

## NMR Studies of Some Liquid Crystal Systems

J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar

Citation: *The Journal of Chemical Physics* **43**, 3442 (1965); doi: 10.1063/1.1696498

View online: <http://dx.doi.org/10.1063/1.1696498>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/43/10?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

[Quasiequilibrium states in thermotropic liquid crystals studied by multiple-quantum NMR](#)

*J. Chem. Phys.* **130**, 024501 (2009); 10.1063/1.3042235

[A PFG-NMR study of polymer diffusion in aqueous systems of some poloxamers.](#)

*AIP Conf. Proc.* **469**, 136 (1999); 10.1063/1.58484

[Dynamics of a nematic liquid crystal constrained by a polymer network: A proton NMR study](#)

*J. Chem. Phys.* **103**, 8726 (1995); 10.1063/1.470129

[The polymorphic phases of the hexaalkanoxyoxytriphenylene liquid crystals, as studied by deuterium NMR spectroscopy](#)

*J. Chem. Phys.* **82**, 5155 (1985); 10.1063/1.448640

[Fluorine-19 FT-NMR studies of CF<sub>3</sub>-containing systems dissolved in smectic liquid crystal solutions](#)

*J. Chem. Phys.* **66**, 1850 (1977); 10.1063/1.434183

---



## NMR Studies of Some Liquid Crystal Systems

J. C. ROWELL, W. D. PHILLIPS, L. R. MELBY, AND M. PANAR

*Central Research Department,\* Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware*

(Received 8 July 1965)

Alignment by electric or magnetic fields of molecules comprising the liquid crystalline phase of a nematogenic material is manifested in proton magnetic resonance spectroscopy by the appearance of nuclear dipole-dipole fine structure. Additionally, much larger splittings ranging up to 300 G are observed in the deuterium magnetic resonance spectrum of deuterium substituted nematogens. These latter splittings arise from perturbation of the Zeeman levels by the quadrupole coupling constant of deuterium and have been of value in elucidating structure and organization in nematic phases. Results of NMR studies on nematogens based on azoxy and carboxylic compounds are presented. Use of nematic phases as ordering matrices for molecules such as benzene, toluene, naphthalene, and stilbene are discussed. Some preliminary results on effects of electric fields and dissolved cholesteryl acetate on orientation and organization of nematogens also are presented. In addition, quadrupole coupling constants for deuterium bound to  $sp^2$  and  $sp^3$  carbon and for deuterium bound to oxygen in a carboxylic acid dimer were determined for a few selected compounds.

## I. INTRODUCTION

EARLY investigations<sup>1-8</sup> of the nematic phases of *p*-azoxyethers by proton magnetic resonance (PMR) spectroscopy yielded broad partially resolved spectra with little structure, e.g., a triplet for *p*-azoxyanisole (PAA). Structure was correctly attributed to proton dipole-dipole interactions. Information relating to molecular organization in these systems was derived also from the NMR studies by analyses of line shapes in terms of second moments. Saupe and Englert<sup>9</sup> reported the first highly resolved PMR spectrum of PAA, similar to that shown in Fig. 1. Although such well-resolved PMR spectra of molecules in nematic phases contain a wealth of information pertaining to the orientation and structure of molecules comprising a liquid crystal phase, they have been regarded generally as too complex to justify detailed analysis. Subsequent work, consequently, has dealt largely with the NMR of compounds dissolved in a nematic phase serving as an ordering matrix. This latter approach has yielded important new information regarding chemical shift anisotropies,<sup>9-13</sup> signs of nuclear spin-spin coupling constants,<sup>9-13</sup> and anisotropic contributions to nucleus-electron interactions in paramagnetic species.<sup>14</sup>

\* Contribution No. 1127.

<sup>1</sup> R. D. Spence, H. A. Moses, and P. L. Jain, *J. Chem. Phys.* **21**, 380 (1953).<sup>2</sup> R. D. Spence, H. S. Gutowsky, and C. H. Holm, *J. Chem. Phys.* **21**, 1891 (1953).<sup>3</sup> P. L. Jain, J. C. Lee, and R. D. Spence, *J. Chem. Phys.* **23**, 878 (1955).<sup>4</sup> P. L. Jain, H. A. Moses, J. C. Lee, and R. D. Spence, *Phys. Rev.* **92**, 844 (1953).<sup>5</sup> H. Lippmann and K. H. Weber, *Ann. Physik* **20**, 265 (1957).<sup>6</sup> H. Lippmann, *Ann. Physik* **2**, 287 (1958).<sup>7</sup> K. H. Weber, *Discussions Faraday Soc.* **25**, 74 (1958).<sup>8</sup> K. H. Weber, *Ann. Physik* **3**, 1 (1959).<sup>9</sup> A. Saupe and G. Englert, *Phys. Rev. Letters* **11**, 462 (1963).<sup>10</sup> A. Saupe, *Z. Naturforsch.* **19A**, 161 (1964).<sup>11</sup> G. Englert and A. Saupe, *Z. Naturforsch.* **19A**, 172 (1964).<sup>12</sup> L. C. Snyder and E. W. Anderson, *J. Am. Chem. Soc.* **86**, 5023 (1964).<sup>13</sup> L. C. Snyder and E. W. Anderson, *J. Chem. Phys.* **42**, 3336 (1965).<sup>14</sup> A. Carrington and G. R. Luckhurst, *Mol. Phys.* **8**, 401 (1964).

In this paper we report NMR studies of both molecules comprising nematic phases and of solutes dissolved and oriented in such phases. PMR spectra of nematic liquid crystals are profoundly simplified by use of selectively deuterated compounds. Observed discrete splittings can then be easily assigned to specific dipole-dipole interactions. In addition, deuterium magnetic resonance (DMR) proved an extremely useful adjunct since the quadrupole splittings are large and uncomplicated. PMR and DMR splittings reveal much detailed information concerning the effect of electric and magnetic fields on molecular orientation, the degree to which these phases are ordered, bond angles and conformation, the ordering of solutes in nematic matrices, and molecular exchange.

## II. EXPERIMENTAL

A standard Varian Associates V-4200B NMR spectrometer was employed for most of the studies reported here. For PMR spectra, a 60-Mc/sec V-4311 rf unit and high-resolution probe insert were used, and for DMR spectra, a V-4210A variable-frequency rf unit was operated at 6.536 Mc/sec. The deuterium resonances generally were weak, and improved signal/noise ratios were sometimes obtained by operating the spectrometer at high power in the dispersion mode. Spacings were measured by calibrating the strip chart either with modulated side bands or by shifting the radio frequency by measured intervals.

Sample temperatures were measured by inserting a thermocouple directly into the sample. In 60-Mc/sec studies the thermocouple was removed while spectra were recorded, and the temperature of the heat-transfer gas stream was monitored. At 6.536 Mc/sec, the thermocouple was left in place near the top of the sample without apparent deleterious effect on the spectra.

The cell employed for NMR study of electric-field orientation effects was constructed as follows. A solid glass plug approximately 11 mm in diameter and 1 $\frac{3}{4}$  in. long was shaped to fit the inside of a sample tube,

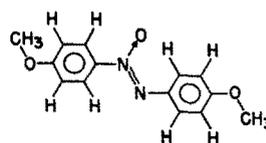
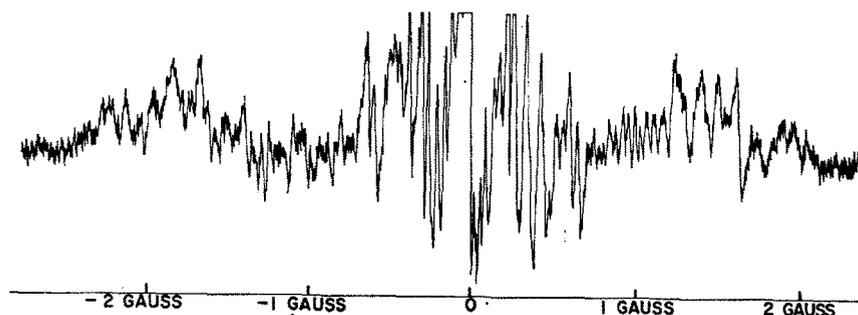
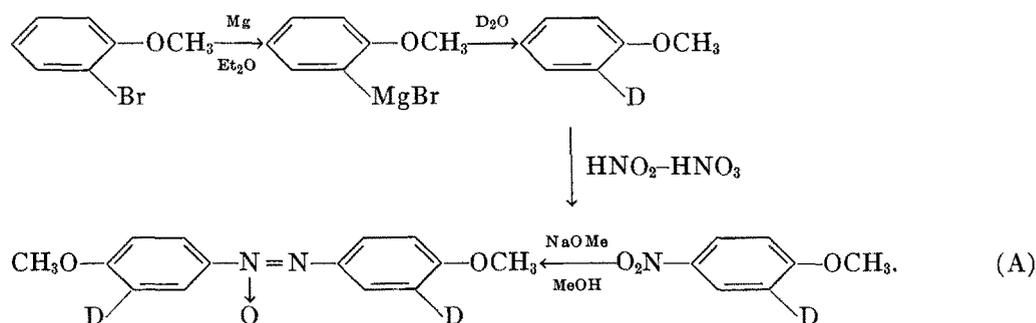


FIG. 1. PMR spectrum of PAA at 126°C and 60 Mc/sec.



leaving only sufficient clearance for easy insertion and withdrawal. A  $\frac{1}{8}$ -in.-wide slot was then cut lengthwise through the center of the plug for a distance of about  $1\frac{1}{4}$  in. from the top, leaving two plane parallel opposed faces. These surfaces were covered with a fired-on platinum coating. An insulated electrical lead was attached to each surface with conducting silver paste. To provide an insulating coating, the electrode assembly was then dipped in Du Pont PI-1200 polyimide high-temperature binder solution and baked at 400°F.

