Deuterium Quadrupolar Parameters from ^{1}H and ^{2}H NMR Spectra for Pyridine-d_5, Benzonitrile-d_5 and Chlorobenzene-d_5 Using Liquid Crystal Solvents*

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The quadrupolar coupling constants (DQCC) and the asymmetry parameters (η) for the *ortho*, *meta* and *para* deuterons in pyridine-d_5, benzonitrile-d_5 and chlorobenzene-d_5 were determined by NMR spectroscopy in oriented phases. The ^{1}H and ^{2}H NMR spectra were recorded in the following solutions in liquid crystal solvents: pyridine + pyridine-d_5 in PCH, in ZLI 1167 and in EBBA; benzonitrile + benzonitrile-d_5 and chlorobenzene + chlorobenzene-d_5 in the same solvents.

The order parameters of the non-deuterated solutes in the various solutions were calculated using the dipolar couplings of the proton spectra and the r^α structures taken from the literature. The same order parameters were assumed to describe also the orientation of the deuterated solute in the corresponding solutions.

Each ^{2}H spectrum yielded three quadrupolar splittings for the three different deuterated positions in the labelled solute. The splittings from the three different solutions of the same solute, together with the order parameters and the r^α structure, were used to determine DQCC and η of the *ortho, meta* and *para* deuterons (Pyridine-d_5: $\mathrm{DQCC}^{\mathrm{ortho}} = 183(1)$ kHz, $\eta^{\mathrm{ortho}} = 0.030(5)$, $\mathrm{DQCC}^{\mathrm{meta}} = 185(1)$ kHz, $\eta^{\mathrm{meta}} = 0.030(10)$, $\mathrm{DQCC}^{\mathrm{para}} = 188(6)$ kHz, $\eta^{\mathrm{para}} = 0.01(5)$. Benzonitrile-$d_5$: $\mathrm{DQCC}^{\mathrm{ortho}} = 171(12)$ kHz, $\eta^{\mathrm{ortho}} = 0.07(3)$, $\mathrm{DQCC}^{\mathrm{meta}} = 175(12)$ kHz, $\eta^{\mathrm{meta}} = 0.05(3)$, $\mathrm{DQCC}^{\mathrm{para}} = 176(4)$ kHz, $\eta^{\mathrm{para}} = 0.10(7)$. Chlorobenzene-$d_5$: $\mathrm{DQCC}^{\mathrm{ortho}} = 180(2)$ kHz, $\eta^{\mathrm{ortho}} = 0.06(1)$, $\mathrm{DQCC}^{\mathrm{meta}} = 174(2)$ kHz, $\eta^{\mathrm{meta}} = 0.09(3)$, $\mathrm{DQCC}^{\mathrm{para}} = 182(4)$ kHz, $\eta^{\mathrm{para}} = 0.06(4)$). The results are discussed, as well as the limits and possibilities of the method used.

Introduction

The general methods for the determination of the deuterium quadrupolar coupling constant (e^2Qq/h = DQCC) and the asymmetry parameter η in the fluid state are based principally on measurements of deuterium spin relaxation in liquids and of quadrupolar splittings in the ^{2}H-NMR spectra of molecules partially oriented in liquid crystal phases [1]. The knowledge of these parameters is very useful both for dynamic studies of liquids and liquid crystals [2] and for orientational order investigations in ordered fluids [3]. The underlying hypothesis for the use of the quadrupolar parameters is that they can be transferred from the solvent where they are determined to other solvents, i.e. that the solvent does not substantially affect their values. Owing to the lack of experimental data, however, quadrupolar parameters from the solid state are often used for the liquid and liquid crystal phases, or "standard" values have to be assumed.

The determination of both DQCC and η in the fluid phase for each deuterated position in a given molecule is not an easy task. In the majority of the studies performed so far η has been neglected or assumed [1]. Recently, however, it has been shown that, provided a good geometry and consequently precise values of the ordering tensor components are available at least in two different liquid crystal solvents, a selective determination of DQCC and η of deuterium is possible [4, 5].

