  $7.8 \pm 0.3$  c.p.s. for  $A_o^{\text{HF}}$ .



**Three Sets of Non-equivalent Nuclei.**—1,3,5-Trifluoro-2,6-dichlorobenzene (VIII) has a fluorine nucleus and a proton (sets a and b) which lie on one plane of symmetry while two fluorine nuclei (set c) lie on a plane of symmetry perpendicular to the first. Because of the symmetry, the two fluorine nuclei in set c are not only equivalent structurally but also equivalent magnetically, *i.e.*, they have the same coupling constants  $A_{ac}$  and  $A_{bc}$ . Moreover, the chemical shift between the two sets of fluorine nuclei (a and c) is large enough that the general form of equation 4 applies. This is a particularly striking example of three sets of nuclei coupled together, so the spectra are reproduced in Fig. 1.

The proton spectrum is a triplet with a splitting of  $8.6 \pm 0.2$  c.p.s., as a result of coupling with the set of two fluorines ( $A_o^{\text{HF}}$ ), while each component of the triplet is a doublet with a splitting of  $2.2 \pm 0.2$  c.p.s. because of coupling with the third fluorine ( $A_b^{\text{HF}}$ ). The spectrum of the two equivalent fluorines is a doublet with a splitting of  $8.6 \pm 0.2$  c.p.s. from coupling with the hydrogen ( $A_o^{\text{HF}}$ ), while each component is split further into a  $1.9 \pm 0.2$  c.p.s. doublet by the coupling with the third fluorine ( $A_m^{\text{FF}}$ ). The spectrum of the third fluorine appears to be a quartet with a splitting of  $2.0 \pm 0.2$  c.p.s. This is because the coupling of this fluorine with the other two ( $A_m^{\text{FF}} = 1.9$  c.p.s.) is very close to its coupling with the proton ( $A_b^{\text{HF}} = 2.2$  c.p.s.); the two fluorines and the proton are thus effectively an equivalent three-spin system insofar as the third fluorine is concerned.

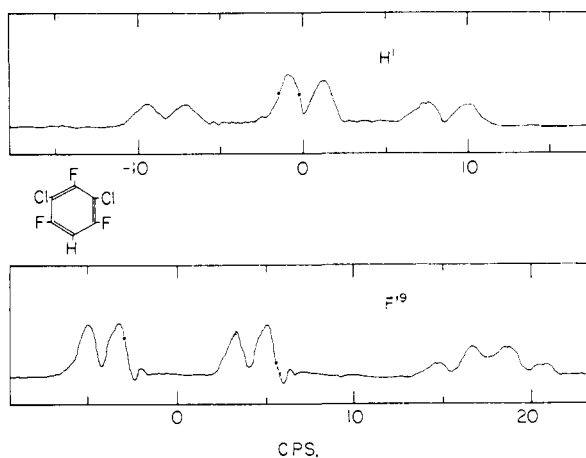
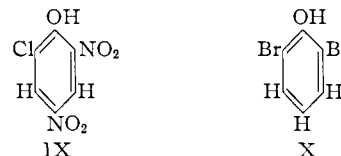


Fig. 1.—The proton and fluorine nuclear magnetic resonance spectra of a system containing three non-equivalent sets of nuclei, observed at a magnetic field of 4165 gauss.

#### Simple Cases in which $\Delta \cong A_{ab}$

In 2,4-dinitro-6-chlorophenol (IX) and 2,6-dibromophenol (X) the spectra of the ring protons do not follow the simple intensity and spacing rules embodied in equation 4. When the chemical shift, in c.p.s., is small, the two sets of nuclei are not very non-equivalent and any coupling between the sets tends further to make them respond as if they were equivalent.



**A Two-spin System.**—In IX there are two ring protons; their spectrum still has four components, but as may be seen in Fig. 2 the center two lines are more intense than the outer two, as described

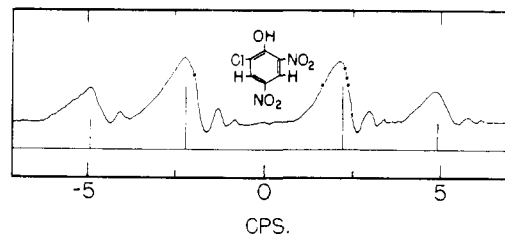


Fig. 2.—The magnetic resonance absorption of the ring protons, a two-spin system with chemical shift and coupling constant of comparable magnitude; observed at 4165 gauss.

in the Introduction. The splitting between both pairs of outer lines is  $2.7 \pm 0.1$  c.p.s. and it is the coupling constant  $A_m^{\text{HH}}$ . The chemical shift between the two protons may be obtained from the spectrum using the theoretical result<sup>4</sup> that the separation between the two center lines is  $(A^2 + \Delta^2)^{1/2} - A$ ; it is found to be 6.6 c.p.s. The relative intensities of the lines were computed<sup>4</sup> using these values for  $A$  and  $\Delta$  and agree well with experiment as shown in Fig. 2.

**A Three-spin System with Two Sets of Nuclei.**—

The three protons in X form two sets of magnetically equivalent nuclei, the two protons *meta* to the hydroxyl in one set and the *para* proton, the other set. According to equation 4, the resonances of these two sets should be, respectively, a doublet, with relative intensities of 4-4 and 1-2-1. However, the chemical shift between the sets is small and, as may be seen in Fig. 3, the doublet and triplet are mixed together to form a group of at least six lines. The most intense components are near the center and the intensities decrease monotonically on both sides. The strong line at the far left is from the OH group.