4,4'-Azoxydianisole was obtained commercially<sup>15</sup> and was recrystallized from ethanol. 4,4'-Azoxydiphenetole was prepared according to a published procedure.<sup>16</sup> 4,4'-Azoxydi(anisole- $\alpha,\alpha,\alpha$ - $d_3$ ) was prepared by alkylation of azoxydiphenol<sup>17</sup> with methyl- $d_3$  iodide and potassium carbonate in refluxing ethanol. The ring deuterated azoxy compounds were prepared by alkoxide reduction of the corresponding nitro compounds into which deuterium had been introduced according to the following reaction sequence:



A similar procedure was employed for preparation of the tetradeuterio analog of (A). In the case of the latter compound, the initial product was grossly contaminated with azo compound derived probably from nitrosophenetole in the nitro precursor. The contaminant was converted to azoxy compound by oxidation with hydrogen peroxide in acetic acid,<sup>18</sup> thus obviating loss of the deuterium. 4,4'-Azoxydi(*n*-hexyloxybenzene) was prepared from *p*-*n*-hexyloxynitrobenzene by reduction with glucose in a refluxing alkaline suspension.<sup>19</sup>

*p*-*n*-Alkoxybenzoic acids were prepared from ethyl *p*-hydroxybenzoate and the appropriate alkyl bromide in refluxing sodium methoxide-ethanol solution.<sup>20</sup>

Alkoxybenzoic acids were deuterated in the positions *ortho* to the alkoxy group by equilibration with refluxing deuterioacetic acid. Carboxyl deuteration was accomplished by exchange or by  $D_2O$  hydrolysis of the acid chloride.

For convenience, the structures of the *p*-azoxyethers and *p*-alkoxybenzoic acids studied, together with their

<sup>15</sup> Aldrich Chemical Company, Milwaukee, Wisconsin.

<sup>16</sup> B. M. Bogolovskii, Akad. Nauk. SSSR **2**, 8 (1952); Chem. Abstr. **48**, 621 (1954).

<sup>17</sup> N. J. Leonard, Jr., and J. W. Curry, J. Org. Chem. **17**, 1071 (1952).

<sup>18</sup> T. Parsons, Jr., and J. C. Bailar, Jr., J. Am. Chem. Soc. **58**, 269 (1936).

<sup>19</sup> H. E. Bigelow and A. Palmer, Org. Syn. **2**, 57 (1943).

<sup>20</sup> J. S. Pierce, J. M. Salsbury, and J. M. Frederickson, J. Am. Chem. Soc. **64**, 1691 (1942).

TABLE I. Structures, symbols, nematic temperature ranges, and reorientation axes for compounds studied.

R	X <sub>2,2'</sub>	X <sub>6,6'</sub>	X <sub>3,3',5,5'</sub>	NAME	SYMBOL	NEMATIC RANGE (°C)
CH <sub>3</sub>	H	H	H	4,4'-azoxydianisole	PAA	117-135
CH <sub>3</sub>	D	H	H	4,4'-azoxydi (anisole-2-d)	PAA-d <sub>2</sub>	117-135
CH <sub>3</sub>	D	D	H	4,4'-azoxydi (anisole-2,6-d <sub>2</sub> )	PAA-d <sub>4</sub>	117-135
CD <sub>3</sub>	H	H	H	4,4'-azoxydi (anisole- <i>a,a,a</i> -d <sub>3</sub> )	PAA-CD <sub>3</sub>	117-135
C <sub>2</sub> H <sub>5</sub>	H	H	H	4,4'-azoxydiphenetole	PAP	136-167
C <sub>2</sub> H <sub>5</sub>	D	D	H	4,4'-azoxydi (phenetole-2,6-d <sub>2</sub> )	PAP-d <sub>4</sub>	136-167
C <sub>2</sub> D <sub>5</sub>	H	H	H	4,4'-azoxydi (phenetole- <i>a,a,β,β,β</i> -d <sub>5</sub> )	PAP-C <sub>2</sub> D <sub>5</sub>	136-167
n-C <sub>6</sub> H <sub>13</sub>	H	H	H	4,4'-azoxydi (n-hexyloxybenzene)	PAHB	81-127

R	X <sub>2,6</sub>	X <sub>3,5</sub>	Y	NAME	SYMBOL	NEMATIC RANGE
n-C <sub>3</sub> H <sub>7</sub>	H	H	D	4-(n-propyloxy) benzoic acid-d	PPBA-d	145-154
n-C <sub>3</sub> H <sub>7</sub>	H	D	H	4-(n-propyloxy) benzoic acid-3,5-d <sub>2</sub>	PPBA-d <sub>2</sub>	145-154
n-C <sub>3</sub> D <sub>7</sub>	H	H	H	4-(n-propyloxy) benzoic acid- <i>a,a,β,β,γ,γ,γ</i> -d <sub>7</sub>	PPBA-C <sub>3</sub> D <sub>7</sub>	145-154
n-C <sub>6</sub> H <sub>13</sub>	H	H	H	4-(n-hexyloxy) benzoic acid	PHBA	106-154
n-C <sub>6</sub> H <sub>13</sub>	H	H	D	4-(n-hexyloxy) benzoic acid-d	PHBA-d	106-154
n-C <sub>6</sub> H <sub>13</sub>	H	D	H	4-(n-hexyloxy) benzoic acid-3,5-d <sub>2</sub>	PHBA-d <sub>2</sub>	106-154

nematic ranges and abbreviations by which they are referred to in the text, are summarized in Table I.

### III. RESULTS AND DISCUSSION

#### A. Nuclear Dipole-Dipole Splittings and Molecular Ordering

Molecules that exhibit nematic phases are for the most part long and flat and contain centers such as phenyl, azoxy, and carboxyl groups that are capable of exerting strong intermolecular attractive interactions. By virtue of these properties, molecules comprising nematic phases form transitory aggregates or clusters in which the order within each cluster appears to be very high.<sup>21ab</sup> These clusters are readily aligned in external electric and magnetic fields because of their shape anisotropies. Molecular characteristics such as absorption band polarizations, nuclear dipole-dipole interactions, chemical shifts, and nuclear quadrupole coupling constants are geometrically anisotropic for most molecules. The ability to orient molecules in

electric and magnetic fields thus offers a number of obvious investigational advantages.

A nematic sample in an ordinary NMR magnetic field of a few thousand gauss is aligned with the long axis approximately parallel to the field.<sup>22</sup> As a consequence of this ordering, the splittings arising from the nuclear dipole-dipole interactions, which are motionally averaged to zero by random tumbling in an isotropic liquid, do not disappear. Lattice expansion and intermolecular motions reduce intermolecular dipole-dipole interactions with the result that sharp, discrete structure arising only from intramolecular dipole-dipole interaction are readily observed in NMR. For a completely protonated compound, the PMR spectrum of the nematic phase usually is extremely complex because of the multiplicity of dipole-dipole interactions possible (Fig. 1). For comparison, the PMR spectrum of PAA-CD<sub>3</sub> is shown in Fig. 2 where the complex CH<sub>3</sub> dipole-dipole splitting pattern is eliminated as are dipolar interactions between methyl and ring protons.

The magnetic dipole-dipole interaction of a pair of protons held in rigid orientation in a magnetic field

<sup>21</sup> (a) G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals* (Academic Press Inc., New York, 1962); (b) H. C. Longuet-Higgins and G. R. Luckhurst, *Mol. Phys.* **8**, 613 (1964).

<sup>22</sup> L. S. Ornstein and W. Kast, *Trans. Faraday Soc.* **29**, 931 (1933).

was treated first by Pake,<sup>23</sup> who showed that splitting of the proton resonance into a doublet should occur in NMR absorption with a total splitting  $\delta H$  given by

$$\delta H = 3\mu_H r_{jk}^{-3} (3 \cos^2 \theta_{jk} - 1), \quad (1)$$

where  $\mu_H$  is the proton nuclear moment,  $r_{jk}$  is the interproton distance, and  $\theta_{jk}$  is the angle between the vector connecting the two protons and the magnetic field. For a liquid crystal the angular-dependence term must be replaced by a mean value for the motions involved:

$$\delta H = 3\mu_H r_{jk}^{-3} \langle 3 \cos^2 \theta_{jk} - 1 \rangle. \quad (2)$$

The crux of the problem is to define  $\langle 3 \cos^2 \theta_{jk} - 1 \rangle$  in terms of parameters which can be directly related to the liquid crystal motion and structure. A solution to this problem is to decompose  $\langle 3 \cos^2 \theta_{jk} - 1 \rangle$  into a number of reorientation terms. This can be done for an  $r_{jk}$  vector of constant length rotating simultaneously about several axes if the frequency of reorientation about each axis,  $\nu_{ci} \leq 1/2\pi\tau_{ci}$ , where  $\tau_{ci}$  is the correlation time, is such that the requirement  $\nu_{ci} > \delta\nu_i$  is fulfilled.  $\delta\nu_i$  in the above inequality is the linewidth produced by the fixed orientation in a rigid system.

