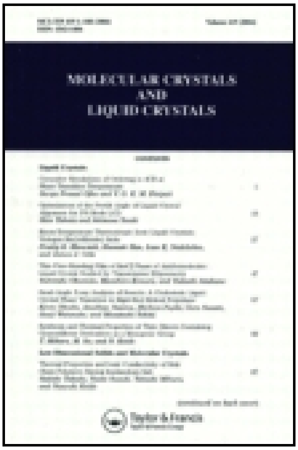

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Molecular Geometry of Acetonitrile, Determined by Proton Magnetic Resonance in Nematic Solutions

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Abstract—The PMR spectra of carbon-13 and nitrogen-15 substituted acetonitrile have been investigated in 3 different nematic solutions. From the direct magnetic spin-spin interactions values for the H—C—H—bond angle of the methyl group and for the other *relative* internuclear distances were calculated under the assumption that the anisotropic part of the indirect spin-spin interactions can be neglected.

Small differences in the molecular geometry were observed in the three nematic solvents and also between the latter and the gas phase (microwave data). Approximate nuclear positions can be calculated if the PMR data are combined with microwave data, e.g. the moment of inertia of the molecule in the gas phase. It is shown that the nuclear positions calculated by this method are in approximate agreement with pure microwave data. Under the assumption that acetonitrile is aligned preferentially parallel to the magnetic field, the absolute signs of the indirect spin couplings ${}^1J_{^{13}C-H}$, ${}^2J_{^{13}C-C-H}$ and ${}^3J_{^{15}N-CCH}$ are found to be positive, negative and negative, respectively.

Introduction

Anisotropic liquid crystals of the nematic type have been found to be extremely useful for the study of the proton magnetic resonance (PMR) spectra of dissolved molecules. Several reviews on this subject have appeared previously (see e.g. ref. (1), (2) and (3)). Whereas the nematic solvent itself produces, in general, only a very broad background signal, the spectrum of dissolved molecules obtained by conventional high resolution technique consists of a number of sharp peaks depending on the number of magnetic nuclei, the molecular geometry and orientation. The observed splittings are not only due to the chemical shifts and the indirect electron-coupled spin-spin interactions, as is the case in isotropic solvents, but are mainly arising from the direct through-space interactions of the magnetic nuclei. The observation of direct spin-spin interactions in nematic solutions has been explained to arise due to an ordering of the solute molecules by the intermolecular forces in the nematic solvent.[4,5] Since the direct magnetic interactions are proportional to $1/r^3$, r being the distance of two magnetic nuclei, accurate values of bond angles and relative internuclear distances can be calculated from these spectra.

At the 1st Conference on Liquid Crystals in 1965 we have reported, among other things, on the PMR spectra of acetonitrile and acetonitrile-2-^{13}C. In the meantime we have investigated further isotopically substituted species, namely with carbon-13 in position 1 and with nitrogen-15. This enabled a complete determination of the relative molecular geometry to be made. In the following, a comparison of our results obtained in three different nematic solvents will be given and discussed with respect to known microwave data.

1. Experimental

The following isotopically substituted molecules were available in mixtures together with the ordinary isotopic species:

A: $H_3{}^{13}C—CN$‡

B: $H_3C—{}^{13}CN + H_3{}^{13}C—CN + (H_3{}^{13}C—{}^{13}CN)$§

The signals of the latter could not be detected because of its low abundance. Since only a small quantity of

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‡ Purchased from Merck, Sharp & Dohme, Canada.

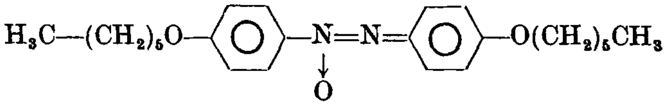
§ Kindly provided by Dr. H. Spiesecke, Ispra, Italy.

specimen B was available, experiments could only be performed in one nematic liquid (see below).