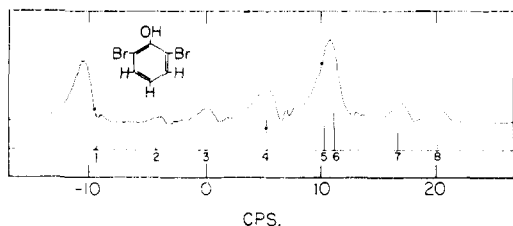


Fig. 3.—The proton magnetic resonance absorption of a two-spin system which is coupled to a one-spin system, with the chemical shift between the two sets of nuclei comparable to the coupling between the sets; at 4165 gauss. The spectrum calculated is shown by the lines below the observed spectrum. The strong line at the far left is from the proton in the OH group.

Several authors<sup>4,11,13</sup> have discussed this type of system for  $\Delta \cong A_{ab}$ . The analysis is straightforward. There are nine transitions possible; they are listed in Table II of reference 13 with explicit

similar in general appearance to that observed. In addition, the calculated spectrum suggested the following. The strongest observed line was probably an overlap of transitions 5 and 6; transitions 1 and 9 were very likely too weak to be observed; the intensity distribution of the observed spectrum places the resonance of the two-spin set at the right, *i.e.*, on the low magnetic field side.

The components in the spectrum were thus numbered to correspond with the transitions producing them, as given in Fig. 3. Various of the observed spacings could then be related to differences in the transition frequencies and the resulting equations solved algebraically for  $A_{ab}$  and  $\Delta$ . The best fit of the observed spacings was obtained with  $A_{ab} = 7.9$  c.p.s. and  $\Delta = 13.7$  c.p.s. These values also give theoretical intensities agreeing well with experiment; the calculated intensities and frequencies are indicated by the line spectrum in Fig. 3. Transition 1 would be detectable if it were not obscured by the OH resonance. It should be noted that because of the symmetry of this system, the coupling between the two equivalent protons ( $A_m^{HH}$ ) produces no observable effects in the spectrum. Moreover, changing the sign of  $A_o^{HH}$  merely permutes the assignment of particular transitions to particular lines in the spectrum, producing no observable effects; the assignment given corresponds to a positive  $A_o^{HH}$  in Anderson's sign convention<sup>13</sup> which is the reverse of that adopted here.

#### Unsymmetrical Three-spin Systems

**Determination of Relative Signs of Coupling Constants.**—A considerable fraction of the compounds studied contain three non-equivalent mag-

TABLE II

ZERO-ORDER SPIN FUNCTIONS AND DIAGONALIZED MATRIX ELEMENTS FOR AN UNSYMMETRICAL THREE-SPIN SYSTEM<sup>a</sup>

Zero-order functions	Elements of diagonalized $\mathcal{H}$ matrix
$\alpha_1\alpha_2\alpha_3$	$\mathcal{H}_{11} = -\frac{\hbar}{2}(\gamma_1H_1 + \gamma_2H_2 + \gamma_3H_3) + \frac{\hbar}{4}(A_{12} + A_{13} + A_{23})$
$\alpha_1\frac{1}{\sqrt{2}}(\alpha_2\beta_3 + \beta_2\alpha_3)$	$\mathcal{H}_{2'2'} = -\frac{\hbar}{2}\gamma_1H_1 - \frac{\hbar}{4}A_{23} + hA_+$
$\alpha_1\frac{1}{\sqrt{2}}(\alpha_2\beta_3 - \beta_2\alpha_3)$	$\mathcal{H}_{3'3'} = -\frac{\hbar}{2}\gamma_1H_1 - \frac{\hbar}{4}A_{23} - hA_-$
$\alpha_1\beta_2\beta_3$	$\mathcal{H}_{44} = -\frac{\hbar}{2}(\gamma_1H_1 - \gamma_2H_2 - \gamma_3H_3) - \frac{\hbar}{4}(A_{12} + A_{13} - A_{23})$
$\beta_1\alpha_2\alpha_3$	$\mathcal{H}_{55} = \frac{\hbar}{2}(\gamma_1H_1 - \gamma_2H_2 - \gamma_3H_3) - \frac{\hbar}{4}(A_{12} + A_{13} - A_{23})$
$\beta_1\frac{1}{\sqrt{2}}(\alpha_2\beta_3 + \beta_2\alpha_3)$	$\mathcal{H}_{6'6'} = \frac{\hbar}{2}\gamma_1H_1 - \frac{\hbar}{4}A_{23} + hA_+$
$\beta_1\frac{1}{\sqrt{2}}(\alpha_2\beta_3 - \beta_2\alpha_3)$	$\mathcal{H}_{7'7'} = \frac{\hbar}{2}\gamma_1H_1 - \frac{\hbar}{4}A_{23} - hA_+$
$\beta_1\beta_2\beta_3$	$\mathcal{H}_{88} = \frac{\hbar}{2}(\gamma_1H_1 + \gamma_2H_2 + \gamma_3H_3) + \frac{\hbar}{4}(A_{12} + A_{13} + A_{23})$
	$A_{\pm\pm} = +\frac{1}{2}\left\{A_{23}^2 + \left[\frac{1}{2\pi}(\gamma_2H_2 - \gamma_3H_3) \pm \frac{1}{2}(A_{12} - A_{13})\right]^2\right\}^{1/2}$

<sup>a</sup> It is assumed that  $\frac{1}{2\pi} |\gamma_1H_1 - \gamma_2H_2| \gg \frac{1}{2\pi} |\gamma_2H_2 - \gamma_3H_3| \cong A_{12}, A_{13}, A_{23}$ .

expressions for the relative intensities.<sup>22</sup> A trial calculation assuming  $\Delta = A_{ab}$  gave a spectrum