Theoretical treatment of the reorientation problem was carried out by Powles and Gutowsky<sup>24</sup> and applied by Weber<sup>8</sup> to liquid crystals in the form of Eq. (3):

$$\langle 3 \cos^2 \theta_{jk} - 1 \rangle = \left(\frac{3}{2} \cos^2 \gamma - \frac{1}{2}\right) \left(\frac{3}{2} \cos^2 \Phi - \frac{1}{2}\right) \times \left(\frac{3}{2} \cos^2 \xi - \frac{1}{2}\right) (3 \cos^2 \theta_0 - 1). \quad (3)$$

In a small volume of the nematic phase, a nearly parallel orientation of the molecular axes exists as a result of the intermolecular forces. The long molecular axes are preferentially oriented in the direction  $P$  shown in Table I and form an angle  $\theta_0$  with the magnetic field.

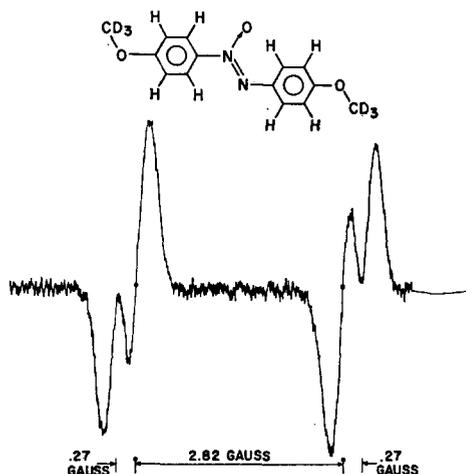


FIG. 2. PMR spectrum of PAA-CD<sub>3</sub> at 120°C and 60 Mc/sec.

<sup>23</sup> G. E. Pake, J. Chem. Phys. **16**, 327 (1948).

<sup>24</sup> J. G. Powles and H. S. Gutowsky, J. Chem. Phys. **21**, 1695 (1953).

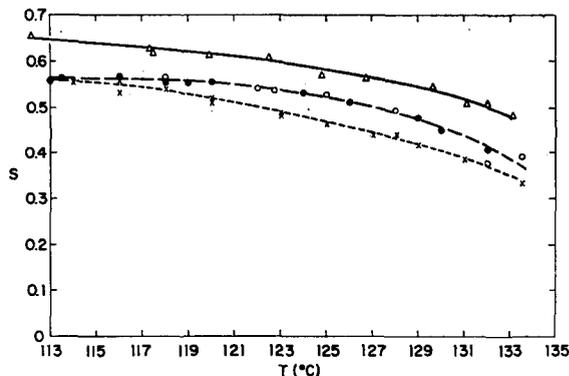


FIG. 3. Temperature dependence of ordering factor ( $S$ ) for PAA;  $\Delta$ , PAA<sup>8</sup>;  $\circ$ , PAA-CD<sub>3</sub>, Table II;  $\bullet$ , PAA-CD<sub>3</sub>, Table VII;  $\times$ , PAA-d<sub>4</sub>, Table VI.

Due to thermal oscillation, a particular molecular axis is inclined at an angle  $\xi$  to the direction of preferred orientation. This oscillation is then decomposed into two opposing rotations. The orientation within this volume is designated as "micro order" while the orientation of volume elements produced by the field is called "macro order" and is also perturbed by thermal motion.

It is also assumed that the molecules involved here are reorienting around their major axes and that both halves of the molecule are reorienting about the *para* axis. These latter reorientations probably occur as a result of the rapid exchange of molecules between ordered sites.  $\gamma$  represents the angle between  $r_{jk}$  and the *para* axis and  $\Phi$ , the angle between the *para* axis and the major molecular axis. Experimental and theoretical evidence<sup>8</sup> leads to the conclusion that, at fields over  $\sim 2000$  G, the macro ordering is perfect, i.e.,  $\theta_0 = 0^\circ$ . The basic equation which is used in this study for nuclear dipole-dipole or deuterium quadrupole splittings is then

$$\delta H = 4\alpha \left(\frac{3}{2} \cos^2 \gamma - \frac{1}{2}\right) \left(\frac{3}{2} \cos^2 \Phi - \frac{1}{2}\right) S, \quad (4)$$

where  $\alpha$  is  $\frac{3}{2}\mu_H r_{H-H}^{-3}$  for proton dipole-dipole interactions. The degree of micro order,  $S$ , usually referred to as the degree of order, is equal to  $\left(\frac{3}{2} \cos^2 \xi - \frac{1}{2}\right)$ . For a perfectly ordered system  $S=1$ , and for complete disorder as in an isotropic system  $S=0$ .

A value of 1.44 G is calculated for  $\alpha$  for dipole-dipole interactions between *ortho* protons of a phenyl ring ( $r_{H-H} = 2.45$  Å). Consideration of the spectrum of PAA-CD<sub>3</sub> (Fig. 2) clearly shows that the major doublet splitting must arise from dipole-dipole interaction between *ortho* pairs ( $H_2-H_3$ ,  $H_2'-H_3'$ ,  $H_6-H_5$ ,  $H_6'-H_5'$ ). From this splitting, determined at different temperatures, values of  $S$  were calculated and are listed in Table II and plotted in Fig. 3. In calculating  $S$ , a value for  $\Phi$  of  $10^\circ$  has been estimated from molecular models,<sup>25</sup> and it was assumed that the *ortho* H-H

<sup>25</sup> W. Maier and A. Saupe, Z. Physik. Chem. **6**, 327 (1956).

TABLE II. PMR *ortho* dipole-dipole splittings and  $S$  values for PAA-CD<sub>3</sub>, PAP-C<sub>2</sub>D<sub>5</sub>, and PPBA-C<sub>3</sub>D<sub>7</sub> at different temperatures.

Temp. (°C)	$\delta H$ (G)	$S$
PAA-CD <sub>3</sub>		
113	3.07	0.559
118	3.12	0.568
122	2.99	0.544
122.75	2.96	0.539
125	2.91	0.530
128	2.73	0.496
132	2.09	0.380
133.5	2.16	0.393
PAP-C <sub>2</sub> D <sub>5</sub>		
128.5	4.15	0.755
137.8	3.99	0.726
141.4	3.91	0.711
146.9	3.76	0.684
150	3.66	0.665
155.3	3.46	0.630
161.1	3.06	0.557
PPBA-C <sub>3</sub> D <sub>7</sub>		
149.8	3.25	0.564

vectors are parallel to the *para* axis so that  $\gamma=0^\circ$ . Also plotted in Fig. 3 are values of  $S$  obtained from the second moment work of Lippman.<sup>6</sup> The lower values found in this study might be expected to be more correct since they were derived from splittings which could be measured rather accurately.

Each component of the major doublet of PAA-CD<sub>3</sub> (Fig. 2) shows an additional small doublet splitting of 0.27 G that is assigned to dipole-dipole interactions between the H<sub>2</sub>-H<sub>6</sub>, H<sub>3</sub>-H<sub>5</sub>, H<sub>2</sub>'-H<sub>6</sub>', H<sub>3</sub>'-H<sub>5</sub>' pairs. Taking the  $S$  value at 120°C from Fig. 2 and an internuclear distance of 4.25 Å for *meta* phenyl protons, a calculated value for this splitting of 0.31 G is obtained, in good agreement with that observed.

Also included in Table II are the splittings and  $S$  values at different temperatures for PAP-C<sub>2</sub>D<sub>5</sub> and PPBA-C<sub>3</sub>D<sub>7</sub>. At 150°C, the ordering in PAP-C<sub>2</sub>D<sub>5</sub> is somewhat greater than in PPBA-C<sub>3</sub>D<sub>7</sub>, whereas at 128°C that of PAP-C<sub>2</sub>D<sub>5</sub> is much greater than that of PAA-CD<sub>3</sub>. The spectra of PAP-C<sub>2</sub>D<sub>5</sub> and PPBA-C<sub>3</sub>D<sub>7</sub> also displayed the minor doublet splitting exhibited by PAA-CD<sub>3</sub>. For PAP-C<sub>2</sub>D<sub>5</sub> this spacing was 0.35 G at 150°C; a value for the splitting of 0.37 G was calculated employing the value of  $S$  derived from the

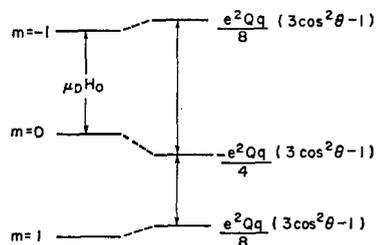


FIG. 4. Deuteron Zeeman levels with quadrupolar perturbation.

major splitting. In the case of PPBA-C<sub>3</sub>D<sub>7</sub>, the observed splitting was 0.26 G at 149.8° compared to a calculated value of 0.31 G. Occurrence of the secondary splitting in both the *p*-azoxyethers and *p*-alkoxybenzoic acids confirms that it arises from the dipole-dipole interaction described above rather than from H<sub>3</sub>-H<sub>3</sub>' and H<sub>5</sub>-H<sub>5</sub>' interactions, since the latter would differ widely between the two types of compounds.

