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Restricted Rotation in Substituted Ethanes as Evidenced by Nuclear Magnetic Resonance

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The fluorine magnetic resonance spectra of four substituted *gem*-difluoroethanes are presented and interpreted in terms of restricted rotation about the ethane C–C linkages. Absolute rotational configurations are assigned on the basis of spin–spin splittings and temperature dependencies of the spectra. With the exception of 1,2-dibromo-2-chloro-1-difluoroethane, only one of the three possible rotational isomers for each of these ethanes is populated over their liquid ranges. The temperature-dependent spectrum of 1,2-dibromo-2-chloro-1,1-difluoroethane is interpreted in terms of "fast" oscillation between two of three possible potential energy minima.

Introduction

The phenomenon of restricted rotation about C–C linkages in ethane and its derivatives has been studied by a variety of physical techniques[1] including infrared, Raman and microwave spectroscopies and dipole moment measurements. The ability of nuclear magnetic resonance spectroscopy to differentiate between like nuclei in different bonding situations or environments in molecules suggests that this technique would be of value in studies of restricted rotation.

In the present study the fluorine magnetic resonance spectra of four substituted ethanes are presented and interpreted in terms of restricted rotation about C–C bonds. Rotational configurations are assigned on the basis of spin–spin splittings and temperature dependencies of the spectra.

Experimental

β,β-Difluorostyrene.—β,β-Difluorostyrene, b.p. 58° (49 mm.), n^{25}_D 1.4890 (reported[2] b.p. 65–66° (61–62 mm.), n^{20}_D 1.4925), was prepared in 33% yield by pyrolysis of 1-phenyl-2,2,3,3-tetrafluorocyclobutane[3,4] at 800° and 2–5 mm. pressure.

1,2-Dibromo-1,1-difluoro-2-phenylethane.—Bromine (17.1 g., 0.107 mole) was added dropwise over a period of five minutes to a stirred solution of 14 g. (0.1 mole) of β,β-difluorostyrene in 150 ml. of carbon tetrachloride. The reaction was maintained at 60–70°. Distillation gave 29 g. (97%) of 1,2-dibromo-1,1-difluoro-2-phenylethane, b.p. 64–65° (0.4–0.5 mm.), n^{25}_D 1.5448.

Anal. Calcd. for $C_8H_6Br_2F_2$: Br, 53.28. Found: Br, 54.18.

1,2-Dichloro-1,1-difluoro-2-phenylethane.—An exothermic reaction took place when chlorine was bubbled into 50 g. (0.36 mole) of β,β-difluorostyrene. The addition of chlorine was discontinued when the temperature of the reaction mixture fell to 25°. Distillation gave 68 g. (90%) of 1,2-dichloro-1,1-difluoro-2-phenylethane, b.p. 200°, n^{25}_D 1.4930.

Anal. Calcd. for $C_8H_6Cl_2F_2$: C, 45.52; H, 2.86. Found: C, 46.01; H, 3.05.

1,2-Dibromo-1-chloro-2,2-difluoroethane.—1-Chloro-2,2-difluoroethylene, purchased from Peninsular Chem. Research, Inc., was bubbled into 3 g. (0.019 mole) of bromine until a colorless solution was obtained. The crude reaction product was distilled to give 4 g. (60%) of 1,2-dibromo-1-chloro-2,2-difluoroethane, b.p. 120°, n^{25}_D 1.4602 (reported[5] 118.7°, n^{20}_D 1.4611).

1,2-Dibromo-1-chloro-1,2,2-trifluoroethane.—1,2-Dibromo-1-chloro-1,1,2-trifluoroethane, b.p. 93.2°, n^{20}_D 1.4278 (reported[6] b.p. 92.9°, n^{20}_D 1.4272) was prepared by the thermal bromination of chlorotrifluoroethylene.

Spectra were obtained by means of a Varian[7] High Resolution nuclear magnetic resonance spectrometer and associated electromagnet. Fluorine magnetic resonance spectra were obtained at 30 Mc. at a field of approximately 7,480 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the fluorine resonance of 1,2-dibromo-1,1,2,2-tetrafluoroethane.