(22) There are several typographical errors in this table; transition 4 should read  $-\delta/2$  instead of  $\delta/2$ , while transitions 5 and 7 should read  $-J/2$  and  $+J/2$ , respectively, instead of  $-J$  and  $J$ ; and in 9,  $m'A$  is  $+1/2$ . We number the transitions in serial order from top to bottom; this order corresponds to the positions of the lines in the observed spectrum.

netic nuclei, fluorine and/or protons, bonded directly to the benzene ring. Such systems are the simplest for which determinations can be made of the relative signs of coupling constants. Equation 1 was used earlier<sup>16</sup> to write the Hamiltonian for the three-spin system, and matrix elements were reported, including two off-diagonal terms, for a

TABLE III  
ALLOWED TRANSITIONS, FREQUENCIES AND RELATIVE INTENSITIES FOR AN UNSYMMETRICAL THREE-SPIN SYSTEM<sup>a</sup>

1—Spin Set			
Transition	Frequency	Transition	Relative intensity <sup>b</sup>
1. 1 → 5	$\nu_1 - \frac{1}{2}(A_{12} + A_{13})$	1,6	1
2. 2' → 6'	$\nu_1 + (A_+ - A_-)$		
3. 2' → 7'	$\nu_1 - (A_+ + A_-)$	2,5	$\frac{\left\{ \left( \frac{A_{23}}{2} + A_+ \right) \left( \frac{A_{23}}{2} + A_- \right) + H_{23}H_{67} \right\}^2}{\left\{ \left( \frac{A_{23}}{2} + A_- \right)^2 + H_{23}^2 \right\} \left\{ \left( \frac{A_{23}}{2} + A_+ \right)^2 + H_{67}^2 \right\}}$
4. 3' → 6'	$\nu_1 + (A_+ + A_-)$		
5. 3' → 7'	$\nu_1 - (A_+ - A_-)$	3,4	$\frac{\left\{ H_{23} \left( \frac{A_{23}}{2} + A_+ \right) - H_{67} \left( \frac{A_{23}}{2} + A_- \right) \right\}^2}{\left\{ \left( \frac{A_{23}}{2} + A_- \right)^2 + H_{23}^2 \right\} \left\{ \left( \frac{A_{23}}{2} + A_+ \right)^2 + H_{67}^2 \right\}}$
6. 4 → 8	$\nu_1 + \frac{1}{2}(A_{12} + A_{13})$		
2—Spin Set			
Transition	Frequency	Transition	Relative intensity <sup>b</sup>
1. 1 → 2'	$\nu_{23} - \frac{1}{4}(A_{12} + A_{13}) - \frac{A_{23}}{2} + A_-$	1,3	$\frac{\left( \frac{A_{23}}{2} + A_- \right)^2}{\left( \frac{A_{23}}{2} + A_- \right)^2 + H_{23}^2}$
2. 1 → 3'	$\nu_{23} - \frac{1}{4}(A_{12} + A_{13}) - \frac{A_{23}}{2} - A_-$		
3. 2' → 4	$\nu_{23} - \frac{1}{4}(A_{12} + A_{13}) + \frac{A_{23}}{2} - A_-$	2,4	$\frac{H_{23}^2}{\left( \frac{A_{23}}{2} + A_- \right)^2 + H_{23}^2}$
4. 3' → 4	$\nu_{23} - \frac{1}{4}(A_{12} + A_{13}) + \frac{A_{23}}{2} + A_-$		
5. 5 → 6'	$\nu_{23} + \frac{1}{4}(A_{12} + A_{13}) - \frac{A_{23}}{2} + A_+$	5,7	$\frac{\left( \frac{A_{23}}{2} + A_+ \right)^2}{\left( \frac{A_{23}}{2} + A_+ \right)^2 + H_{67}^2}$
6. 5 → 7'	$\nu_{23} + \frac{1}{4}(A_{12} + A_{13}) - \frac{A_{23}}{2} - A_+$		
7. 6' → 8	$\nu_{23} + \frac{1}{4}(A_{12} + A_{13}) + \frac{A_{23}}{2} - A_+$	6,8	$\frac{H_{67}^2}{\left( \frac{A_{23}}{2} + A_+ \right)^2 + H_{67}^2}$
8. 7' → 8	$\nu_{23} + \frac{1}{4}(A_{12} + A_{13}) + \frac{A_{23}}{2} + A_+$		

$$\nu_{23} = \frac{1}{2}(\nu_2 + \nu_3), H_{23} = -\frac{1}{2}(\nu_2 - \nu_3) + \frac{1}{4}(A_{12} - A_{13}), H_{67} = -\frac{1}{2}(\nu_2 - \nu_3) - \frac{1}{4}(A_{12} - A_{13})$$

<sup>a</sup> It is assumed that  $|\nu_1 - \nu_2| \gg |\nu_2 - \nu_3| \cong |A_{12}, A_{13}, A_{23}|$ . <sup>b</sup> The absolute value of  $A_{23}$  is used in these calculations.

molecule with one proton and two fluorine nuclei. It is not essential for determination of relative signs of the coupling constants that there be different nuclear species in the three-spin system. However, the mathematical analysis of the spectra is much simpler and complete results are more readily obtained if the resonance frequencies satisfy the condition  $|\nu_1 - \nu_2| \gg |\nu_2 - \nu_3|, A_{12}, A_{13}, A_{23}$ .

When this criterion is satisfied, the eight zero-order wave functions are taken most simply as the products of the doublet state functions of nucleus 1 and the singlet and triplet state functions of nuclei 2, 3. Off-diagonal matrix elements in this representation then arise only from the mixing of the  $M = 0$ , singlet and triplet states of nuclei 2, 3. The zero-order wave functions and the elements of the diagonalized  $\mathcal{H}$  matrix are given in Table II, while the frequencies of the allowed transitions and their relative intensities are listed in Table III.