### B. Quadrupole Splittings in DMR Spectra

Perturbation of deuteron Zeeman levels arising from interaction of the deuteron quadrupole moment with the asymmetric electric-field gradient of the bond by which the deuteron is attached to a molecule should be manifested in the DMR spectra of deuterated nematic phases. The energy levels of a deuteron rigidly fixed in a magnetic field and including the first-order quadrupolar perturbation are given by Eq. (5) and shown

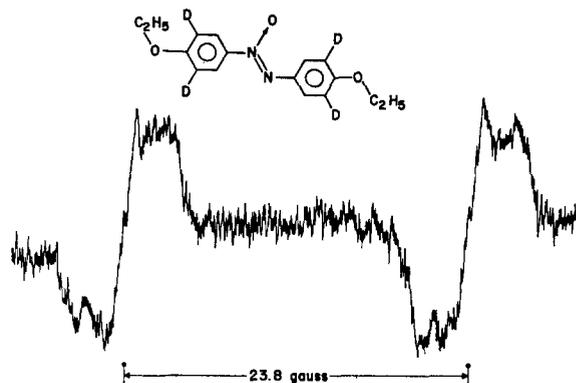


FIG. 5. DMR spectrum of PAP-*d*<sub>4</sub> at 140°C and 6.536 Mc/sec.

in Fig. 4:

$$E_m = -m\mu_D H_0 + \frac{1}{8}(e^2 q Q / \mu_D)(3m^2 - 2)(3 \cos^2 \theta - 1). \quad (5)$$

$q$  is the electric-field gradient experienced by the deuteron quadrupole moment  $Q$ , and  $\theta$  is the angle between  $q$  and the magnetic-field direction. For the sake of simplicity the asymmetry of the tensor quantity  $q$  has been ignored. In any event, because of the absence of  $\pi$  bonding,  $q$  should be cylindrically symmetrical to a good approximation for at least the C-D bond. A doublet splitting is predicted, the magnitude of which is given by

$$H^* = H_0 \pm \frac{3}{8}(e^2 q Q / \mu_D)(3 \cos^2 \theta - 1). \quad (6)$$

$e^2 q Q / \mu_D$  is the quadrupole coupling constant. The expected splitting for a nematic system is again given by Eq. (4), in which  $\alpha$  is replaced by  $\frac{3}{8}e^2 q Q / \mu_D$  and  $\gamma$  is the angle between the C-D bond direction and the *para* axis of the molecule. In all of the deuterated compounds investigated, deuterons of a specific type were indeed found to yield a single doublet. Examples are given in Figs. 5, 6, and 7 of the doublets arising, respec-

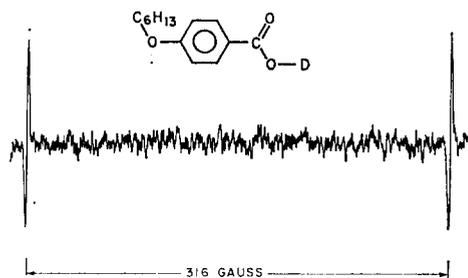


FIG. 6. DMR spectrum of PHBA-*d* at 125°C and 6.536 Mc/sec.

tively, from aromatic ring deuterons,<sup>26</sup> carboxyl deuterons, and aliphatic side-chain deuterons.

In order to translate the experimental quadrupole splittings for the nematic phase systems into more meaningful quantities such as degree of ordering, bond angles, and orientation, it is necessary to employ appropriate deuteron quadrupole coupling constants in Eqs. (6) and (4). Very little has been available in the way of magnitudes and variations of deuterium quadrupole coupling constants in different bonding situations. Values were determined in this study for a few selected examples from perturbations on the DMR spectra of polycrystalline perdeutero compounds. Experimentally, quadrupole doublets in the DMR spectra of polycrystalline solids are usually broad. Nevertheless, the outer edges of the doublet that gives rise to peaks in the derivative of the DMR absorption spectrum are usually quite sharp so that the doublet separation can be measured rather accurately. The quadrupole coupling constant can be calculated from the observed splitting and Eq. (7) if the molecules are

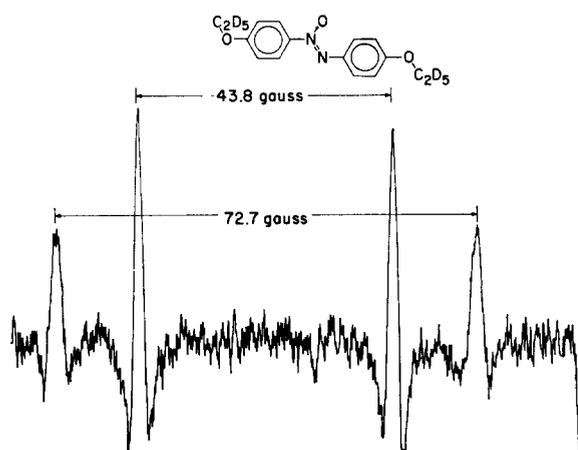


FIG. 7. DMR spectrum of PAP-C<sub>2</sub>D<sub>5</sub> at 153°C and 6.536 Mc/sec, dispersion mode.

<sup>26</sup> W. D. Phillips, J. C. Rowell, and L. R. Melby, *J. Chem. Phys.* **41**, 2551 (1964). First-order perturbation treatment of H-D dipolar interaction appears to produce in the DMR spectrum a pattern more complex than the triplet reported earlier.

TABLE III. Temperature dependence of quadrupole splitting in the DMR spectrum of polycrystalline benzene-*d*<sub>6</sub>.

Temp. (°C)	$\delta H$ (G)	Receiver mode	$e^2qQ/\mu_D$ (G)	$e^2qQ/h$ (kc/sec)
-3.8	107.8	Absorption	288	188
-18.0	107.5	Dispersion	287	187
-19.8	107.2	Absorption	286	187
-39.7	111.0	Absorption	296	193
-82.3	112.0	Absorption	299	195
-118.2	112.3	Absorption	299	196
-118.9	112.5	Dispersion	300	196
-119.1	113.2	Absorption	302	197
-126.0	113.7	Dispersion	303	198
-132.3	114.5	Dispersion	305	199
-137.9	114.0	Dispersion	304	199
-144.3	226.0 ( $2 \times \delta H$ also) ( $\frac{2}{3} \delta H$ also)	Dispersion	302	197
-158.3	219	Dispersion	292	190
-164.5	220	Dispersion	294	192
Av.			295 ± 4	193 ± 2.6

rigidly bound in the crystal:

$$e^2qQ/\mu_D = \frac{4}{3} \delta H. \quad (7)$$

If rapid reorientation or internal rotation occurs about some axis forming an angle  $\theta$  with the deuteron bond, then Eq. (8) applies:

$$e^2qQ/\mu_D = \frac{4}{3} \delta H / (\frac{2}{3} \cos^2 \theta - \frac{1}{2}). \quad (8)$$

The quadrupole coupling constant for a deuteron bound to  $sp^2$  carbon was determined from the DMR of polycrystalline benzene-*d*<sub>6</sub>. The temperature dependence of the quadrupole splitting is given in Table III and a typical spectrum is presented in Fig. 8. Above -138°C the benzene molecules are reorienting about an axis perpendicular to the C-D vectors and, therefore, to the plane of the molecule. Below this temperature reorientation effects have begun to diminish and have completely disappeared at -158.3°C with a resulting doubling of magnitude of the splitting. Motion in solid benzene earlier had been studied by Andrew and Eades<sup>27</sup> using PMR second moments. Because the DMR absorption of benzene-*d*<sub>6</sub> was much sharper and the spacings better defined above the transition occurring around -138°C, the quadrupole

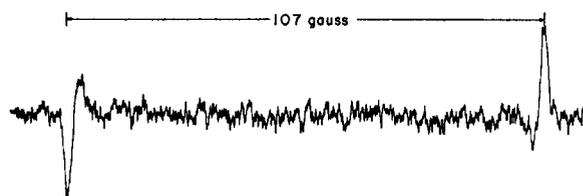


FIG. 8. DMR spectrum of polycrystalline benzene-*d*<sub>6</sub> at -19.8°C and 6.536 Mc/sec.

<sup>27</sup> E. R. Andrew and R. G. Eades, *Proc. Roy. Soc. (London)* **A218**, 537 (1953).

TABLE IV. Temperature dependence of quadrupole splitting in the DMR spectrum of polycrystalline cyclohexane- $d_{12}$ .

Temp. (°C)	$\delta H_1$ (G)	$\delta H_2$ (G)	$\delta H_3$ (G)	Mode	$e^2qQ/\mu_D$ (G)	$e^2qQ/h$ (kc/sec)
-88.8	194.5	131.5 (weak)	0 (strong)	Abs.	...	...
-93.5	195.0	131.2 (weak)	...	Abs.	...	...
-104.5	196.3	...	...	Abs.	262	171
-112.8	197.3	...	...	Abs.	263	172
-115.1	200	...	...	Abs.	267	174.5
-116.0	203.9	...	...	Abs.	272	178
-156.3	210.2	...	...	Disp.	...	...
				Av.	266±4	174±2

coupling constant actually was calculated from the results over the temperature range where rotation about the hexad axis was occurring. The resulting quadrupole coupling constant is  $193 \pm 3$  kc/sec. This value is appreciably larger and probably more accurate than the one of 138 kc/sec which was estimated from spin-lattice relaxation studies.<sup>28</sup>

The quadrupole coupling constants for deuterium bound to  $sp^3$  carbon were determined for cyclohexane- $d_{12}$  and toluene- $\alpha$ - $d_3$ . The splittings observed at different temperatures for cyclohexane- $d_{12}$  are shown in Table IV together with the average value of the derived quadrupole coupling constant ( $174 \pm 2$  kc/sec). At the two highest temperatures reorientation of cyclohexane- $d_{12}$  is occurring in the solid as evidenced by the appearance of a center line and a weak doublet with a spacing of 131 G. The quadrupole coupling constant was derived from splittings at lower temperatures where motional averaging effects appear to be absent. There appears to be a slight increase in splitting with reduction of temperature, but the largest splitting obtained at  $-156.3^\circ\text{C}$  is not considered to be very accurate because of saturation effects; saturation effects become progressively greater at lower temperatures and distort the resonances badly. DMR spectra for polycrystalline toluene- $\alpha$ - $d_3$  were recorded at  $-153^\circ$  and  $-162^\circ\text{C}$ , at which temperatures ring reorientation has ceased but rotation of the methyl group persists.<sup>29</sup> Insertion of the  $109.5^\circ$  tetrahedral angle for  $\theta$  and the measured CD<sub>3</sub>

splitting into Eq. (8) produces a value of 165 kc/sec for the quadrupole coupling constant of deuterium bound to an  $sp^3$  carbon, a value which is slightly less than that obtained for cyclohexane- $d_{12}$ . As is shown later, there is evidence that  $\theta$  for toluene is closer to  $111^\circ$  than  $109.5^\circ$ . A value of  $110.6^\circ$  for  $\theta$  brings the quadrupole coupling constants derived from the two sets of measurements into exact agreement. Inspection of Table V suggests that quadrupole coupling constants for deuterium bonded to carbon will not be sensitive functions of carbon electronegativities and orbital hybridizations.