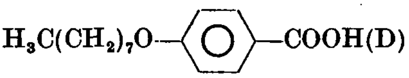
C: $H_3{}^{13}C$—CN + H_3C—$C^{15}N$ + $H_3{}^{13}C$—$C^{15}N$‡

As solvents we used the following compounds:

I: *p,p'*-di-*n*-hexyloxy-azoxybenzene

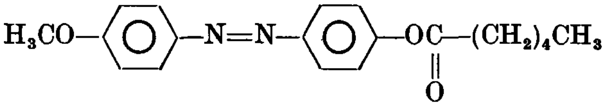


II: *p*-*n*-octyloxy-benzoic acid (partially deuterated)

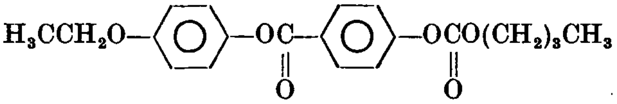


III: A 3 : 3 : 1 mixture§ (by weight) of

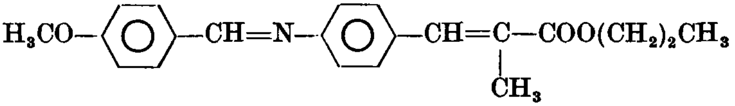
(a)



(b)



(c)



The latter solvent can be used at 27 °C (probe temperature of the HA 100 spectrometer) without heating. Since the sample tube can be left in the magnet over a long period in order to attain a good temperature equilibrium, solvent III has been found to give a very constant degree of orientation of the dissolved molecules. The use of similar mixtures of low melting point has been described elsewhere.[6,7,8]

‡ Synthesized by Dr. J. Würsch, Basle. Starting material was $H_3{}^{13}C$—CN and NO_2Na with *ca.* 30% ^{15}N.

§ These compounds were obtained from Dres. H. Els, H. Linde and E. Grell, Basle.

In general, several concentrations were used between 15 and 35 Mol %. Measurements have been done over the temperature range of 68 to 85 °C with solvent I, between 86 and 110 °C with solvent II, and at 27 °C with solvent III. In some cases spinning of the sample with about 150 r.p.m. was found to give sharper lines in the outer parts of the spectra.

2. Qualitative Discussion

In Fig. 1 we present as examples two PMR spectra of acetonitrile and of some of its isotopically substituted molecules partially oriented in the nematic phase of *p*-*n*-octyloxy-benzoic acid at 96 °C. The concentrations were 24 (above) and 28 Mol % (below). As has been shown previously,[9,10] the PMR spectrum of the first molecule consists of a triplet with relative intensities of 1 : 2 : 1. The splitting is only caused by the dipolar coupling of the equivalent protons of the rotating methyl group.

Each component of the triplet is further split into a doublet upon introduction of a carbon-13 of spin 1/2. The splitting now depends both on the direct and indirect spin-spin couplings. The latter are, however, in general smaller. A further splitting is observed upon substitution of a nitrogen-15 nucleus. The splitting is much smaller since the nitrogen is more distant from the protons. Typical values for the three splittings are given in the spectra. They depend on the concentrations, the temperatures and the solvent. In these spectra no splitting is observed due to the ^{14}N nucleus. It should be pointed out here that this nucleus should, in principle, split the lines into triplets, because it possesses spin $I = 1$. This has actually been observed by Spiesecke in the case of a similar molecule, namely methyl isocyanide $H_3C—NC$.[7] With acetonitrile, the ^{14}N-nucleus is effectively decoupled from the methyl protons due to rapid quadrupolar relaxation. It has no effect on the splittings but causes the relatively large line widths of the central components of the triplets compared to the outer lines which are assigned to the ^{15}N-molecules.

