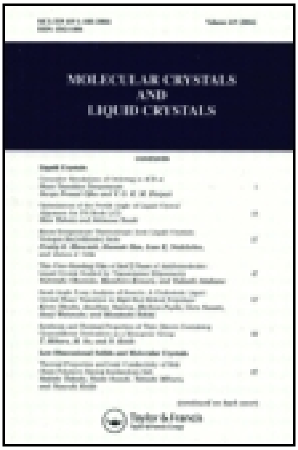


Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Proton Magnetic Resonance Spectra of Oriented Molecules: Acetylenic Compounds, Acetonitrile and Methanol

Gerhard Englert [a] & Alfred Saupe [b]

[a] Physical Department of F. Hoffmann-La, Roche & Co. Ltd., Basle, Switzerland

[b] Physical Institute of the University, Freiburg 1, Br., Germany

Version of record first published: 21 Mar 2007.

To cite this article: Gerhard Englert & Alfred Saupe (1966): Proton Magnetic Resonance Spectra of Oriented Molecules: Acetylenic Compounds, Acetonitrile and Methanol, Molecular Crystals, 1:4, 503-514

To link to this article: http://dx.doi.org/10.1080/15421406608083289

Molecular Crystals. 1966. Vol. 1, pp. 503–514

Printed in Great Britain

Proton Magnetic Resonance Spectra of Oriented Molecules: Acetylenic Compounds, Acetonitrile and Methanol

GERHARD ENGLERT
Physical Department of F. Hoffmann-La Roche & Co. Ltd., Basle, Switzerland
and
ALFRED SAUPE
Physical Institute of the University, Freiburg i. Br., Germany

Received December 27, 1965

Abstract—The proton magnetic resonance spectra of some acetylenic compounds, acetonitrile and methanol, oriented in the nematic phase of 4,4-di-n-hexyloxy-azoxybenzene or 4-n-octyloxy-benzoic acid have been investigated. From the chemical shift difference of the signals of the acetylenic proton in the isotropic and nematic phase a value of 12 ± 1.5 ppm is obtained for the anisotropy of the chemical shift. From the spectra of oriented acetontrile-2-^{13}C and methanol-^{13}C accurate values for the H—C—H bond angle of the methyl groups are derived. The absolute sign of the indirect spin coupling constant $J_{^{13}\mathrm{CH}}$ in acetonitrile-2-^{13}C has been found to be positive.

Introduction

We have previously shown in a number of publications[1–5] that the use of nematic liquids as solvent provides a simple technique for the study of the n.m.r. spectra of oriented molecules. These consist of sharp lines superimposed on a very broad background signal which is due to the molecules of the nematic matrix. The highly resolved spectra of the solute molecules are of considerable interest not only to the n.m.r. spectroscopist, but also to the chemist who is interested in studying the properties of nematic liquids.

The sharpness of these signals, which is in contrast to observations made on solids, arises because the local magnetic fields of *inter*molecular origin are reduced by the molecular motions as in ordinary liquids. The partial orientation of the solute molecules—

on the other hand—gives rise to *intra*molecular, direct magnetic dipole–dipole couplings ranging from a few c/s up to a few kc/s. Their magnitudes depend on the distances between magnetic nuclei and on the degree of order. The analysis of such highly resolved n.m.r. spectra of oriented molecules can therefore give detailed insight into the molecular geometry and the molecular orientation.

In the following contribution we should like to discuss some results obtained from the proton magnetic resonance spectra of some acetylenic compounds, acetonitrile and methanol. This discussion will demonstrate that the study of the spectra of molecules, oriented in a nematic phase is not confined to aromatic compounds. From our experiments we rather conclude that all other compounds are equally well suited provided their molecular structure sufficiently deviates from a spherical shape. This means that the anisotropy of the molecular polarizability must be sufficiently pronounced in order to obtain a molecular orientation by the intermolecular dispersion forces which is also a requirement for pure nematic liquids.

I. Description of the Average Molecular Orientation

The coupling constant of the direct magnetic coupling between two magnetic nuclei (distance r) is given by

$$D = \frac{h\gamma^2}{4\pi^2 r^3}\cdot\tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle = \frac{h\gamma^2}{4\pi^2 r^3}S$$

Here θ denotes the angle between the internuclear vector and the magnetic field, the latter being parallel to the optical axis. The degrees of order S of the internuclear vectors between different pairs of magnetic nuclei in a given molecule are correlated with the degrees of order of the three molecular principal axis. As has been shown previously[2,3] these three S-values completely describe the average molecular orientation.