Results and Discussion

A. Spectra of Substituted *gem*-Difluoroethanes.—The fluorine magnetic resonance spectrum of 1,2-dibromo-1,1-difluoro-2-phenylethane would be expected to consist of a simple doublet in the event of free or rapid rotation about the ethane C–C linkage. As a result of "rapid" rotation, the environments of the two 1-fluorine atoms averaged over the rotation would become identical. The fluorine resonance would be a doublet by virtue of electron-coupled spin–spin interaction with the 2-proton. The observed room temperature fluorine magnetic resonance spectra of 1,2-dibromo-1,1-difluoro-2-phenylethane (Fig. 1) and similarly substituted *gem*-difluoroethanes consist in general of eight distinct resonances. The observed complex patterns are reminiscent of the spectra exhibited by CF_2 groups in cyclic[8] and olefinic[9] structures where the environmental averaging process is prevented by the rigidity of the molecule. It appears that the complexity of spectra in

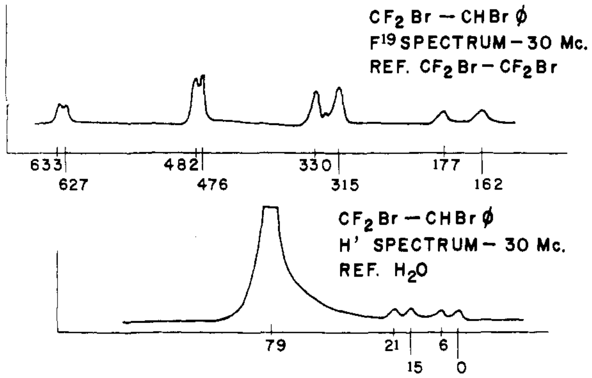

Fig. 1.—F^{19} and H^1 spectra of 1,2-dibromo-1,1-difluoro-2-phenylethane.

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(1) For a general review of the subject, see S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954.

(2) M. Goober, THIS JOURNAL, **75**, 968 (1953).

(3) D. D. Coffman, *et al.*, *ibid.*, **71**, 490 (1949).

(4) J. L. Anderson, U. S. Patent 2,733,278, January 31, 1956.

(5) A. L. Henne and E. C. Todd, THIS JOURNAL, **58**, 402 (1936).

(6) E. G. Locke, W. R. Brode and A. L. Henne, *ibid.*, **56**, 1726 (1934).

(7) Varian Associates, Palo Alto, California.

(8) W. D. Phillips, *J. Chem. Phys.*, **24**, Dec. (1956).

(9) H. M. McConnell, A. D. McLean and C. A. Reilly, *ibid.*, **23**, 1152 (1955).

these molecules is a manifestation of the phenomenon of hindered rotation about the C–C bonds of ethane and its derivatives.

The three most probable rotational configurations of 1,2-dibromo-1,1-difluoro-2-phenylethane are those shown in Fig. 2. It can be seen that in the event of hindered rotation about the C–C bond, the environments of the two 1-fluorine atoms in each of the three configurations are different, and they would therefore exhibit a chemical shift relative to each other. As the spins of the non-equivalent 1-fluorine atoms would be expected to be strongly coupled, a rather large spin–spin splitting would overlay the chemical shift.

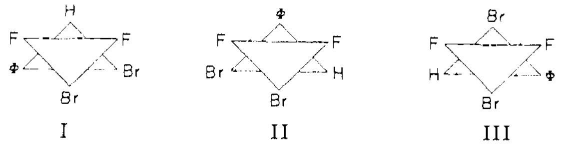

Fig. 2.—Rotational configurations of 1,2-dibromo-1,1-difluoro-2-phenylethane.