Satisfactory DMR spectra were not obtained for polycrystalline compounds containing a carboxyl deuterium, presumably because of relaxation effects. A value for the quadrupole coupling constant of a carboxyl deuterium was, however, estimated by combining PMR results on PPBA- $\text{C}_3\text{D}_7$  and DMR results on PPBA- $d$ , both in the nematic phase. The latter yielded a quadrupole splitting of 238 G. From this splitting the quadrupole coupling constant can, in principle, be calculated if the angle  $\gamma_{\text{O-D}}$  is known. In the absence of accurate data concerning this angle, the O-D bond was assumed to be colinear with the *para* axis and oriented parallel to the magnetic field. A value of 184 kc/sec for the carboxyl dimer deuterium quadrupole coupling constant was then calculated from Eq. (4) using  $S=0.564$  obtained from the PMR of PPBA- $\text{C}_3\text{D}_7$ . For comparison, the values of the quadrupole coupling constants determined here are listed in Table V together with those which were available from the literature.

TABLE V. Quadrupole coupling constants for deuterium bonded to carbon.

Compound	$e^2qQ/h$ (kc/sec)
Formaldehyde- $d$	$170.0 \pm 2.0^a$
Monochloroacetylene- $d$	$175 \pm 20^b$
Benzene- $d_6$	$193 \pm 2.6^c$
Cyclohexane- $d_{12}$	$174 \pm 2^c$
Toluene- $\alpha$ - $d_3$	$165^c$

<sup>a</sup> P. Thaddeus, L. C. Krisher, and J. H. N. Loubser, *J. Chem. Phys.* **40**, 257 (1964).

<sup>b</sup> R. L. White, *J. Chem. Phys.* **23**, 253 (1954).

<sup>c</sup> Present work.  $\text{C}_{\text{ar}}\text{-C-D}$  bond angle assumed to be  $109.5^\circ$  for toluene- $\alpha$ - $d_3$ .

<sup>28</sup> D. E. Woessner, *J. Chem. Phys.* **40**, 2341 (1964).

<sup>29</sup> E. R. Andrew, *J. Chem. Phys.* **18**, 607 (1950).

### C. Quadrupole Splittings and Molecular Ordering

Values of  $S$  for the ring deuterated compounds PAA- $d_2$ , PAA- $d_4$ , and PAP- $d_4$  were calculated from the observed DMR splittings and assumed hexagonal angles. These values were appreciably lower than those obtained from the proton dipole-dipole splittings of the side-chain deuterated compounds at comparable temperatures. Accordingly, the following calculations were carried out to ascertain how small a departure of  $\gamma_{\text{C-D}}$  from  $60^\circ$  would account for the discrepancy in  $S$  values obtained from the two approaches. At  $113^\circ\text{C}$  the dipole-dipole splitting  $\delta H_{\text{H-H}}$  for PAA- $\text{CD}_3$

and the quadrupole splitting  $\delta H_{C-D}$  for PAA- $d_4$  are 3.07 and 15.85 G, respectively. Splittings from the lower end of the nematic temperature range were selected for the calculation because of the slower variation of splitting with temperature in this region.  $\gamma_{C-D}$  was then obtained from

$$\frac{\delta H_{H-H}}{\delta H_{C-D}} = \frac{(\frac{3}{2} \cos^2 \gamma_{H-H} - \frac{1}{2}) \alpha_{H-H}}{(\frac{3}{2} \cos^2 \gamma_{C-D} - \frac{1}{2}) \alpha_{C-D}} \quad (9)$$

In this and subsequent calculations of angles, it should be borne in mind that the sign of a  $(\frac{3}{2} \cos^2 \gamma - \frac{1}{2})$  term cannot be determined in the absence of angular dependences of splittings. Therefore, two angles are obtained as a solution of the equation, one on each side of the angle  $54^\circ 46'$  at which  $(\frac{3}{2} \cos^2 \gamma - \frac{1}{2})$  vanishes. In the absence of other evidence, it is assumed that the angle closest to the value of typical known bond angles represents the proper solution.<sup>30</sup> Taking  $\gamma_{H-H} = 0^\circ$ , the above experimental splittings and Eq. (9) yield a value of  $\gamma_{C-D} = 57.5^\circ$ . Splittings and values of  $S$  calculated with  $\gamma_{C-D} = 57.5^\circ$  are listed in Table VI for various temperatures and are plotted in Fig. 3.

Values of  $S$  based on ring deuteron quadrupole splitting fall off somewhat more rapidly with increasing temperature than those derived from proton-proton dipole interaction. A feature encountered throughout this work was that  $S$  values involving a vector direction along the *ortho*- or *meta*-C-D bonds showed slightly greater temperature dependence than those based on a vector direction coincident with a *para* axis or involving a group attached to the *para* position. This behavior very likely stems from a difference in motional or exchange averaging processes for the two types of nuclei that also requires the calculated *ortho*- and *meta*-C-D bond angles to differ slightly from  $60^\circ$ . Similar results were obtained for PAP- $d_4$  and PPBA- $d_2$ .  $\gamma_{C-D}$  was about  $58^\circ$ , and in all cases the calculated value for this angle tended to approach  $60^\circ$  as the temperature was decreased.

Some interesting conclusions concerning the conformation of the side chains can be drawn from the DMR results. The quadrupole doublet splittings for

TABLE VI. Temperature dependences of DMR quadrupole splittings and  $S$  values for PAA- $d_4$ .

Temp. ( $^\circ\text{C}$ )	$\delta H$ (G)	$S(\gamma_{C-D}=60^\circ)$	$S(\gamma_{C-D}=57.5^\circ)$
113	15.85	0.300	0.560
116	15.90	0.300	0.561
118	15.40	0.291	0.544
120	14.80	0.280	0.523
123	13.90	0.262	0.491
128	12.50	0.236	0.441
131.5	10.95	0.207	0.387
133.5	9.50	0.180	0.335

<sup>30</sup> The alternate solution was inadvertently reported in Ref. 26.

TABLE VII. Temperature dependences of DMR quadrupole splittings and  $S$  values for PAA- $\text{CD}_3$ .

Temp. ( $^\circ\text{C}$ )	$\delta H$ (G)	$S(\sigma=123.1^\circ, \epsilon=109.5^\circ)$
113.5	3.79	0.565
116	3.82	0.570
118	3.73	0.557
119	3.73	0.557
120	3.74	0.558
124	3.57	0.533
126	3.44	0.513
129	3.21	0.479
130	3.03	0.452
132	2.75	0.410

the DMR of PAA- $\text{CD}_3$  at different temperatures are shown in Table VII. One may conclude from the appearance of the sharp doublet splitting that, in addition to previously discussed molecular motions, rotation of the  $\text{CD}_3$  group around the O- $\text{C}_\alpha$  axis is occurring at a rate which satisfies the  $\nu_c > \delta\nu$  condition. Calculations to determine whether reasonable bond angles account for the observed splitting were carried out by combining the forms of Eq. (4) for dipole-dipole and quadrupole splittings to obtain

$$\frac{\delta H_{H-H}}{\delta H_{C_\alpha-D}} = \frac{(\frac{3}{2} \cos^2 \gamma_{H-H} - \frac{1}{2}) \alpha_{H-H}}{(\frac{3}{2} \cos^2 \sigma - \frac{1}{2}) (\frac{3}{2} \cos^2 \epsilon - \frac{1}{2}) \alpha_{C_\alpha-D}} \quad (10)$$

where  $\sigma$  and  $\epsilon$  represent, respectively,  $\text{C}_{ar}$ -O- $\text{C}_\alpha$  and O- $\text{C}_\alpha$ -D angles. Ether bond angles as large as  $124^\circ$  are known,<sup>31</sup> but the carbon tetrahedral bond varies relatively little in alkyl groups. Consequently  $\epsilon$  was taken to be  $109.5^\circ$ ,  $\gamma_{H-H}$  was assumed equal to  $0^\circ$ , and  $\sigma$  was calculated from the following experimental data and Eq. (10).  $\alpha_{C-D}$  is 101 G. At  $113.5^\circ$ ,  $\delta H_{H-H}$  and  $\delta H_{C_\alpha-D}$  for PAA- $\text{CD}_3$  are 3.11 and 3.79 G, respectively.  $\sigma$  was found to be  $123.1^\circ$  (or  $127.3^\circ$ ), which is somewhat larger than the  $119^\circ$  obtained by Weber<sup>3</sup> from second-moment studies.  $S$  values were then calculated from Eq. (4) with the results shown in Table VII and plotted in Fig. 3. The temperature dependence agrees well with that obtained from the ring dipole-dipole splittings.