If the molecular geometry is known, e.g. from X-ray or microwave data, accurate values for the degrees of order can therefore be derived from the analysis of the n.m.r. spectra of oriented molecules. In certain cases of molecular symmetry the molecular order is completely described by only one independent S-value. If more than one value of the direct dipolar coupling can be obtained from the spectrum, their ratios may be used to derive ratios of internuclear distances, as will be seen from the examples discussed below.

First, we should like to make some remarks concerning the intuitive meaning of these S-values. A positive S-value indicates that the corresponding axis is preferably parallel to the magnetic field. A maximum value of $+1$ would correspond to an ideal, perfect alignment of this axis. Experimentally, the values usually observed are between approximately 0.05 and 0.7, the latter being expected for pure nematic liquids.

A negative S-value (maximum $|S| = \frac{1}{2}$) indicates that the corresponding axis is preferably oriented perpendicular to the magnetic field direction.

In the next section we should like to present and to discuss briefly some of the spectra, and in the last section we shall summarize all preliminary results obtained from the detailed analysis of our spectra. The results of the quantum mechanical treatment of the respective 3-, 4- and 6-spin systems and a more extensive discussion of the experimental data will be given elsewhere.[5, 6]

II. PMR Spectra of some Oriented Acetylenic Compounds and of Acetonitrile

In Fig. 1 we present the typical 100 Mc/s spectrum of an oriented 3-spin system, namely of 3-chloro-propyne (propargylchloride) dissolved in 4,4-di-n-hexyloxy-azoxybenzene at 72° C. The experimental spectrum consists of seven lines and an additional signal which is assigned to a very small quantity of tetramethylsilane (TMS). As has been shown in previous communications, spherically shaped TMS will not be oriented in a nematic liquid and its single signal† therefore may serve as an internal reference for the measurement of chemical shifts as it is usually the case in normal high-resolution spectroscopy.[1, 3]

† Note added in proof: Very recently, a small splitting of a few c/s of the signal of TMS in a nematic solution has been observed (L. C. Snyder and S. Meiboom, private communication).

Since the inter-proton distance r of the CH_2-group is smaller than the distance from the acetylenic proton R, the former direct coupling (B) is expected to be large compared to the latter (A). The resulting spectrum therefore should consist of a doublet of doublets with a large and a small splitting, assigned to the CH_2-protons. The triplet is due to the acetylenic proton. The central line of the triplet is shifted with respect to the centre of gravity of the CH_2-lines by $\Delta\nu$, the chemical shift difference. The result of an exact analysis of this 3-spin problem is given in Fig. 1 together with the resulting theoretical spectrum.

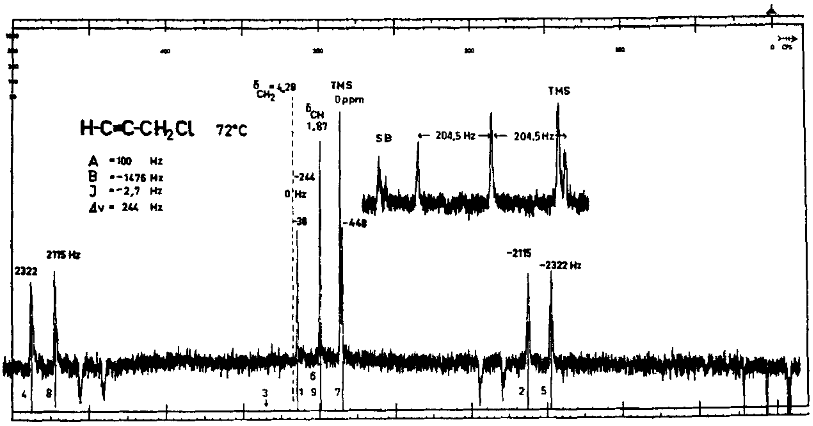


Figure 1. Experimental and theoretical 100 Mc/s spectrum of 3-chloropropyne (15 mol %) in 4,4-di-n-hexyloxy-azoxybenzene at 72° C. Signals with negative intensities are audio sidebands at $n \cdot 2001$ c/s ($n = 2$), introduced by the V 3521 A Integrator-Baseline Stabilizer Unit of the HA 100 spectrometer.