In Fig. 1, the resonances occurring at 630 and 479 c.p.s. are the two components of the spin–spin doublet arising from one of the *gem*-fluorine atoms, and the resonances occurring at 322.5 and 169.5 c.p.s. are the doublet components arising from the other *gem*-fluorine atom. The spectrum is typical of that for two non-equivalent fluorine atoms of a rigid CF_2 group in which J, the spin–spin coupling, is of the same order of magnitude as δ, the chemical shift between the fluorine atoms.[8] The separation between doublet centers is not δ but $(J^2 + \delta^2)^{1/2}$ and the doublet intensity ratio, R, is given[10] by the expression

$$R = \frac{1 + (Q')^2}{1 + Q^2} \qquad (1)$$

where

$$Q = \frac{J - (J^2 + \delta^2)^{1/2}}{\delta} \text{ and } Q' = \frac{J + (J^2 + \delta^2)^{1/2}}{\delta}$$

For 1,2-dibromo-1,1-difluoro-2-phenylethane, $(J^2 + \delta^2)^{1/2}$ is 308 c.p.s., J is 152 c.p.s., δ is 268 c.p.s., and R(calcd.) is 2.94. Each of the doublet components is seen to be further split into secondary doublets as a result of nuclear spin coupling between the 1-fluorine and 2-hydrogen atoms. The secondary spin doublet spacings for the two 1-fluorine atoms are not equal, one being of 6 c.p.s. and the other of 15 c.p.s., indicating that the nuclear spin coupling between the 2-hydrogen atom and each of the two 1-fluorine atoms is not the same.

The above analysis of the F^{19} spectrum of 1,2-dibromo-1,1-difluoro-2-phenylethane is confirmed by the H^1 spectrum of the molecule given in Fig. 1. The strong resonance at 79 c.p.s. arises from the protons of the phenyl group. The 2-proton, however, exhibits a resonance consisting of four separate components at frequencies of 21, 15, 6 and 0 c.p.s. The four components of the H^1 resonance result from non-equal nuclear spin couplings between the 2-proton and each of the non-equivalent 1-fluorine atoms to yield successive doublet splittings of 15 and 6 c.p.s.

Results of analysis of the room temperature fluorine magnetic resonance spectra of four substituted *gem*-difluoroethanes are presented in Table I. In each case the results clearly indicate that rotation about the ethane C–C linkage is hindered. While the values of δ vary widely, J, the CF_2 nuclear spin coupling constant, is seen to be very nearly the same for the four ethanes. As has been noted before,[8] values of J appear to be sensitive to bond angles and hydridizations. However, for given ring systems and other structural configurations in which bond angles and hybridizations are known to be similar, values of J are found to be very nearly constant throughout a series.

B. Rotational Configuration of Hindered Ethanes.—If two or all three of the rotational configurations of 1,2-dibromo-1,1-difluoro-2-phenylethane were populated, the fluorine magnetic resonance spectrum would consist not of the observed eight resonances, but of 16 or 24 lines, respectively, perhaps somewhat less because of accidental coincidences. The observation of only eight lines for 1,2-dibromo-1,1-difluoro-2-phenylethane permits the conclusion that, at least for this highly hindered ethane, only one of the three possible rotational isomers is populated at room temperature.

In configuration I of Fig. 2, the 2-hydrogen atom is symmetrically situated with respect to the two 1-fluorine atoms. The two hydrogen-fluorine coupling constants, j_1 and j_2, would be expected to be very nearly equal, and the secondary doublet splittings of Fig. 1 should be the same. Configuration I may therefore be discarded as the one populated at room temperature. Both configurations II and III would, however, be expected to exhibit unequal nuclear spin couplings between the 2-hydrogen and the two 1-fluorine atoms as the result of the non-symmetrical situation of the hydrogen atom with respect to the two fluorine atoms.

A choice cannot be made between II and III as to the correct rotational configuration of 1,2-dibromo-1,1-difluoro-2-phenylethane on the basis of *n-m-r* results alone. However, I has been shown to be excluded, undoubtedly as the result of the proximity of the large bromine atoms in this configuration. Probably II can be eliminated on the same basis, leaving the *trans* configuration III as the most probable, single populated rotational configuration of 1,2-dibromo-1,1-difluoro-2-phenylethane at room temperature.