Increasing the length of the alkyl group introduces a doublet in the DMR spectrum for each additional  $-\text{CD}_2-$  group. The observed DMR splittings for PAP- $\text{C}_2\text{D}_5$  and PPBA- $\text{C}_3\text{D}_7$  are shown in Table VIII, with a PAA- $\text{CD}_3$  splitting included for comparison. Striking features of these spectra are the large difference in  $\alpha$ -deuteron splitting and the similarity of the  $-\text{CD}_3$  splittings for PAA- $\text{CD}_3$  and PPBA- $\text{C}_3\text{D}_7$ . This behavior indicates that for more than one carbon atom the alkyl chain tends to be fully extended and that while rotation of a terminal methyl group about its C-C bond always occurs in these systems motion about the other C-C and C-O bonds is limited to small amplitude oscillations. Similar conclusions were

<sup>31</sup> *Interatomic Distances* (The Chemical Society, London, 1958).

TABLE VIII. Side-chain ordering factors and ether bond angles for PAA-CD<sub>3</sub>, PAP-C<sub>2</sub>D<sub>5</sub>, and PPBA-C<sub>3</sub>D<sub>7</sub>. (See text for explanation of symbols.)

	PAA-CD <sub>3</sub>	PAP-C <sub>2</sub> D <sub>5</sub>	PPBA-C <sub>3</sub> D <sub>7</sub>
Temp. (°C)	113.5	144	149.5
<i>S</i>	0.565	0.702	0.564
δ <i>H</i> <sub>C<sub>α</sub>-D</sub> (G)	3.79	79.1	65.2
σ	123.1° (127.3°)	127.5°	129.3°
δ <i>H</i> <sub>C<sub>β</sub>-D</sub> (G)	...	48.5	53.1
δ <i>H</i> <sub>C<sub>γ</sub>-D</sub> (G)	...	...	3.97
<i>S</i> '	...	0.634	0.617
<i>S</i> ''	...	...	0.815

drawn by Weber,<sup>8</sup> from second-moment studies. Analysis of the splittings is complicated by the additional degrees of freedom conferred on the vectors of interest by the mobility of the chain.

Approximate calculations were performed by introducing additional ordering terms similar to the *S* values representing motion of the long molecular axis. The splittings for PPBA-C<sub>3</sub>D<sub>7</sub> are given by

$$\delta H_{C_{\alpha}-D} = 4\alpha S S' \left[ \frac{3}{2} (0.577)^2 \cos^2(54.7^\circ + \eta) - \frac{1}{2} \right], \quad (11)$$

$$\delta H_{C_{\beta}-D} = 4\alpha S S' S'' \left[ \frac{3}{2} (0.577)^2 \cos^2(54.7^\circ + \eta) - \frac{1}{2} \right], \quad (12)$$

$$\delta H_{C_{\gamma}-D} = 4\alpha S S' S'' \left[ \frac{3}{2} \cos^2 109.5^\circ - \frac{1}{2} \right] \times \left[ \frac{3}{2} \cos^2(109.5^\circ + \eta) - \frac{1}{2} \right]. \quad (13)$$

In these equations *S*' reflects rapid oscillations of the C<sub>α</sub>-C<sub>β</sub> bond about the O-C<sub>α</sub> axis, *S*'' reflects the motion of the C<sub>α</sub>-C<sub>β</sub> axis, the C<sub>ar</sub>-O-C<sub>α</sub> angle is σ (σ = 109.5° + η), and all other bond angles are assumed to be 109.5°. The angular terms involving η result from simple geometrical considerations based on the above model. Calculated values of *S*', *S*'', and σ are listed in Table VIII, along with results from similar calculations for PAP-C<sub>2</sub>D<sub>5</sub>. Values of *S*' for the two compounds agree well. In addition, data for PAP-C<sub>2</sub>D<sub>5</sub> at several temperatures revealed that the ratio δ*H*<sub>C<sub>α</sub>-D</sub>/δ*H*<sub>C<sub>β</sub>-D</sub> is constant, a fact which indicates that both types of deuterons experience the same motional averaging effects. *S*' also exhibited little variation with temperature.

The temperature dependence of the doublet splitting in the DMR of PHBA-*d*<sup>26</sup> is given in Table IX together

TABLE IX. Temperature dependences of DMR quadrupole splittings and *S* values for PHBA-*d*.

Temp. (°C)	δ <i>H</i> <sub>COOD</sub> (G)	<i>S</i>
104.0	338.0	0.805
111.0	331.4	0.790
118.0	323.3	0.770
125.0	315.9	0.752
132.0	304.4	0.725
140.0	286.4	0.683

with *S* values calculated from Eq. (4) using α = 105 G (from carboxyl deuteron coupling constant of 184 kc/sec obtained with PPBA-*d*).

#### D. Ordering of Solutes by Nematogenic Solvents

Benzoic acid dissolved in a nematogenic carboxylic acid constitutes a somewhat atypical solute system because the solute can be strongly bound to the solvent in a specific orientation as a consequence of carboxyl dimer formation. A higher degree of solute orientation would therefore be expected to occur in this instance than with a more nonspecifically interacting solute. Three distinct quadrupole splitting doublets occur in the DMR spectrum of a 27.5-mole % solution of benzoic acid-*d*<sub>6</sub> (BA-*d*<sub>6</sub>) dissolved in PHBA-*d* (Fig. 9). The least intense doublet is assigned to the *para* deuteron of BA-*d*<sub>6</sub>. The widest doublet is attributed to the carboxyl deuteron since it is absent in the spectrum of benzoic acid-*d*<sub>5</sub> (BA-*d*<sub>5</sub>) dissolved in PHBA. The most intense but smallest splitting therefore arises

TABLE X. Temperature dependences of DMR quadrupole splittings and calculated values of γ<sub>o-m</sub> for BA-*d*<sub>6</sub> in PHBA-*d*.

Temp. (°C)	δ <i>H</i> <sub>D<sub>o-m</sub></sub> (G)	δ <i>H</i> <sub>D<sub>p</sub></sub> (G)	δ <i>H</i> <sub>COOD</sub> (G)	γ <sub>o-m</sub>
69.8	24.6	287	311	58.3°
74.9	23.2	282	306	58.2°
80.9	21.8	275	305	58°
86.6	21.6	270	302	58°
94.5	18.3	250	287	57.7°
97.2	17.9	237	274	57.9°
100.4	15.1	226	268	57.6°
105.9	12.7	207	250	57.3°
112.1	9.55	180	221	57°

from the *ortho*- and *meta* deuterons in the BA-*d*<sub>6</sub>. Three different dimers are present in this solution and their concentrations, assuming a statistical distribution, are in the proportions

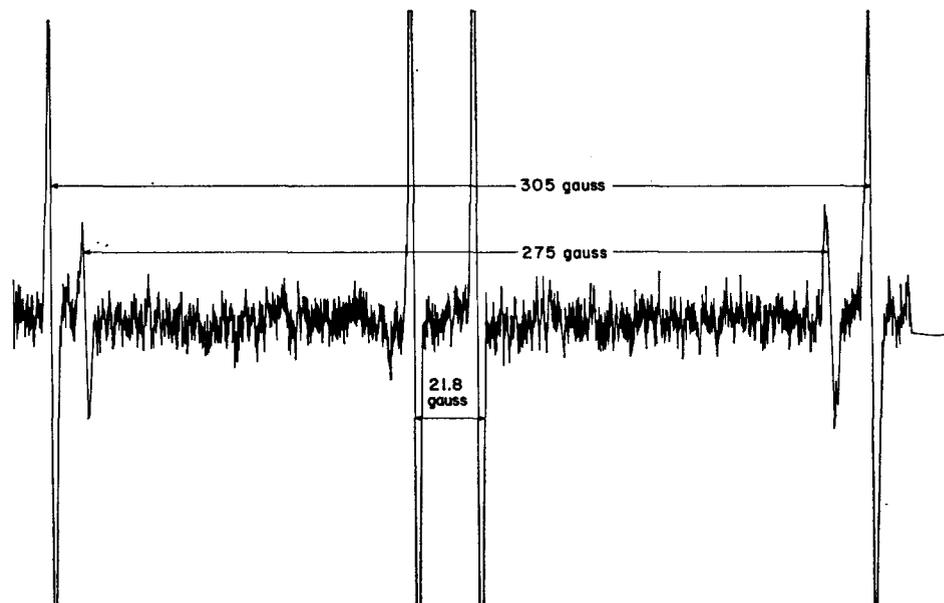
$$(\text{BA-}d_6)_2 / (\text{PHBA-}d \cdot \text{BA-}d_6) / (\text{PHBA-}d)_2$$

$$:: 0.0755 / 0.399 / 0.525.$$

Different degrees of ordering would be expected for each of these species leading, in the absence of exchange averaging, to more lines than are observed. The presence of only three doublets, one for each type of deuteron, means that rapid exchange of acid molecules among the dimers occurs and that the observed splittings are exchange averaged. A summary of the splittings at different temperatures is given in Table X.