In the following section we shall briefly show how the values of

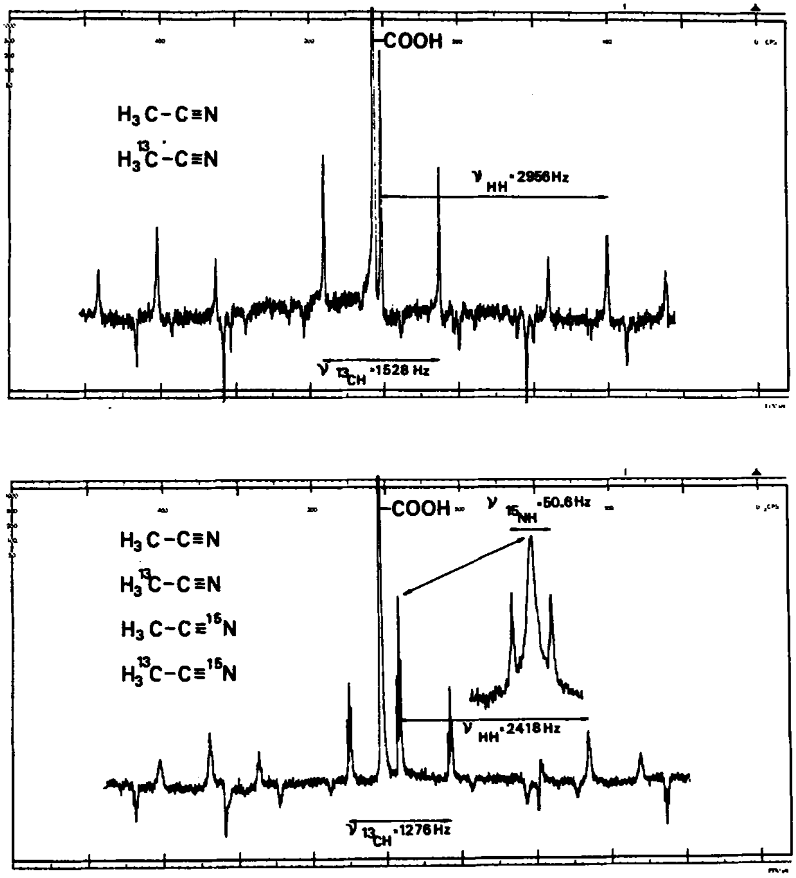


Figure 1. PMR spectra of isotopically substituted acetonitrile in *p*-*n*-octyloxybenzoic acid (COOH partly deuterated) at 96 °C.
upper part: 24.5 Mol %
lower part: 28 Mol %
The strongest line is due to the rapidly exchanging COOH-protons of the solvent. Signals with negative intensity are modulation sidebands ($n \times 2000$ Hz) introduced by the baseline stabilizer. Both spectra were recorded with spinning samples (*ca.* 150 r/m).

the direct dipolar couplings can be calculated from the observed splittings and which conclusions can be drawn concerning the relative signs of the direct and indirect spin-spin couplings.

3. Theoretical Background

The theory of the PMR spectra of oriented molecules has been extensively treated elsewhere.[1,5,9,10,11] We only have to put together here some fundamental equations which will be used later in the analysis of the spectra.

As has been shown,[9,10] the splitting ν_{HH} is given by

$$\nu_{\mathrm{HH}} = 3\,|\,B_{\mathrm{HH}}\,| \tag{1}$$

with the direct spin-spin coupling B_{HH} between the methyl protons defined by

$$B_{\mathrm{HH}} = \frac{h}{8\pi^2}\,\gamma_{\mathrm{P}}^2\,\frac{1}{r^3}\,S_{\mathrm{C}_3} \tag{2}$$

Here γ_{P} designates the gyromagnetic ratio of the proton, S_{C_3} the degree of orientation of the C_3-symmetry axis, r the interproton distance. Strictly, the direct dipolar coupling is proportional to $\langle 1/r^3 \rangle$, where the angular brackets imply an average over the molecular vibrations. This has to be kept in mind if one compares NMR data with the values obtained by other techniques, e.g. x-ray, electron diffraction or microwave spectroscopy. We assume that the influence of the molecular vibrations on the relative nuclear distances is not important with acetonitrile and we therefore neglect their influence in the following discussion.

We assume furthermore that the anisotropy of the indirect spin-spin coupling can be neglected and that their scalar values can be taken from the isotropic solution. Both assumptions seem to be justified since the structure parameters derived are in good agreement with those obtained by microwave spectroscopy.