The non-equal secondary splitting parameters, j_1 and j_2, for 1,2-dibromo-1,1-difluoro-2-phenylethane and 1,2-dibromo-1-chloro-2,2-difluoroethane indicate that the most probable configurations for these ethanes are those in which the largest halogen substituents are *trans*. From the near equality of j_1 and j_2 for 1,2-dibromo-1-chloro-1,2,2-trifluoroethane, it is possible that the populated configuration for this molecule is that in which the 2-bromine and 1-fluorine atoms are *trans*. On the other hand, due to the large dimensions of the substituents in this molecule, it would seem to be more probable that a "twisted" analog of configuration III of Fig. 2 is the populated rotational isomer of 1,2-

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(10) E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952).

dibromo-1-chloro-1,2,2-trifluoroethane. A "twisted" analog of configuration III for 1,2-dibromo-1-chloro-1,2,2-trifluoroethane conceivably could result in approximately equal spin coupling parameters, j_1 and j_2, between the 1-fluorine and the two 2-fluorine atoms. The temperature dependency of the fluorine magnetic resonance spectrum of 1,2-dichloro-1,1-difluoro-2-phenylethane, to be discussed in the next section, indicates that two of the three rotational configurations of this molecule are populated.

TABLE I

ANALYSIS OF THE FLUORINE MAGNETIC RESONANCE SPECTRA OF SOME SUBSTITUTED *gem*-DIFLUOROETHANES

Frequency: 30 Mc.

	$(J^2 + \delta^2)^{1/2}$ [a]	J [b]	δ [c]	R (calcd.) [d]	R (expt.) [d]	j_1 [e]	j_2 [e]
$CF_2BrCHBrC_6H_5$	308	152	268	2.94	2.9	15	6
$CF_2BrCHBrCl$	182	154	97	12.0	11	10	7
$CF_2ClCHC_6H_5Cl$	182	158	90	14.3	16	9	6
$CF_2BrCFBrCl$	166	159	48	45.8	45	14	13

[a] $(J^2 + \delta^2)^{1/2}$ is the separation in c.p.s. between doublet centers of the two *gem*-fluorine atoms. [b] J is the spin–spin coupling in c.p.s. between the two *gem*-fluorine atoms. [c] δ is the chemical shift in c.p.s. between the two *gem*-fluorine atoms. [d] R is the intensity ratio between the J doublet components for each of the two *gem*-fluorine atoms. [e] j_1 and j_2 are the spin–spin coupling constants in c.p.s. between each of the two *gem*-fluorine atoms bonded to one of the ethane carbons and the fluorine or hydrogen atom bonded to the other.

C. Temperature Dependence of Spectra of Hindered Ethanes.—It has been shown that environmental exchange of nuclei of sufficiently high frequency is capable of collapsing a complex *n–m–r* pattern into a simpler one.[11] As the 48 c.p.s. chemical shift of 1,2-dibromo-1-chloro-1,2,2-trifluoroethane is the smallest in the fluorine magnetic resonance spectra of the four substituted ethanes studied, it may be concluded that 360° rotation about the hindered C–C linkages in these molecules must proceed at frequencies of less than $48\ (2\pi) = 301\ \text{sec.}^{-1}$ at room temperature. A maximum rotational frequency of this order of magnitude imposes a minimum barrier to rotation of something of the order of 15 kcal.

Attempts to confer a rotational velocity sufficient to collapse the complex F^{19} patterns of the bromofluoroethanes into simpler ones by temperature elevations were not successful at temperatures below 200°. However, a definite and rather unexpected temperature dependency of the F^{19} spectrum of 1,2-dichloro-1,1-difluoro-2-phenylethane was observed. Spectra of this molecule at temperatures over the range 0 to 200° are shown in Fig. 3. As the weak doublet components are only $^1/_{16}$ the intensity of the strong components at 20°, only the strong CF_2 doublet components centering around 142 and 118 c.p.s. were recorded in the temperature studies.