An unusual feature of these spectra is that the carboxyl deuteron splitting is greater than that for the *para* deuteron. Since the effective quadrupole coupling constant for a carboxyl deuteron was found to be 184 kc/sec and that of an aromatic deuteron 193 kc/sec, and the field gradients experienced by both are similarly oriented with respect to the external field, the *para* deuteron would be expected to exhibit the larger

FIG. 9. DMR spectrum of a 27.5-mole % solution of benzoic acid- $d_6$  dissolved in PHBA- $d$  at 80.9°C and 6.536 Mc/sec.



splitting. This apparent anomaly is a consequence of the exchange process, as shown by the following considerations. Splittings for the three types of dimers are given by Eqs. (14) through (16), where  $S_B$  is the ordering factor for  $(BA-d_6)_2$ ,  $S_P$  that for  $(PHBA-d)_2$ , and  $S_M$  that for the mixed dimer

$$\delta H_{D_{o-m}} = (0.725 S_M + 0.275 S_B) 4 \times 111 \left( \frac{3}{2} \cos^2 \gamma_{o-m} - \frac{1}{2} \right), \quad (14)$$

$$\delta H_{D_p} = (0.725 S_M + 0.275 S_B) 4 \times 111, \quad (15)$$

$$\delta H_{COOD} = (0.0755 S_B + 0.399 S_M + 0.525 S_P) 4 \times 105. \quad (16)$$

It is immediately clear that the carboxyl deuteron is more abundantly distributed among the better ordered species than is the *para* deuteron, thus accounting for its larger quadrupole splitting.

The angle  $\gamma_{o-m}$  is readily obtained by a combination of Eqs. (14) and (15) using only the experimentally observed splittings. The values and temperature dependence of  $\gamma_{o-m}$ , included in Table X, are in good agreement with results discussed earlier for azoxy compounds. The ring deuteron splittings at different temperatures for BA- $d_5$  in PHBA were essentially the same as those for BA- $d_6$  dissolved in PHBA- $d$ .

TABLE XI. Effect of dimer exchange on the DMR quadrupole splittings of benzoic acid in PHBA- $d_2$  and benzoic acid- $d_5$  in PHBA.

Sample	$\delta H_{D_{o-m}}$ (G)	Temp. (°C)
PHBA- $d_2$	32.9	109.0
27.5 mole % BA in PHBA- $d_2$	24.9	109.0
27.5 mole % BA- $d_5$ in PHBA	15.3	109.0
27.5 mole % BA in PHBA- $d_2$	31.3	84.0
27.5 mole % BA- $d_5$ in PHBA	23.8	84.0

To confirm the effect of exchange between dimers on the size of splittings, DMR spectra were obtained for mixtures of benzoic acid (BA) and PHBA in which one or the other of the acids was ring deuterated. Results are shown in Table XI. Although the mole fraction of each of the three dimer types is the same for both mixtures, the distribution of the deuterium among them is quite different because the deuterium-containing acid can only exchange between two of the three dimers. For BA in PHBA- $d_2$  72.5% of the deuterium is in the  $(PHBA-d_2)_2$  dimer and 27.5% in the  $(PHBA-d_2 \cdot BA)$  mixed dimer. Since the preponderance of the deuterium is in the better-ordered dimers, a larger splitting should therefore result from this mixture than from the BA- $d_5$  in PHBA in which 72.5% of the deuterium is in the mixed dimer  $(PHBA \cdot BA-d_5)$  and 27.5% in the  $(BA-d_5)_2$ . The observed splittings clearly support this conclusion.

The DMR spectrum of benzene- $d_6$  in PAHB at 67°C (Fig. 10) exhibits a single doublet quadrupole splitting of 28.4 G. The doublet separation decreased

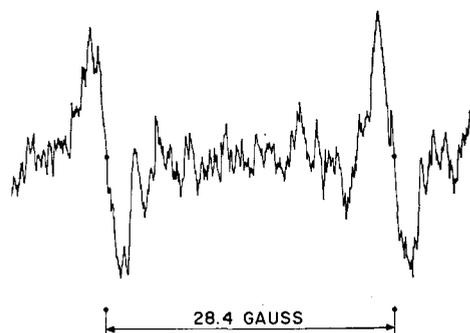


FIG. 10. DMR spectrum of benzene- $d_6$  in PAHB at 67°C and 6.536 Mc/sec.

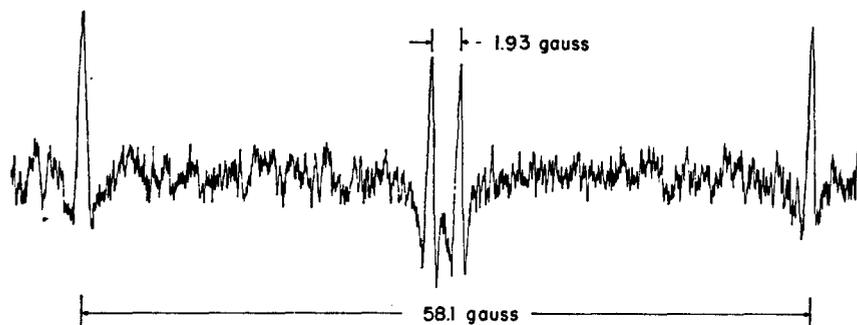
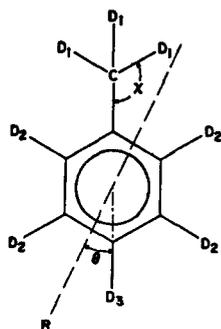


Fig. 11. DMR spectrum of a 25-mole % solution of naphthalene- $d_8$  in PAHB at 81.1°C and 6.536 Mc/sec, dispersion mode.

when either the concentration<sup>32</sup> or temperature was increased. The appearance of only one doublet shows that the benzene is rapidly reorienting about at least a threefold or, more likely, a sixfold axis perpendicular to its molecular plane so that each deuteron on the ring experiences the same averaging process. From the nature of the structure of the nematic phase it would be expected that the preferred orientation of the benzene molecular plane would be parallel to the magnetic field. On the basis of this assumption an  $S$  value of 0.26 can be calculated.

The DMR spectrum of toluene- $d_8$  in PAHB exhibits three doublets with spacings at 76°C of 11.4, 13.6, and 42.9 G. The 42.9-G doublet was assigned to the *para* deuteron on an intensity basis. Since a splitting identical with the smallest was found for toluene- $\alpha$ - $d_3$ , the 13.6-G splitting must arise from the *o* and *m* deuterons. Reorientation of solute molecules embedded in a nematic solvent can result from rapid exchange of solute molecules between ordered regions of the nematic phase. Reorientation of toluene about an axis  $R$  forming an angle  $\theta$  with its *para* axis averages all the  $D_2$  deuteron splittings to the same value. In addition, the  $D_1$  and  $D_3$  deuteron splittings



are related by

$$\delta H_{D_1} / \delta H_{D_3} = \frac{3}{2} \cos^2 \chi - \frac{1}{2}. \quad (17)$$

Experimental splittings inserted in Eq. (17) yield a value for  $\chi$  of 111.9° (136.6°) which is close to the normal tetrahedral angle of 109.5°. A C—C—D angle

<sup>32</sup> Concentrations of benzene are not specified because of its high vapor pressure at the temperature used (63°–80°C).

of 111.0° was recently obtained from electron-diffraction studies of deuterioethane.<sup>33</sup> Toluene is also oriented in PHBA as evidenced by a 20.1-G doublet observed in the DMR spectrum at 95°C of a 25-mole % solution of toluene- $\alpha$ - $d_3$  in PHBA.

Two quadrupole doublets occur in the DMR of a 25-mole % solution of naphthalene- $d_8$  in PAHB (Fig. 11) with separations of 1.93 and 58.1 G at 81.1°C. The smaller splittings is identical with that obtained for naphthalene-1,4- $d_2$  under the same conditions, so assignment is obvious. The corresponding splittings for a 17-mole % solution of naphthalene- $d_8$  in PHBA are 2.63 and 75.2 G at 102.6°C and 4.65 and 81.6 G at 94°C. Reorientation and exchange have made the splittings from the 1,4,5,8-deuterons equivalent as well as those from the 2,3,6,7-deuterons.

The DMR spectrum of a 15.6 mole % solution of stilbene- $d_{12}$  exhibits only two resolvable quadrupole doublets with 2.80 and 34.8 G separations at 58.1°C. Intensity relationships permit assignment of the 34.8-G doublet to the *para* deuterons and the 2.80-G doublet to the 10 remaining phenyl and ethylenic deuterons. Failure to resolve a third doublet is undoubtedly due to the fact that the angle which the ethylenic C—D vectors make with the *para* axis is nearly the same as that assumed by the *ortho* and *meta* C—D vectors of the two rings.

#### E. Ordering of Nematic Phases of Cholesteryl Acetate

Friedel, much earlier, had reported<sup>34</sup> that a small amount of cholesteryl acetate added to *p*-azoxyanisole induced very high optical activity in the nematic phase mixture. These results suggested a strong ordering influence of small amounts of the optically active cholesteric material on the nematogen. Some preliminary studies have shown that small amounts of cholesteryl acetate profoundly alter the PMR spectrum of PAA. Further study of the perturbing action of cholesteryl acetate on the nematic phase was performed by employing the DMR of deuterated compounds which exhibit a simple quadrupole doublet so that altered

<sup>33</sup> L. S. Bartell and H. K. Higginbotham, *J. Chem. Phys.* **42**, 851 (1965).