The splittings $\nu_{^{13}\mathrm{CH}}$ and $\nu_{^{15}\mathrm{NH}}$ are given by[9]

$$\nu_{XH} = |\,2B_{XH} + J_{XH}\,| \tag{3}$$

For the calculation of the direct coupling the relative signs of the direct and indirect couplings B_{XH} and J_{XH} must be known. The former is given by

$$B_{\mathrm{XH}} = \frac{-h}{4\pi^2}\gamma_{\mathrm{X}}\gamma_{\mathrm{P}}\left(1 - \frac{3}{2}\sin^2\delta\right)\cdot S_{C_3}\cdot\frac{1}{r_{\mathrm{XH}}^3} \qquad (4)$$

Here δ denotes the angle between the internuclear vector r_{XH} and the C_3-symmetry axis.

Since the degree of orientation is not known, only the ratio of internuclear distances can be calculated. Combination of Eqs. (2) and (4) leads to

$$\frac{B_{\mathrm{XH}}}{B_{\mathrm{HH}}} = \frac{\gamma_{\mathrm{X}}}{\gamma_{\mathrm{P}}}\frac{r_{\mathrm{HH}}^3}{r_{\mathrm{XH}}^3}\left(\frac{r_{\mathrm{HH}}^2}{r_{\mathrm{XH}}^2} - 2\right) \qquad (5)$$

From the ratio of the distances the angle between the X,H-vector and the symmetry axis can be calculated. The H—C—C-angle β and the H—C—H-bond angle α of the methyl group are obtained from the relation

$$\frac{r_{\mathrm{HH}}}{r_{\mathrm{CH}}} = \sqrt{3}\sin\beta = 2\sin\frac{\alpha}{2} \qquad (6)$$

For the calculation of the direct couplings B_{XH} from Eq. (3) we used the following indirect coupling constants, measured in $\mathrm{CDCl_3}$-solution:

$$^1J_{^{13}\mathrm{CH}} = +\,136.0\ \mathrm{Hz}$$
$$^2J_{^{13}\mathrm{C-C-H}} = -\,10.0\ \mathrm{Hz}$$
$$^3J_{^{15}\mathrm{N-C-C-H}} = -\,1.75\ \mathrm{Hz}$$

Their relative signs have been determined by McFarlane[12] applying double resonance techniques in isotropic solution. As is discussed later, they are in agreement with our own measurements. Under the assumption that the long molecular axis of acetonitrile is preferentially oriented parallel to the magnetic field—as has already been found for similar shaped molecules[13]—the absolute sign of the first coupling was already proved to be positive.[9,10] It should be pointed out, however, that only the *relative* signs of B_{XH} and J_{XH} enter Eq. (3) and therefore the conclusions concerning the molecular structure are independent of the assumption of the absolute signs of the J's.

If the magnitude of J_{XH} is not too small compared to B_{XH}, the relative signs of both can be obtained by application of one of the following criteria:

(1) Only the correct combination of signs leads to reasonable values for the ratios of the internuclear distances.

(2) The wrong sign combination can be distinguished from the correct one since the former may result in a strong dependence of the ratios and bond angles on the concentration and temperature of the sample.

In the case of acetonitrile the following relative signs have been found to be correct:

$B_{^{13}\mathrm{CH}}$, $^{1}J_{^{13}\mathrm{CH}}$: like signs

$B_{^{13}\mathrm{C-CH}}$, $^{2}J_{^{13}\mathrm{CCH}}$: like signs

$B_{^{15}\mathrm{HN}}$, $^{3}J_{^{15}\mathrm{NH}}$: opposite signs

If one assumes a parallel orientation of the molecule with respect to the magnetic field, the three direct couplings $B_{^{13}\mathrm{CH}}$, $B_{^{13}\mathrm{C-C-H}}$ and $B_{^{15}\mathrm{NH}}$ will be positive, negative and positive, respectively. This is easily seen from Eq. (4). Therefore, the above given absolute signs of the indirect couplings are confirmed. The sign conversion of $B_{^{15}\mathrm{CH}}$ is due to the fact that the gyromagnetic ratio of this nucleus is negative.