There are 14 allowed transitions. Six are associated with nucleus 1; of these, two are often of

very low intensity and not observed. The four lines usually found may be considered approximately as arising from the splitting of the resonance, first into a doublet by the coupling  $A_{12}$  with nucleus 2, and then each component split further into a doublet by the coupling  $A_{13}$  with nucleus 3. Similarly, the resonance of nuclei 2,3 has eight lines which may be considered as a pair of 4-line spectra. The coupling among the two nuclei,  $A_{23}$ , and their chemical shift  $\Delta_{23}$  give a symmetrical 4-line spectrum such as that shown in Fig. 2 for IX. However, this quartet is split further into a pair of quartets by the average of the coupling of nuclei 2,3 with nucleus 1, *i.e.*, by  $\frac{1}{2}(A_{12} + A_{13})$ . Therefore, if the splitting of the pair of quartets can be assigned and if there are independent absolute values for  $A_{12}$  and  $A_{13}$ , their relative signs can be found.

**1,4-Difluoro-2,3,5-trichlorobenzene (XI).**—This compound provides one of the best examples to illustrate the main features of relative sign deter-

mination. A brief account of the analysis has been published.<sup>16</sup> The proton is taken to be nucleus 1; the 1-fluorine, nucleus 2; and the 4-fluorine nucleus 3; so  $A_{12} = A_o^{\text{HF}}$ ,  $A_{13} = A_m^{\text{HF}}$  and  $A_{23} = A_p^{\text{FF}}$ . In the proton spectrum the transitions are symmetric about the center. Inspection of the relative transition probabilities in Table III for the 1-spin system reveals that transitions 1 and 6 are always observed, with a splitting of  $(A_{12} + A_{13})$ . Transitions 3 and 4 approach zero intensity when  $|\nu_2 - \nu_3| \gg \frac{1}{2}|A_{12} - A_{13}|$ ; while if the reverse is true and  $A_{23} \cong 0$ , transitions 2 and 5 are not observed. The separation of transitions 2-5 is  $2(A_+ - A_-)$ ; that of transitions 3-4 is  $2(A_+ + A_-)$ . However, if only one pair of these transitions is observed, expansion of  $A_+$  and  $A_-$  under the appropriate conditions shows that the splitting of this pair is always approximately  $(A_{12} - A_{13})$ .

The observed proton and fluorine spectra of XI are given in Fig. 4. The proton spectrum has only four lines of equal intensity with splittings, between pairs, of 2.0 and 14.6 c.p.s. One of these

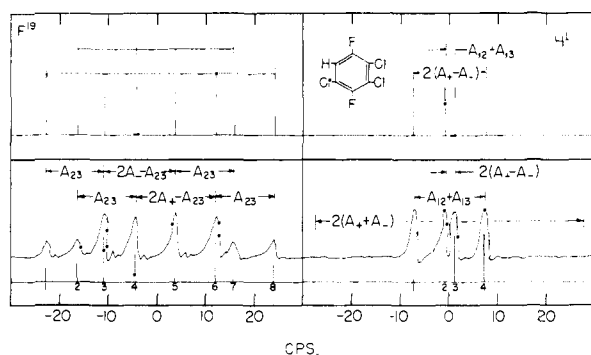
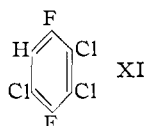


Fig. 4.—The proton and fluorine nuclear magnetic resonance spectra of an unsymmetrical three-spin system for which the relative signs of two of the coupling constants can be obtained. The lines represent calculated spectra, the top set for  $A_o^{\text{HF}}$  and  $A_m^{\text{HF}}$  of unlike sign, the bottom for like signs. The spectra given at the bottom were observed at 4165 gauss.

is  $(A_{12} + A_{13})$ , the other approximately  $(A_{12} - A_{13})$ ; so we can now give approximate values to the two constants of 8.3 and 6.4 c.p.s. One cannot at this point assign these to  $A_{12}$  or  $A_{13}$  nor give signs to them. It will be shown later that transitions 2 and 5 are the other pair observed so the exact value of the second proton splitting is  $2(A_+ - A_-)$ . In this discussion it must be remembered that ordinarily only the magnitudes of the observed splittings are known.



The fluorine spectrum has eight lines which are to be assigned to two quartets, each symmetrical about its center. Inspection of the transitions in Table III for the 2-spin set shows that the splitting of the outer two pairs of lines in each quartet is  $A_{23}$  (Transitions 1-4, 2-3, 5-8 and 6-7). This is the usual case for a 2-spin system with a chemical

shift and coupling between the spins. In the observed spectrum reproduced in Fig. 4, the eight lines can be paired in only one way to give four identical splittings, lines 1-3, 2-4, 5-7 and 6-8. The observed splitting is  $12 \pm 0.2$  c.p.s. which is  $A_p^{\text{FF}}$ . However, there are still two ways in which the four pairs of lines can be combined to give two symmetrical quartets: 1357 and 2468 (assignment i) or 1368 and 2457 (assignment ii).

The observed line separations alone do not distinguish between these two assignments. One quartet has a central spacing of  $2A_+ - A_{23}$  and the other quartet  $2A_- - A_{23}$ ; the difference in central spacings is thus  $2(A_+ - A_-)$ . Another useful relation is that the separation between the centers of the two quartets is  $\frac{1}{2}(A_{12} + A_{13})$ . For assignment i, the experimental data give  $\frac{1}{2}(A_{12} + A_{13}) = 7.4$  c.p.s. and  $2(A_+ - A_-) = 2.4$  c.p.s.; assignment ii reverses these values giving  $\frac{1}{2}(A_{12} + A_{13}) = 1$  c.p.s. and  $2(A_+ - A_-) = 15$  c.p.s. Within experimental error these two assignments are identical with the two possible assignments of the proton spectrum. This supports the earlier analysis of the proton spectrum which assumed that the two missing proton transitions are 3 and 4. Otherwise one of the proton splittings would have disagreed with the fluorine values; it would have been  $2(A_+ + A_-)$  instead of  $2(A_+ - A_-)$ . Moreover,  $A_{23}$  was found in the fluorine spectrum to be comparable in magnitude to the various other terms and this ensures that transitions 2 and 5 are not weak.