The relative signs of A and B ($A \cdot B < 0$) have been obtained from the intensity ratio of the central lines of the spectrum. Their absolute signs can be derived from the anisotropy of the chemical shift of the acetylenic proton. In the nematic phase we obtained

$$\delta = 1.87 \text{ ppm below TMS}$$

In the isotropic phase at 120° C we found

$$\delta = 2.40 \text{ ppm below TMS}$$

A comparison of these values shows that the signal of the oriented molecule has suffered a considerable upfield shift. This can be explained by the assumption that the long axis of the molecule is preferably oriented parallel to the magnetic field direction. In this case the known diamagnetic anisotropy of the carbon triple bond will cause an upfield shift of the observed order of magnitude as will be seen in the last section. From the known molecular orientation which has also been found for all other acetylenic compounds, we conclude that the absolute signs of A and B are positive and negative, respectively. For the calculation of the theoretical spectrum we have assumed that the indirect J-coupling is negative. Although the agreement between experimental and theoretical spectrum is excellent, the negative sign of J can unfortunately, however, not be confirmed beyond doubt, for the influence of the sign of J on the spectrum is rather small.

In Fig. 2 we present the 100 Mc/s spectrum of a typical 4-spin system, namely of 25 mol % of 1,3-pentadiyne (methyl-diacetylene) dissolved in 4,4-di-n-hexyloxy-azoxybenzene at 76° C. The upper trace shows the central- and low-field part of the spectrum; the lower trace gives the three sections of the total spectrum with higher resolution. The spectrum is determined by three parameters:

(1) the direct dipole coupling of the protons of the methyl group, denoted by B

(2) the coupling of the acetylenic and the methyl protons, denoted by A

(3) the chemical shift difference between both types of protons.

The indirect J-coupling has still been neglected here. Because of the high molecular symmetry the orientation of the molecule is completely described by only one S-value. Using an internuclear distance of $r = 1.805$ Å for the protons of the methyl group, taken from the microwave data of propyne,[7] we obtain for the degree of order of the long molecular axis

$$S_{\parallel} = 0.18 = -2S_{\perp} \quad (\perp : \text{perpendicular axis})$$

Since both direct couplings are proportional to this S-value, their ratio is independent of S and can therefore be used to calculate the ratio of the distance r between the methyl protons and the distance R between the methyl and the acetylenic protons[5]