The separation between the two doublet centers is seen to be 31 c.p.s. at 0°, 24.5 c.p.s. at 20°, and 7.5 c.p.s. at 200°. This temperature dependence can be ascribed solely to a decrease of δ, the chemical shift between the two 1-fluorine atoms, with increasing temperature inasmuch as J, the spin–spin interaction between the two 1-fluorine atoms, remains constant over the temperature range investigated. This behavior of the fluorine magnetic resonance spectrum of 1,2-dichloro-1,1-difluoro-2-phenylethane as a function of temperature is in striking contrast to the behavior of the proton magnetic resonance spectrum of N,N-dimethylformamide[12,13] in which the proton resonances of the non-equivalent methyl groups merge at the temperature at which the frequency of rotation about the C–N bond is of the same order of magnitude as the chemical shift separating the methyl resonances. For 1,2-dichloro-1,1-difluorophenylethane there is a progressive decrease in the chemical shift separating the two 1-fluorine atoms with increasing temperature. Onset of "rapid" 360° rotation may be discarded as the cause of the lessened chemical shift at elevated temperature inasmuch as rotation would remove rather than simply decrease the chemical shift between the two 1-fluorine atoms.

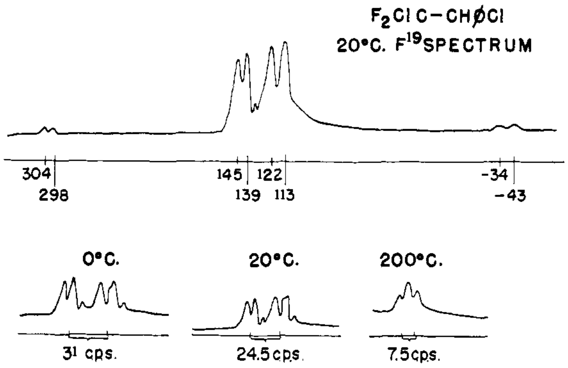

Fig. 3.—Effect of temperature on the 30 Mc. F^{19} spectrum of 1,2-dichloro-1,1-difluoro-2-phenylethane.

Torsional oscillations about the C–C axis between the two extreme configurations shown in Fig. 4 with an amplitude of 120° or less could, however, account for the observed temperature dependency of the fluorine magnetic resonance spectrum. Increasing amplitude of this oscillation plus altered relative populations of the two rotational configurations with temperature elevation would be expected to result in a partial averaging, though not obliteration, of the chemical shift between the two 1-fluorine atoms. When averaged over the 120° oscillation shown in Fig. 4, the environments

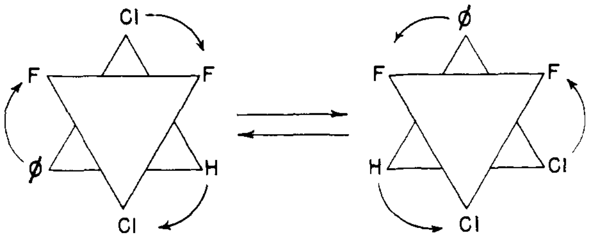

Fig. 4.—Torsional oscillations of 1,2-dichloro-1,1-difluoro-2-phenylethane.

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(11) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

(12) W. D. Phillips, *ibid.*, **23**, 1363 (1955).

(13) Unpublished results.

of the two 1-fluorine atoms are more nearly the same than if only one of the two rotational configurations alone were populated. The environments averaged over the oscillation, however, are not identical. Increased frequency of oscillation with temperature elevation would have no effect on the chemical shift since presumably the frequency is sufficiently high even at the lowest temperature studied to prohibit observation of fluorine resonances characteristic of the two configurations at frequencies of 30 Mc. or less.

Of the four substituted *gem*-difluoroethanes studied, only 1,2-dichloro-1,1-difluoro-2-phenylethane exhibited the temperature dependent spectra discussed above. Spectra for the other ethanes appeared to be temperature independent over their liquid ranges. Of the four substituted ethanes examined, 1,2-dichloro-1,1-difluoro-2-phenylethane with two small chloro substituents rather than with two large bromo substituents would be expected to exhibit the lowest barrier to the 120° torsional oscillation postulated in Fig. 4, and consequently to be most likely to exhibit a temperature dependent spectrum over the accessible temperature range.