The choice between the two assignments can be based upon the intensities of the lines in the fluorine spectrum. Each of the two quartets must be symmetrical not only in terms of splittings but also in the intensities. On this basis, inspection of the spectrum in Fig. 4 is almost enough to convince one that the quartets are 1357 and 2468 (assignment i). Intensities were calculated for both assignments; the results are shown by the line spectra in Fig. 4. It is clear that assignment i is the correct one.<sup>23</sup> Therefore, we find that  $(A_{12} + A_{13}) = 14.7$  c.p.s. and  $2(A_+ - A_-) = 2.4$  c.p.s., which is approximately  $(A_{12} - A_{13})$ . Numerical values can be obtained for  $A_{\pm}$  from the center spacings of the quartets and the value of  $A_{23}$ . We conclude that the coupling constants are of like sign. An accurate solution of the equations in  $A_{\pm}$  and  $(A_{12} + A_{13})$  gives values of  $8.4 \pm 2$  and  $6.3 \pm 0.2$  c.p.s. for the coupling constants and 24.8 c.p.s. for the chemical shift between the fluorines.

Even though we now know that the relative signs of  $A_{12}$  and  $A_{13}$  are the same, there appears to be no way in which we can learn absolute signs from the observed spectra.<sup>24</sup> Reversing the sign of  $\frac{1}{4}(A_{12} + A_{13})$  interchanges the sign of this term between the first four and the second four transitions of the 2-spin set. However, the sign change

(23) The assignment of the lines into quartets also can be made on the basis of data taken at two different magnetic fields, since only the chemical shift, in c.p.s., is field dependent. Data at 6300 gauss confirmed the assignment given.

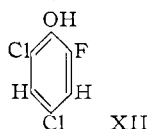
(24) Some information on absolute signs may be gained from cases in which the Hamiltonian of equation 1 does not apply, *e. g.*, when  $\mathcal{H}^{(1)} \cong \mathcal{H}^{(2)}$ . When equation 1 applies, symmetry considerations indicate that the predicted spectra do not change upon reversing the signs of all  $A$ 's.

also interchanges the magnitudes of  $A_+$  and  $A_-$  so the net effect is a complete interchange of the frequencies and intensities of the two groups of four transitions, with no observable change in the spectrum. Similarly, a change in the sign of  $A_{23}$  interchanges assignments of particular transitions to particular lines within each quartet but produces no observable effect. The spectrum of the 1-spin system is equally unhelpful.

There is, however, an asymmetry in the spectrum of the 2-spin system which depends upon the chemical shift of the nucleus which is coupled most strongly to the 1-spin system. In terms of the transitions in Table III, the asymmetry depends upon the sign of the chemical shift ( $\nu_2 - \nu_3$ ) and also upon the relative signs of  $(A_{12} + A_{13})$  and  $(A_{12} - A_{13})$ . A change in either of these features inverts the observed spectrum; a change in both leaves the spectrum unchanged. It is useful to note that determination of the relative signs of  $(A_{12} + A_{13})$  and  $(A_{12} - A_{13})$  will tell us which of our two numerical values (8.4 and 6.3 c.p.s.) is  $A_{12}$  and which is  $A_{13}$ .

In order to analyze the asymmetry we can assume, without loss of generality, that  $(A_{12} + A_{13})$  is positive. The quartet toward the high frequency end of the spectrum then has a central separation<sup>25</sup> of  $2A_+ - A_{23}$  while the low frequency quartet has  $2A_- - A_{23}$ , as shown in Fig. 4. Inspection of the definition of  $A_{\pm}$  in Table II shows that  $A_+ > A_-$  providing both  $(\nu_1 - \nu_3)$  and  $(A_{12} - A_{13})$  are positive. In the general case,  $(A_{12} - A_{13})$  need not be positive but it must have the same sign as  $(A_{12} + A_{13})$ . Experimentally it is found that the larger of the two central separations does occur at the high frequency (low magnetic field) end of the spectrum. The additive effects of substituents upon the fluorine resonance in substituted fluorobenzenes<sup>19</sup> can be used to estimate  $(\nu_2 - \nu_3)$ , giving a value of +90 c.p.s. This is compatible with an observed value of +25 c.p.s. but not with -25 c.p.s. A positive chemical shift implies here that  $(A_{12} - A_{13})$  has the same sign as  $(A_{12} + A_{13})$ ; this plus the previous finding that  $A_{12}$  and  $A_{13}$  are of like sign requires that  $A_{12}$  be larger than  $A_{13}$ . The final conclusion is that  $A_o^{\text{HF}} = 8.4 \pm 0.2$  c.p.s. and  $A_m^{\text{HF}} = 6.3 \pm 0.2$ . It is gratifying, in view of the rather intricate details of the analysis, to note that in Table I the values of  $A_o^{\text{HF}}$  obtained from simple spectra are consistently larger than  $A_m^{\text{HF}}$ .

**2-Fluoro-4,6-dichlorophenol (XII).**—In this compound the 2-spin set contains protons rather than fluorines. The fluorine is nucleus 1, the 3-proton is taken as nucleus 2 and the 5-proton as nucleus 3, so  $A_{12} = A_o^{\text{HF}}$ ,  $A_{13} = A_p^{\text{HF}}$  and  $A_{23} = A_m^{\text{HH}}$ .