$$\frac{A}{B} = \frac{r^3}{R^3}\left(\frac{r^2}{R^2} - 2\right)$$

With the given values for A and B we obtained

$$\frac{\mathrm{R}}{r} = 3.703 \pm 0.7\%$$

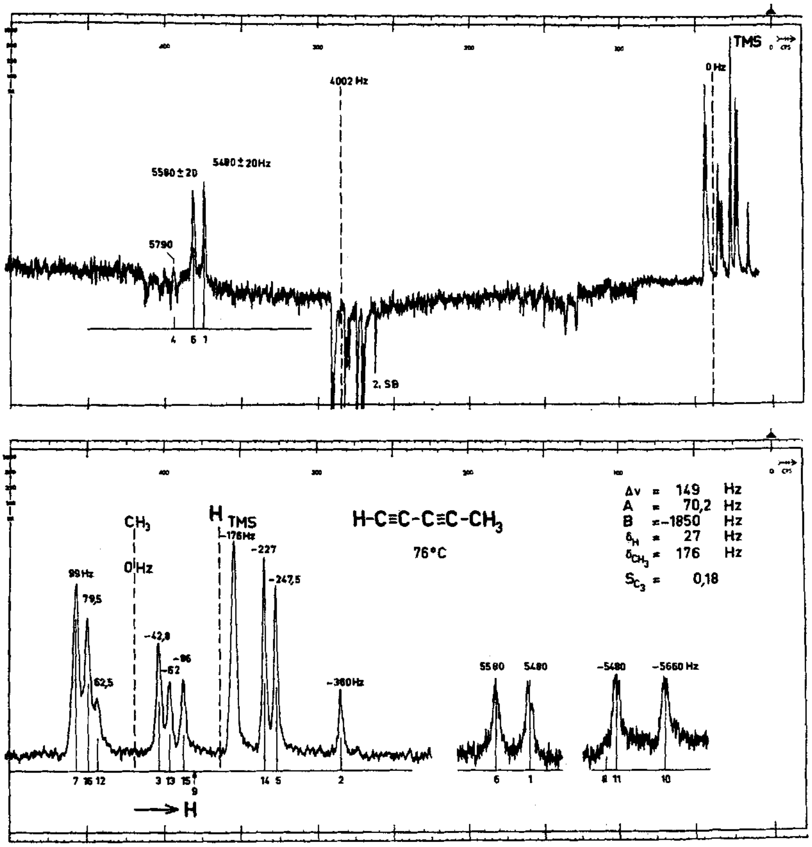


Figure 2. Experimental and theoretical 100 Mc/s spectrum of 25 mol % of 1,3-pentadiyne, dissolved in 4,4-di-n-hexyloxy-azoxybenzene at 76° C. Upper trace: central- and low-field part; lower trace: all sections of the spectrum with higher resolution.

Since we have neglected the indirect coupling of $|J| = 1.25$ c/s, a more refined analysis of the spectrum will probably result in a slightly altered ratio.[6]

In Fig. 3 we show the 6-spin spectrum of 2,4-hexadiyne (dimethyl diacetylene) dissolved in a concentration of 20 mol % in 4,4-di-n-hexyloxy-azoxybenzene at 76° C. A theoretical analysis of this problem indicates that the spectrum should consist of thirty-four lines symmetrically arranged with respect to the centre of gravity of the total spectrum.[6] Some of the lines at low and high field have almost identical frequencies and their intensities have therefore been added in the theoretical spectrum. In order to demonstrate the influence of a change of B, we used a value of $B = -2920$ c/s for the calculation of the low-field part of the theoretical spectrum. Assuming again a proton distance in the methyl group of $r = 1.805$ Å, we obtain from the coupling B of the methyl protons a degree of order of the long molecular axis of

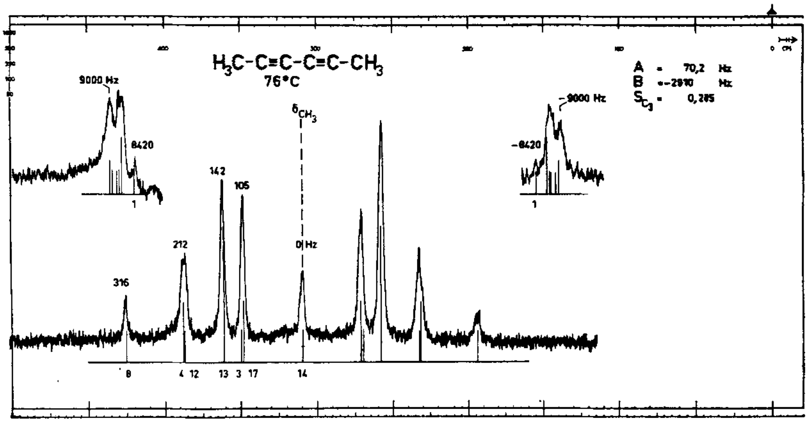


Figure 3. Experimental and theoretical spectrum of 20 mol % of 2,4-hexadiyne, dissolved in 4,4-di-n-hexyloxy-azoxybenzene at 76° C.

$$S_{\parallel} = 0.28 = -2S_{\perp}$$

To conclude this short discussion of some experimental results, we present in Fig. 4 the 100 Mc/s spectra of acetonitrile (upper trace) and of acetonitrile-2-^{13}C, dissolved in a concentration of about 15 mol % in 4,4-di-n-hexyloxy-azoxybenzene. The spectrum of the unlabelled compound consists—as is expected for a rotating methyl group[3]—of three lines with an intensity ratio of 1 : 2 : 1. The lower trace shows the same triplet and two further triplets arising