In the following sections we confine our discussion of the results to the correct sign combinations given above. The values of the orientation parameter S_{C_3} in a given solvent is a function of temperature and concentration. In solvent I and II the observed range for S_{C_3} was between approximately 0.08 and 0.1. In solvent III a slightly lower S_{C_3}-value of 0.06 was observed. However, this does not seem to reflect any remarkable difference in the orientation properties of the latter solvent.

4. Determination of the Ratios of Internuclear Distances

As has already been mentioned only the ratios of internuclear distances can be determined from the ratios of the direct spin-spin couplings. In Table 1 we have put together the ratios of the different direct spin-spin couplings, obtained from the spectra of the isotopically substituted molecules in three nematic solvents. Since a significant dependence of these values on the concentrations and temperatures has not been found (with the correct sign combinations of the direct and indirect couplings), the measurements have been averaged. The standard deviations are given without consideration of systematic errors in the indirect coupling constants, which can be neglected. Since acetonitrile-1-^{13}C was available only in a small quantity, two values of the second column are missing and a comparison is possible only of the values in the first and third column. It is seen that the ratios of the direct couplings are slightly different in the three solvents and therefore the molecular geometry should be slightly different.

Table 1 Measured Ratios (absolute values) of the Direct Dipolar Couplings of Isotopically Substituted Acetonitriles in 3 Nematic Solvents

Solvent	$\left\lvert \frac{B_{^{13}\mathrm{CH}}}{B_{\mathrm{HH}}} \right\rvert$	$\left\lvert \frac{B_{^{13}\mathrm{C-C-H}}}{B_{\mathrm{HH}}} \right\rvert$	$\left\lvert \frac{B_{^{15}\mathrm{NH}}}{B_{\mathrm{HH}}} \right\rvert$
p,p-di-*n*-hexyloxyazoxybenzene I 68–85 °C	0.7096 ± 0.0004	0.2000 ± 0.0004	0.03248 ± 0.00008
p-*n*-octyloxybenzoic acid II 86–110 °C	0.7063 ± 0.0007	—	0.03214 ± 0.0002
mixture III 27 °C	0.7159 ± 0.0007	—	0.03183 ± 0.00009

The magnitude of the deviations can be better visualized from Table 2, which contains the calculated bond angles and ratios of the internuclear distances. From the PMR values it is seen that the molecular geometry in the three nematic solvents is actually slightly different. For example, the H—C—H-bond angle of the methyl group varies by about 12′ on passing from solvent II to III.

TABLE 2 Structural Parameters of Acetonitrile, obtained by PMR in 3 Different Nematic Solvents, and Comparison with Known Microwave Data (r_0- and r_s-structures; see ref. (14)).

Parameter	PMR Data			Microwave Data (Gas Phase)	
	Solvent I	Solvent II	Solvent III	r_0	r_s
$\sphericalangle$(H—C—H)	109° (3.5 ± 0.5)′	108° (59.5 ± 0.5)′	109° (11.3 ± 1)′	109° 16.5′	109° 29.5′
$\sphericalangle$(H—C—C)	109° (52.9 ± 0.5)′	109° (56.8 ± 0.5)′	109° (45.4 ± 1.2)′	109° 40′	109° 27′
r_{HH}/r_{CH}	1.62882 ± 0.00009	1.62815 ± 0.00017	1.6301 ± 0.0002	1.6310	1.6332
r_{HH}/r_{CCH}	0.8563 ± 0.0009	—	—	0.85935	0.8576
r_{HH}/r_{NH}	0.5772 ± 0.0005	0.575 ± 0.0014	0.5727 ± 0.0006	0.57255	0.5705

For comparison, the last two columns present the microwave data[14] of the r_0- and r_s-structure. Here the limits of error are not stated, however it is seen that especially the value of the H—C—H-bond angle considerably depends on the method applied for its calculation. The bond angles of the r_0-structure closely agrees with those obtained in solvent III. It should be pointed out that the microwave data are calculated from molecules in the vibrational groundstate, whereas the PMR values might also be influenced to a very small extent by excited vibrational states. However, since the frequency of the CH_3-deformation is rather high, we can assume that its contribution can be neglected.