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Structure of ClF_3 and Exchange Studies on Some Halogen Fluorides by Nuclear Magnetic Resonance[1]

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The high resolution F^{19} magnetic resonance spectra of ClF_3 at 10, 30 and 40 Mc. are presented and interpreted in terms of the structure of C_{2v} symmetry for the molecule. Observed temperature dependencies of the spectra of ClF_3 and IF_5 are interpreted in terms of fluorine exchange. Activation energies for exchange of 4.8 kcal. for ClF_3 and 13 kcal. for IF_5 are estimated from the *n–m–r* temperature-dependence results. It is concluded that fluorine exchange occurs in these halogen fluorides through a dimer intermediate.

Introduction

Electron diffraction[2] and microwave[3] studies of ClF_3 have indicated that the molecule is planar with two long and a short Cl–F bond and exhibits C_{2v} symmetry. Fluorine exchange between HF and ClF_3 and IF_5, and between F_2 and ClF_3 and IF_5 previously has been demonstrated[4] using radioactive F^{18}.

In the present study, the complex F^{19} magnetic resonance spectrum of ClF_3 is analyzed and shown to be consistent with a structure possessing C_{2v} symmetry. An observed dependence of the number, widths and positions of the F^{19} resonances of ClF_3 and IF_5 on temperature is interpreted in terms of fluorine exchange in these molecules. Activation energies for fluorine exchange are estimated for ClF_3 and IF_5 from the temperature dependencies of the F^{19} magnetic resonance spectra.

Experimental

Materials.—The commercial grade of chlorine trifluoride yielded a fluorine *n–m–r* spectrum consisting of a single, broad, relatively temperature-insensitive peak. The fluoride was purified by a series (twelve) of bulb-to-bulb vacuum distillations in quartz equipment that had been previously dried at 400° under high vacuum. It was necessary to exercise extreme precautions in the distillation of the fluoride in order to obtain a pure sample. Samples for analysis were obtained by distilling the fluoride into quartz capillaries (2 mm. i.d.) which were then sealed off. A sample prepared by this method was found to be "stable" (in contact with quartz) indefinitely. The color of the liquid was an extremely pale yellow; the solid melted sharply at −76° (uncor.).

Bromide trifluoride and bromine pentafluoride were purified in the same manner as chlorine trifluoride. Elimination (by purification) of very slow attack of the quartz by bromine trifluoride at 25° was never achieved. The pentafluoride was stable in quartz.

Iodine pentafluoride was treated with silver(I) fluoride to remove elemental iodine and then distilled in a glass–platinum spinning band column.

Method.—The fluorine magnetic resonance spectra were obtained using a Varian high resolution *n–m–r* spectrometer and electromagnet[5] at frequencies of 10, 30 and 40 Mc. and fields of 2,500, 7,500 and 10,000 gauss, respectively. The spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the fluorine resonance of SF_6. Positive frequency displacements indicate resonances occurring at lower fields than the fluorine resonance of SF_6. Calibration was accomplished by superimposing an audiofrequency on the sweep field to produce side band peaks to the SF_6 resonance.[6]

Results and Discussion

1. Spectrum and Structure of ClF_3.—Microwave[3] and electron diffraction[2] studies of ClF_3 concur in assigning the molecule the structure possessing C_{2v} symmetry shown in Fig. 1. On the basis of this structure and to the approximation that the nuclear spin coupling between the two non-equivalent sets of fluorine atoms is much less than the chemical shift separating the two sets,[7] the expected fluorine magnetic resonance spectrum of ClF_3 would consist of a doublet and triplet of relative integrated intensities of 2 and 1, respectively. The doublet would arise from the equiva-

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(1) Presented before the Division of Industrial and Engineering Chemistry, National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

(2) R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, **21**, 602 (1953).

(3) D. F. Smith, *ibid.*, **21**, 609 (1953).

(4) M. T. Rogers and J. J. Katz, THIS JOURNAL, **74**, 1375 (1952).

(5) Varian Associates, Palo Alto, California.

(6) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 6108 (1951).

(7) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *ibid.*, **21**, 279 (1953).