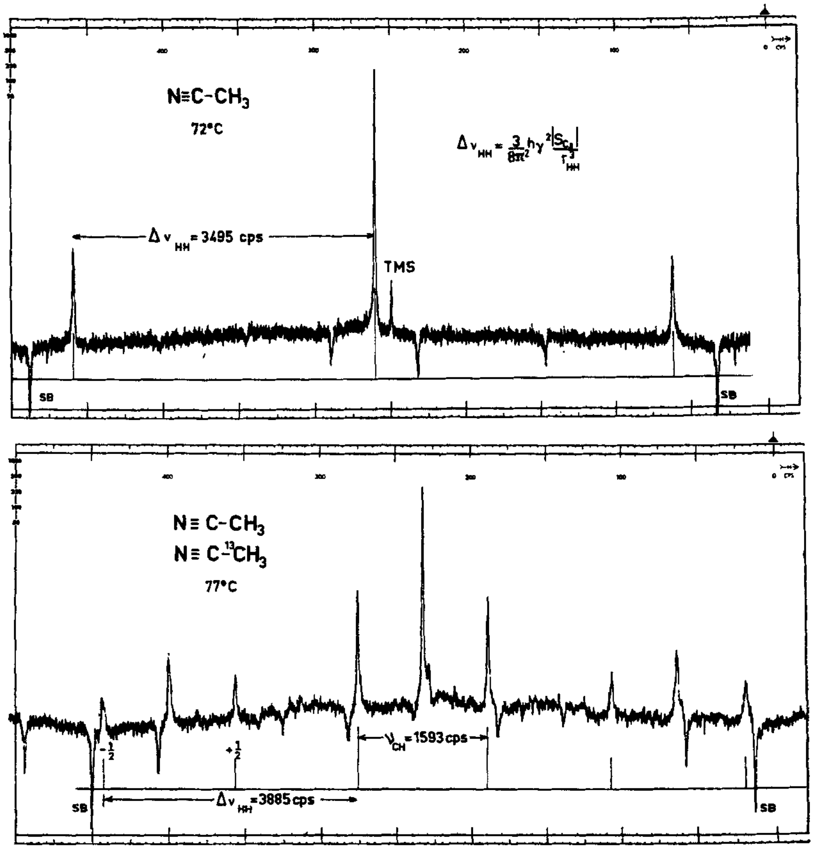


Figure 4. Experimental and theoretical spectrum of 20 mol % of acetonitrile at 72° C and of about 15 mol % of acetonitrile-2-^{13}C at 77° C, dissolved in 4,4-di-n-hexyloxy-azoxybenzene.

from about 60% of the molecules containing a fourth magnetic nucleus, namely a carbon-13 in the methyl group. The latter two triplets correspond to the two possible orientations of carbon-13 spin with respect to the magnetic field. The splitting ν_{CH} which can be observed three times in the spectrum is caused by the direct magnetic coupling of the carbon-13 nucleus with the methyl protons plus or minus the indirect coupling of $|J| = 136.5$ c/s, depending on the relative sign of the two parameters. If we assume that the long molecular axis is again oriented parallel to the magnetic field direction —as it was the case with the acetylenic compounds—then we can deduce that the absolute sign of the indirect coupling J is positive. This is in agreement with predictions derived from theoretical considerations and from determinations of relative signs of proton–proton- and proton–carbon-13 coupling constants.

III. Summary of the Results

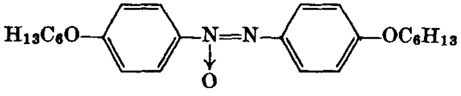
In Table 1 we present a survey of our preliminary results obtained for five different acetylenes, acetonitrile and methanol. In the second column we have summarized the anisotropy of the chemical shift of the acetylenic protons, defined as the difference of the shielding for a parallel and perpendicular orientation of the triple bond with respect to the magnetic field. With compounds (1) and (2) only approximate values could be obtained, for we had to assume that the screening tensor of the acetylenic proton is rotationally symmetric. Furthermore, instead of the S-value of the triple bond, we have used the S-value of the axis between the acetylenic and the methylene protons. The angle between these two axis is only about 14°. These assumptions seem to be justified since the $\Delta\sigma$-values are in qualitative agreement with the value obtained for compounds (3) and (4). Theoretical predictions of Pople[8] have shown that the diamagnetic anisotropy of the carbon triple bond gives rise to a $\Delta\sigma$-value of the order of 10 ppm, which is in excellent agreement with our experimental values. The anisotropy of compound (4) is slightly larger, partly due to the combined effect of both carbon triple bonds.