<sup>34</sup> G. Friedel, *Ann. Phys. (Paris)* **18**, 272 (1922); *Compt. Rend.* **176**, 475 (1923).

characteristics of the spectrum of the nematogen subsequent to introduction of the cholesteric material could be more readily observed and interpreted. The sharp doublet of PHBA-*d* disappeared when 0.53 mole % of cholesteryl acetate was added. With PAA-*d*<sub>4</sub> an increasing concentration of cholesteryl acetate (0.6 to 4.7 mole %) caused a broadening of the lines of the original 13.4-G doublet, followed by the appearance of what seemed to be an additional doublet nearer the center. Finally, at 4.7 mole %, the various broadened structures coalesced to form a single broad line, 3.9 G wide. Detailed interpretation of this behavior has not yet been made but is the subject of further investigation.

#### F. Ordering by Electric and Magnetic Fields

In order to investigate the effect of electric fields on the NMR spectra of nematic phases, it was desirable to ascertain the minimum value of the magnetic field which would produce macro ordering. The PMR spectrum of PAA-CD<sub>3</sub> at 120°C was recorded at different field strengths with the results shown in Table XII. Macroordering was not significantly reduced until the field dropped below 764 G. At 705 G the lines of the doublet persisted but a center line of comparable width and intensity appeared. Further reduction of the field strength resulted in a broad resonance, about 4 G wide, on which was superimposed weak, poorly resolved structure.

Considerable difference of opinion is to be found in the literature<sup>21,35</sup> as to whether molecules in the nematic state are oriented with their long axes parallel or perpendicular to the direction of an applied electric field. Since orientation can be determined from NMR measurements, it seemed feasible to investigate the nature of electric field effects by NMR methods. In order to optimize the orienting influence of the electric field it was desirable to reduce the competing magnetic orientation as much as possible. The spectrometer was operated at 940 G (4 Mc/sec). At this field strength the PMR dipole-dipole doublet of PAA-CD<sub>3</sub> is well resolved.

TABLE XII. Dependence of PMR dipole-dipole splitting of PAA-CD<sub>3</sub> on magnetic-field strength.

Resonance frequency (Mc/sec)	Resonance field (G)	$\delta H$ (G)
16.00	3760	2.91
8.00	1880	2.95
4.00	940	2.83
3.50	823	2.76
3.25	764	2.75
3.00	705	0, 2.75
2.00	470	Broad line, some structure

<sup>35</sup> E. F. Carr, J. Chem. Phys. **39**, 1979 (1963).

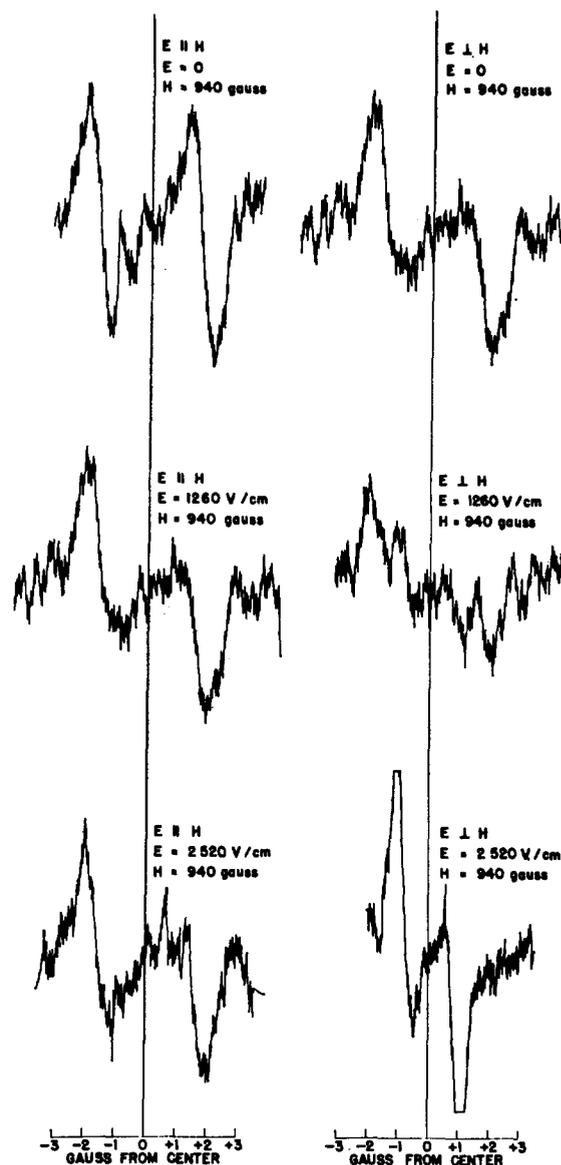


FIG. 12. Effect of electric fields on the PMR of PAP-C<sub>2</sub>D<sub>5</sub> at 150°C.

PMR spectra of PAP-C<sub>2</sub>D<sub>5</sub> at 150°C and at several electric-field strengths with the electric field parallel and perpendicular to the magnetic field are shown in Fig. 12. Similar results were obtained with PAA-CD<sub>3</sub>. With PAP-C<sub>2</sub>D<sub>5</sub> the well-resolved doublet structure disappears when the field is applied in either direction. Instead, the spectrum appears to be a broad line with rather sharp edges. The reason for the apparent loss of resolution is not known with certainty, but turbulence created by application of the field may be responsible. When the electric field is parallel to the magnetic field, the points of maximum slope of the broad line are separated by 4.0 G compared to a 4.2-G separation of the outer peaks in the derivative curve when no electric field is applied. Orienting the electric field perpen-

dicular to the magnetic field reduced the above spacing to 2.1 G, one-half of the value observed in the absence of an electric field. The transition from the wide to narrow line appears to commence at a field just above 940 V/cm and is complete at 1885 V/cm. These results confirm that the long axes of the nematic molecules are oriented parallel to the electric field. If the orientation of the long axis is parallel to the electric-field direction then  $\theta_0$  would be equal to  $0^\circ$  when the direction of the two fields are coincident, and application of such an electric field would not change the spacing. When the two field directions are normal to each other and the

electric field dominates  $\theta_0$  would be  $90^\circ$  and the splitting would be reduced by one-half [see Eq. (3)].

Competitive orienting influences of electric and magnetic fields also were demonstrated with PAA-CD<sub>3</sub>. With a magnetic field of 940 G and an electric field of 1885 V/cm, spectra of the same type as shown in Fig. 12 were observed for PAA-CD<sub>3</sub> for the two electric-field orientations. When the magnetic field was increased to 1880 G the magnetic orientation became dominant and the spectra reverted to the original doublet type obtained in the absence of the electric field.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 43, NUMBER 10 15 NOVEMBER 1965

## Microwave Spectrum and Molecular Structure of Nitrosobenzene\*

YOSHIKI HANYU AND JAMES E. BOGGS

Department of Chemistry, The University of Texas, Austin, Texas

(Received 9 August 1965)

The microwave spectrum of nitrosobenzene has been studied in the frequency region between 13 000 and 24 000 Mc/sec. Numerous *a*-type, *R*-branch transitions have been identified, and the rotational constants have been determined. The molecule is completely planar with the C-N=O group bent at an angle of about  $116^\circ$  in the plane of the ring.

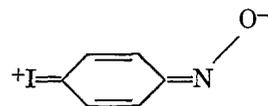
### INTRODUCTION

VERY little detailed structural information is available on organic nitroso compounds, although the C-N=O group is generally considered to be bent with a bond angle on the order of  $120^\circ$ . A recent electron-diffraction study<sup>1</sup> of CF<sub>3</sub>NO has shown an angle of  $121.0^\circ \pm 1.6^\circ$ .

In nitrosobenzene, one would expect a considerable degree of interaction between the  $\pi$ -orbital system of the benzene ring and the double bond of the nitroso group. In fact, it has been suggested<sup>2</sup> on the basis of dipole-moment measurements that conjugation with the ring widens the C-N=O angle to essentially  $180^\circ$ . It is unlikely, however, that the group is entirely linear since a proton nuclear magnetic resonance study<sup>3</sup> of the very similar compound *p*-nitrosodimethylaniline has shown changes with temperature of the observed pattern which can be correlated with hindered rotation of the nitroso group. The barrier to rotation was calculated to be  $11.2 \pm 1.1$  kcal. Similar large barriers are observed in benzaldehyde and benzaldehyde deriva-

tives where the carbonyl group can interact with the ring.

An x-ray-diffraction study<sup>4</sup> of *p*-iodonitrosobenzene has shown the nitroso group to be coplanar with the ring in the solid state. The iodine substituent is a strong electron donor, and it is suggested that there is a large contribution from the structure



The C-N bond length is shortened from the normal single bond distance of about 1.47 to 1.28 Å, which would be expected for partial double-bond character. The expected shortening of the lateral C-C bonds in the ring due to partial bond character is not observed; in fact they are longer by about 0.02 Å than the bonds adjacent to the substituents. The N=O bond length is reported to be 1.28 Å, and the C-N=O angle is  $125^\circ$ . As the authors point out, these parameters are probably strongly influenced by the presence of the iodine substituent.

### EXPERIMENTAL

The microwave spectrum of nitrosobenzene has been observed using a commercial sample which was purified

\* M. S. Webster, J. Chem. Soc. **1956**, 2841.

\* This research was made possible by support extended by The Robert A. Welch Foundation.

<sup>1</sup> M. I. Davis, J. E. Boggs, D. Coffey, Jr., and H. P. Hanson, "An Electron Diffraction Study of Trifluoronitrosomethane," J. Phys. Chem. (to be published).

<sup>2</sup> C. P. Smyth, *Dielectric Behavior and Structure* (McGraw-Hill Book Company, Inc., New York, 1955), pp. 318-319, 324.

<sup>3</sup> D. D. MacNichol, R. Wallace, and J. C. D. Brand, Trans. Faraday Soc. **61**, 1 (1965).