The analysis is simplified considerably by the appearance in the fluorine spectrum, given in Fig. 5, of all six lines possible for the 1-spin system.

(25) The asymmetry in the observed spectrum in Fig. 4 is most readily apparent in the different separations of lines 2-3 and 6-7.

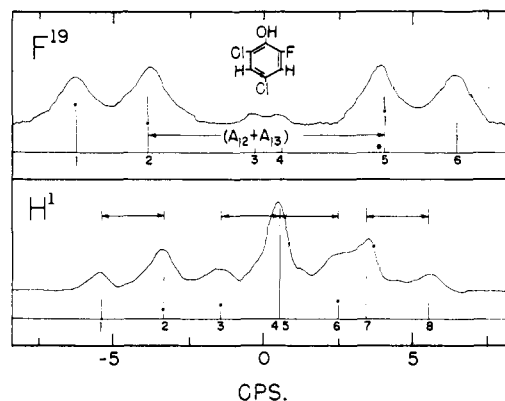


Fig. 5.—Observed and calculated proton and fluorine nuclear magnetic resonance spectra at 4165 gauss for an unsymmetrical three-spin system. The results show that  $A_o^{\text{HF}}$  and  $A_p^{\text{HF}}$  are of unlike sign.

The strongest pair must be transitions 1 and 6; their splitting of 7.9 c.p.s. is  $(A_{12} + A_{13})$ . The other two splittings of 12.6 and 0.9 c.p.s. cannot as yet be assigned to  $2(A_+ - A_-)$  and  $2(A_+ + A_-)$ .

The pairing of proton lines for the quartets is done readily on the basis of intensities and splittings; they are 12, 34, 56 and 78. The splittings of these lines are 2.4, 2.28, 2.36 and 2.36 c.p.s., giving  $A_{23} = 2.3 \pm 0.1$  c.p.s. The pairs can be grouped into quartets in two ways: 1278 and 3456 or 1256 and 3478. The first assignment gives a separation between quartet centers of 0.4 c.p.s. and the second, 3.9 c.p.s. The correct spacing is  $\frac{1}{2}(A_{12} + A_{13})$  which we know from the fluorine spectrum to be  $\frac{1}{2}(7.9)$  c.p.s.; therefore, the second assignment is correct. The difference in the central spacings of the two quartets gives  $2(A_+ - A_-) = 0.8$  c.p.s., which agrees well with the 0.9 c.p.s. doublet splitting in the fluorine spectrum. The other fluorine splitting, 12.6 c.p.s. must then be  $2(A_+ + A_-)$ ; moreover, since these lines are strong we know that  $2(A_+ + A_-) \cong (A_{12} - A_{13})$ . We conclude that since  $(A_{12} + A_{13}) = 7.85$  c.p.s. and  $(A_{12} - A_{13}) \cong 12.6$  c.p.s.,  $A_{12}$  and  $A_{13}$  are of opposite sign. Detailed calculations give numerical values of 9.6 and 2.1 c.p.s. for the two coupling constants and a proton chemical shift of 0.75 c.p.s. These values were used in preparing the theoretical spectra in Fig. 5.

The proton chemical shift is too small for its sign to be predicted by the methods used on the fluorines in XI. However, the values in Table I for  $A_o^{\text{HF}}$  and  $A_p^{\text{HF}}$  make it certain in this case that the *ortho* and *para* constants are 9.6 and 2.1 c.p.s., respectively. The asymmetry of the proton spectrum thus indicates that the resonance of the 3-proton occurs at a lower frequency than the 5-proton.

**2-Amino-3,5-difluoro-4-chloronitrobenzene (XIII).**—The spectra of this compound are very similar to the preceding case, except that the 2-spin set contains fluorines instead of protons. The experimental results are shown graphically in Fig. 6. The proton spectrum exhibits all of the six possible lines of the 1-spin set. The splitting of the strongest pair of lines gives  $(A_o^{\text{HF}} + A_p^{\text{HF}}) =$



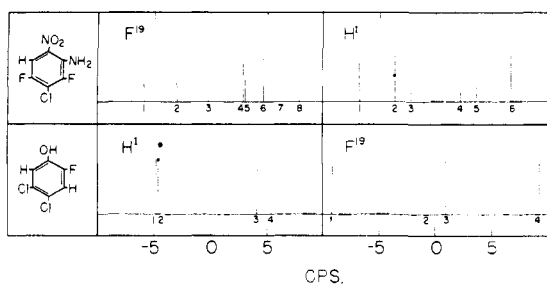
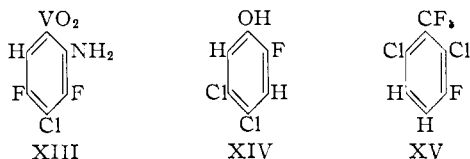


Fig. 6.—Graphical representations of the proton and fluorine nuclear magnetic resonance spectra observed at 4165 gauss for two cases in which relative signs of coupling constants are determined. In the top fluorine spectrum and the bottom proton spectrum, lines 4, 5 and 1, 2, respectively, were not resolved.