An unexpected behaviour has been found for acetonitrile. Here the methyl signal is shifted downfield in the nematic phase of 4,4-di-n-hexyloxy-azoxybenzene whereas in 4-n-octyloxy-benzoic acid no shift has been observed. Therefore, the diamagnetic contribution

TABLE 1 Preliminary Results Obtained for Seven Compounds

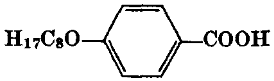
	Compound	$\equiv$C—H $\Delta\sigma_H = \sigma_{\parallel} - \sigma_{\perp}$	$S_{\parallel}, S_{C_3}$	Results	
				N.m.r.	MW-data
(1)	$H—C\equiv C—CH_2Cl$	$\sim 12.4 \cdot 10^{-6}$	~ 0.06		
(2)	$H—C\equiv C—CH_2Br$	~ 12.4	~ 0.05		
(3)	$H—C\equiv C—CH_3$	10.8	0·08	$\frac{R}{r} = 2.345 \pm 0.5\%$†	$\frac{R}{r} = 2.352$[7]
(4)	$H—C\equiv C—C\equiv C—CH_3$	13.0	0.18	$\frac{R}{r} = 3.705 \pm 0.7\%$	
(5)	$H_3C—C\equiv C—C\equiv C—CH_3$	—	0.28		
(6)	$^{13}N\equiv C—CH_3$ in I	—	0.12	$\measuredangle_{HCH} = 109°\ 2' \pm 2'$	109°16′[10]
	$N\equiv C—^{13}CH_3$ in II	—	0.10	$= 108°54' \pm 2'$	
(7)	$H—O—^{13}CH_3$ in II	—	0.005	$= 110°\ 3' \pm 8'$	109°2′ ± 45′[11]

I:



m.p. 80.5° C; c.p. 128° C

II:



m.p. 100° C; c.p. 144° C

† Note added in proof: In the meantime, an improved analysis, including the indirect coupling of $J = -2.7$ c/s gave $\frac{R}{r} = 2.353 \pm 0.2\%$.

of the triple bond is evidently compensated by a paramagnetic contribution, the magnitude of which depends on the specific nematic compound being used. An exact explanation of this behaviour is at present not possible. However, it seems likely that the difference between the two solvents is due to a partial protonation of the nitrogen atom in the nematic phase of 4-n-octyloxybenzoic acid (see below).

In the third column we have indicated the degree of order of the long molecular axis and of the C_3-symmetry axis of the methyl group, respectively. For their calculation we have made use of known microwave data for compounds (1), (2), (3) and (6). The data for compounds (4) and (5) have been assumed from the respective values of compound (3). A comparison of the S-values, which have been measured using similar concentrations and temperatures, qualitatively shows that the more elongated molecules possess a higher degree of order and one might speculate whether or not a compound with three acetylenic bonds will possess liquid crystalline properties.

A last and very important application of the technique of oriented molecules can only be mentioned here very briefly. From the two direct dipole–dipole couplings observed in the spectra of carbon-13 labelled methyl groups it is possible to obtain the ratio of the proton–proton and the carbon-13–proton distances and therefore, very accurate values for the H—C—H bond angle of the methyl group can be calculated. Our results for acetonitrile-2-^{13}C are given in the table: the H—C—H bond angle of the methyl group in acetonitrile has been found to be $108° 58' \pm 6'$ in two different nematic liquids. This is in excellent agreement with the value of $109° 16'$ as derived by microwave spectroscopy (r_0-structure, gas phase).[7] Since the experimental error is only $\pm 2'$ we presently believe that the difference of the bond angle in the two liquid crystals is real and again caused by the protonation as mentioned before. From similar measurements with methanol-^{13}C we obtained a bond angle of $110° 3' \pm 8'$. A more detailed discussion of these results including measurements on other carbon-13 labelled compounds as $N \equiv {}^{13}C—CH_3$ and $^{13}CH_3J$ will soon be published.[9]

REFERENCES

1. Saupe, A. and Englert, G., *Phys. Rev. Lett.* **11**, 462 (1963).
2. Saupe, A., *Z. Naturf.* **19a**, 161 (1964).
3. Englert, G. and Saupe, A., *Z. Naturf.* **19a**, 172 (1964).
4. Saupe, A., *Z. Naturf.* **20a**, 572 (1965).
5. Englert, G. and Saupe, A., *Z. Naturf.* **20a**, 40 (1965).
6. Englert, G., Saupe, A., and Weber, J.-P., to be published.
7. Costain, C. C., *J. Chem. Phys.* **29**, 864 (1958).
8. Pople, J. A., *Proc. Roy. Soc.* (*Lond.*) A **239**, 541 (1957).
9. Saupe, A. and Englert, G., submitted for publication in: *Advances in Chemistry Series.*
10. Thomas, L. F., Sherrard, E. I. S., and Sheridan, J., *Trans. Farad. Soc.* **51**, 619 (1955).
11. Venkatesvarlu, P. and Gordy, W., *J. Chem. Phys.* **23**, 1200 (1955).