More important will be the influence of the zero-point vibrations. They should result in small deviations of the internuclear distances obtained by different methods even in the case of the vibrational groundstate and a harmonical potential. These effects are, however, difficult to be calculated. They may partly explain some of the deviations between the PMR and microwave data summarized in Table 2, but they will not explain the difference between the PMR values of different solvents obtained at equal S-values.

As is seen, the best agreement was achieved between the r_0-

structure and the values obtained in solvent III. Here the bond angle and the two ratios differ only by 0.08, 0.06 and 0.03%. This indicates that the different assumptions involved in the determination of relative internuclear distances by PMR spectroscopy must be essentially correct. We believe that some of the differences between the molecular geometry in the three nematic solvents and between the latter and the microwave data correspond to real changes that are caused by changes in the intermolecular forces.

5. Calculation of Absolute Internuclear Distances

It has already been pointed out that absolute internuclear distances cannot directly be obtained from PMR measurements in nematic liquids since the degree of orientation cannot be derived with sufficient accuracy. If one internuclear distance is precisely known from other methods, the remaining ones can be calculated, although considerable errors may be introduced by this.

We have chosen another way to obtain the absolute internuclear distances. We assume that the moment of inertia, which is easily obtained with high precision by microwave spectroscopy, is not changed on passing from the gas phase to the liquid. It is furthermore assumed that by isotropic substitution the internuclear distances will not be changed. Then, we use the rotational constant of acetonitrile in the vibrational groundstate[15]

$$B_0 = 9.19883 \cdot 10^9 \text{ Hz}$$

to calculate the moment of inertia referred to an axis perpendicular to the molecular symmetry axis:

$$I_0 = 9.1223 \cdot 10^{-39} \text{ g} \cdot \text{cm}^2.$$

With the relative internuclear distances obtained in *p,p*-di-*n*-hexyloxy-azoxybenzene (I) summarized in column 2 of Table 2, we finally calculated the internuclear distances presented in Table 3. The bond angles of Table 2 are also given here together with the pure microwave data.

TABLE 3 Comparison of the Combined PMR (solvent I)/Microwave—and Pure Microwave Data for Acetonitrile

	PMR/MW	MW	
		r_0	r_s
∢H—C—C	109°(52.9 ± 0.5)′	109° 40′	109° 27′
r_{CH}	1.125 Å	1.112 Å	1.1036 Å
r_{CC}	1.477 Å	1.4582 Å	1.4584 Å
r_{CN}	1.133 Å	1.1572 Å	1.1571 Å

It is seen that the internuclear distances obtained by the two different methods are in reasonable agreement with deviations between 0.013 and 0.024 Å. It is at present not yet possible to quantitatively estimate the different sources of these deviations.

Part of the deviations observed in Table 3 are certainly caused by the influence of molecular vibrations, mainly zero-point vibrations, but another part of the differences is due to real changes of the molecular geometry in the liquid phase. This is actually to be expected. Polar bonds, for instance, such as the CN-bond will be affected in the liquid phase because of an electric reaction field which tends to increase the bond polarity. By this, the hybridisation of the two atoms will be altered and slight changes in the internuclear distances might therefore occur. Our results indicate indeed a shortening of the C≡N bond distance in solvent I.

6. Conclusions

We have shown that PMR investigations on molecules dissolved in nematic liquids can provide valuable insight into the molecular geometry in the liquid phase. In the case of acetonitrile the precision of this technique is sufficient as to allow the detection of very small changes in the bond angles and in the relative internuclear distances observed in different solvents. A comparison with known microwave data indicates that the molecular structure is also slightly different in the liquid and the gas phase. Further work has to be done, however, before these rather small differences will be completely understood.

Aknowledgement

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