7.2 c.p.s. The splitting of the next strongest pair gives  $(A_o^{HF} - A_p^{HF}) \cong 13.3$  c.p.s.; therefore,  $A_o^{HF}$  and  $A_p^{HF}$  are of opposite sign. In the fluorine spectrum, the separation of lines 1 and 2 establishes  $A_m^{FF}$  as about 3 c.p.s. This, as well as the intensities of the various lines readily gives the assignment of quartets as 1247 and 3568. It is of interest to note that the fluorine spectrum gives  $2(A_+ - A_-) = 4.3$  c.p.s. so the 13.3 c.p.s. splitting in the proton spectrum is  $2(A_+ + A_-)$ . Assuming that  $A_o^{HF} > A_p^{HF}$  as found in other cases, final values for the various constants are  $A_o^{HF} = 9.4 \pm 0.3$ ,  $A_p^{HF} = 2.2 \pm 0.3$ ,  $A_m^{FF} = 3.1 \pm 0.1$  and  $\Delta = (\nu_{5-F} - \nu_{3-F}) = -2.5 \pm 0.3$  c.p.s. The spectrum calculated for these values agrees with that observed, well within experimental error.



**2-Fluoro-4,5-dichlorophenol (XIV).**—The observed proton and fluorine spectra of this compound are given graphically in Fig. 6. The proton spectrum, the 2-spin set, is unusual in that there are only three lines well resolved; one of these is double the intensity of the other two and thus is an accidental overlap of two lines.  $A_{23}$  in this case is  $A_p^{HH}$  which we know to be vanishingly small, which accounts for the presence of only four lines. The four lines can be assigned to pairs giving  $1/x$  ( $A_o^{HF} + A_m^{HF}$ ) = 9.3 or 0.7 c.p.s. (12,34 or 13,24, respectively) but in either event the difference in the splittings of the pairs gives  $2(A_+ - A_-)$  as 1.4 c.p.s.

The splittings observed in the fluorine spectrum are 18.4 and 1.9 c.p.s. The 1.9 c.p.s. splitting differs from the 1.4 or  $2 \times 0.7$  c.p.s. splittings of the proton spectrum by 0.5 c.p.s., which is well outside of experimental error. Therefore, the 1.9 c.p.s. fluorine splitting would seem to be  $2(A_+ + A_-)$  rather than  $2(A_+ - A_-)$  or  $(A_o^{HF} + A_m^{HF})$ . This requires that the 18.4 c.p.s. splitting be  $(A_o^{HF} + A_m^{HF})$  and shows that  $A_o^{HF}$  and  $A_m^{HF}$  are of like sign. A detailed solution gives  $A_o^{HF} = 10.1 \pm 0.2$ ,  $A_m^{HF} = 8.3 \pm 0.2$ ,  $A_p^{HH} = 0.4 \pm 0.2$ , and  $\Delta = (\nu_{2-H} - \nu_{6-H}) = +0.9 \pm 0.2$  c.p.s. In making

the assignment it was assumed that  $A_o^{HF} > A_m^{HF}$ , as found in other compounds. Calculations of intensities with these values show that the center "pair" of fluorine lines must be the pair  $2(A_+ - A_-)$  as well as the pair  $2(A_+ + A_-)$ , of equal intensity and unresolved.  $2(A_+ + A_-)$  is thus actually about 2.2 c.p.s.

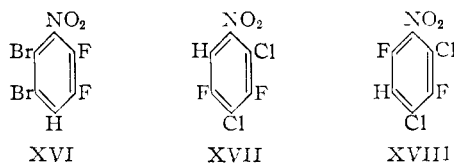
Under conditions of particularly good resolution, the two high frequency proton lines were partially resolved into two doublets, of equal intensity and a splitting of  $0.3 \pm 0.1$  c.p.s. ( $A_p^{HH}$ ), which confirms the analysis and assignments given.

**2,6-Dichloro-3-fluorobenzotrifluoride (XV).**—The spectra of this compound apparently follow equation 4. The fluorine resonance (the 1-spin set) is a 1-2-1 triplet with a splitting between outer lines of  $12.0 \pm 0.5$  c.p.s. and the proton resonance (the 2-spin set) is a doublet with a splitting of  $6.3 \pm 0.2$  c.p.s. These spectra suggest that even though the protons are different structurally, they are equivalent magnetically. Magnetic equivalence here would mean no chemical shift ( $\nu_2 - \nu_3$ )  $\cong 0$ ; and the two protons would have to be coupled equally with the fluorine, *i.e.*,  $A_{12}$  and  $A_{13}$  of like sign and equal magnitude.

However, the relative signs of  $A_{12}$  and  $A_{13}$  are important only if there is some other interaction present which combines with them. If  $A_{23} \cong 0$ , as well as  $(\nu_2 - \nu_3) \cong 0$ , the two protons cannot tell us that their interactions with the fluorine are of different signs; the protons are pseudo-equivalent and the spectra will also be simple as observed.

In other compounds where independent, complete analyses have been made of the spectra we have found that  $A_o^{HH} \cong 8$  c.p.s. In XV this is  $A_{23}$ , so we conclude that its simple spectra result from "full" equivalence of the protons.  $A_{12}$  and  $A_{13}$  are of like sign and about equal magnitude. The large value of  $A_{23}$  overcomes even moderate differences in the values of  $A_{12}$  and  $A_{13}$  so accurate separate values of the latter cannot be obtained. The line width of the center component in the fluorine spectrum places an upper limit on  $2(A_+ - A_-)$  of 1 c.p.s.; this is approximately  $(A_{12} - A_{13})$ . We conclude that  $A_o^{HF} \geq 6.2$  c.p.s. and that  $A_m^{HF} \leq 6.2$  c.p.s.; they are of like sign. The chemical shift between the protons is less than 1 c.p.s.

**Unsymmetrical 3-Spin Systems with  $|\nu_2 - \nu_3|$  Too Large for Relative Sign Determinations.**—In the limit, as  $|\nu_2 - \nu_3|$  becomes large, the spectrum of the 3-spin system consists of three groups of four lines, one group for each nucleus and all lines of equal intensity. The two splittings within each group, if assigned correctly, are the coupling constants of that nucleus with the other two nuclei. The three observed proton and fluorine spectra given schematically in Fig. 7 are of this variety. The compounds are all difluorobenzenes; 2,3-difluoro-5,6-dibromo-nitrobenzene (XVI), 2,4-di-



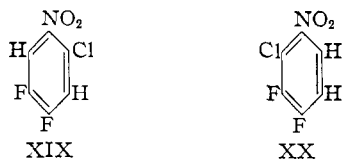
chloro-3,5-difluoronitrobenzene (XVII) and 2,4-dichloro-3,6-difluoronitrobenzene (XVIII).

In the fluorine spectra, the pairs of lines separated by the F-F coupling,  $A_{23}$ , are readily identified by the fact that this spacing is common to both fluorine resonances. Moreover, the lines in these pairs have small differences in intensity; which, however, are virtually the same for all pairs and thus insufficient for determining relative signs of the coupling constants. The separation of the centers of the  $A_{23}$  pairs for a given fluorine is, of course, the coupling constant of that fluorine with the proton.

In XVII and XVIII the chemical shift predicted between the two fluorines is too small to tell which end of the observed spectrum corresponds to which fluorine. In XVI, the situation is more favorable; the resonance of the 2-fluorine is predicted at a frequency of 150 c.p.s. less than that of the 3-fluorine. The shift observed is 205 c.p.s., permitting us to assign the lower frequency resonance to the 2-fluorine and giving the larger H-F coupling as  $A_o^{HF}$ .

In XVII and XVIII, it is assumed that  $A_o^{HF} > A_m^{HF}$ ,  $A_p^{HF}$  as found unambiguously in other compounds. This permits assignment of the fluorine shifts given in Fig. 7; the numerical values are simply the separations between the centers of the two 4-line fluorine spectra, 65 and 120 c.p.s. for XVII and XVIII, respectively. The average values found for the coupling constants are included in Table I.

**2-Chloro-4,5-difluoronitrobenzene (XIX).**—This compound combines features of the preceding four compounds. The two fluorines have resonances chemically shifted by a relatively large amount,  $(\nu_{4-F} - \nu_{5-F}) \cong +130$  c.p.s. Moreover, the two protons are *para*; and with  $A_p^{HH} \cong 0$ , they act as separate spins in their coupling with the fluorines. Therefore, each of the four nuclear spins may be considered as a separate set. However, by virtue of the molecular symmetry insofar as the couplings are concerned, the resonances of the two protons are mirror images as are the resonances of the two fluorines.



The chemical shift between the two protons is only about 7 c.p.s., too small to prevent overlapping of the two 4-line spectra. The splittings of the latter give values for the H-F coupling constants of  $9.4 \pm 0.2$  and  $7.1 \pm 0.2$  c.p.s.; these are assigned as  $A_o^{HF}$  and  $A_m^{HF}$ , respectively, on the basis of their relative magnitudes. The absence of any other structure shows that  $A_p^{HH} < 1$  c.p.s. Each of the two fluorine resonances has eight lines,

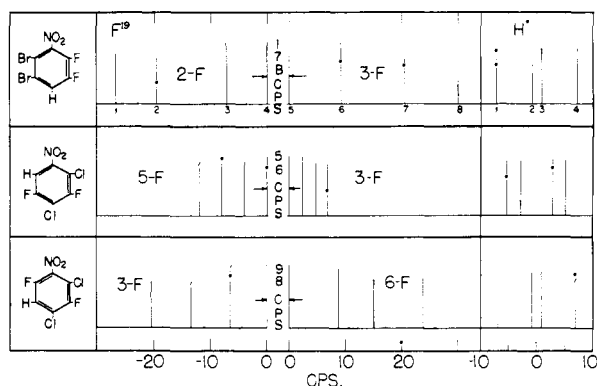


Fig. 7.—Graphical representations of the proton and fluorine nuclear magnetic resonance spectra observed at 4165 gauss for three cases where the chemical shift between the nuclei in the two-spin set is too large to permit determination of relative signs of coupling constants.

two 4-line groups separated by  $20.8 \pm 0.3$  c.p.s. The splittings within each group correspond to those found in the proton spectra. Thus the 20.8 c.p.s. splitting is  $A_o^{FF}$ .

There was some uncertainty regarding the positions of the substituents in this compound. The fluorine chemical shifts alone were unable to differentiate<sup>10</sup> between XIX and XX, although they eliminated all other isomers. However, the H-F splittings of the resonances of the two fluorines show conclusively that each fluorine is *ortho* to one proton and *para* to another, eliminating XX.

#### General Comments

Early observations<sup>14,15</sup> of the spectra of several fluorobenzenes, such as fluorobenzene itself and 1,4-difluorobenzene gave deceptively simple results. One interpretation<sup>15</sup> of the results was that the various H-F coupling constants were equal and that the coupling was therefore *via* the  $\pi$  electrons. However, it is clear from the present work that the coupling constants depend upon orientation and atomic species in a complex manner which cannot be explained by assigning either the  $\pi$ - or the  $\sigma$ -electrons the major role in a simple coupling mechanism. The "simple" spectra of some of the "simpler" fluorobenzenes, e.g., 1,3,5-trifluorobenzene, have been analyzed in detail<sup>2,7</sup> and the resulting values of the coupling constants agree with the range of values given here.

The theoretical significance of these results will be treated in another article.<sup>7</sup> It is hoped that the values found for the various coupling constants and the methods given for analyzing the spectra will be useful in determining the structure of unknowns.

**Acknowledgment.**—We wish to thank Mr. J. P. Heeschen for making the measurements on compounds IV, IX and X as well as repeating the fluorine measurements on V.

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