Some assumptions are implicit in the procedure we followed in this work: (a) the direction of maximum electric field gradient (e.f.g.) is supposed to coincide with the C−D bond direction and the labelled molecule is assumed to have the same bond

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angles as the unlabelled species; (b) the deuterated molecule is supposed to be oriented in the same way as the unlabelled one in the liquid crystal phase; (c) DQCC and η are supposed not to differ significantly in various solvents. The validity of these assumptions is difficult to assess. It is undoubtedly necessary to choose solvents that do not show apparent distorting effects on the molecular geometry due to the presence of many-site exchange [6] or non-negligible rotation-vibration correlation [7–9]. However, even if this precaution is taken, some of our assumptions could be inadequate.

In order to test the limits and the possibilities of the method, we have undertaken an investigation of a series of aromatic molecules in various liquid crystal solvents. Here we present the results for pyridine (Py), benzonitrile (CNB) and chlorobenzene (ClB). These results will be discussed as far as the cited assumptions are concerned and compared with the data available in the literature.

Experimental

The ^{1}H and ^{2}H NMR spectra of the following nematic solutions were recorded at 28 °C: (I) Py + Py-d_5 in the mixture ZLI 1167 (Merck), (II) Py + Py-d_5 in trans-4-n-heptyl-(4′-cyanophenyl)cyclohexane, PCH (Merck), (III) Py + Py-d_5 in 4-ethoxybenzylidene-4′-n-butylaniline, EBBA, (IV) CNB + CNB-d_5 in ZLI 1167, (V) CNB + CNB-d_5 in PCH, (VI) CNB + CNB-d_5 in EBBA, (VII) ClB + ClB-d_5 in ZLI 1167, (VIII) ClB + ClB-d_5 in PCH, and (IX) ClB + ClB-d_5 in EBBA. In each solution the concentrations of the unlabelled and deuterated solute were 6% and 9% by weight, respectively. Solutions (VII) and (VIII) were prepared in a 5 mm tube and the related spectra were recorded on a VARIAN XL 400 spectrometer in an unlocked operation. Solutions (III) and (IX) were prepared in a double wall tube and their spectra were recorded on a Jeol GX 270 instrument. In this case, for the ^{1}H spectra, the ^{1}H decoupling coil in the ^{2}H probe was used; the signal for the internal ^{2}H lock was supplied by D_2O put in the interval space of the tube. The spectra of the remaining solutions (contained in 10 mm tubes) were recorded on a VARIAN XL 100 spectrometer with external ^{19}F lock. The sample was spun whenever allowed by the instrumental characteristics and by the ordering properties of the nematic solvent, i.e. for solutions (I), (III), (IV), (VIII) and (IX). Some pairs of measurements (^{1}H- and ^{2}H-spectra of the same solution) were repeated twice in order to verify the reproducibility and stability of the experimental conditions.

Spectral Analysis and Determination of Quadrupolar Parameters

The analysis of the proton spectra was performed using the LEQUOR program, with indirect *J* couplings taken from the literature [10–12]. The analysis of the ^{2}H spectra [13] furnished the quadrupolar splittings listed in Table 1. The experimental ^{2}H-NMR spectrum of ClB in PCH is shown in Figure 1.

The possibility of extracting reliable orientational parameters from a set of dipolar couplings is wholly dependent on the knowledge of the precise molecular geometry. The r^α structures of Py (refs. [14, 15], partial structures), CNB [11] and ClB [16] are known from accurate NMR studies in liquid crystal phases. In these works ZLI 1167 and PCH are shown to be non-distorting solvents for the solutes of interest, since the yielded r^α structures are in excellent agreement with the microwave results. The microwave geometry of Py [17] and the r^α structures for CNB and ClB were used throughout the present work, when structural parameters were required, for both labelled and unlabelled solutes.

The dipolar couplings obtained from the proton spectra were corrected for the effect of harmonic vibration according to the procedure proposed by Lucas [18], using the vibrational frequencies and

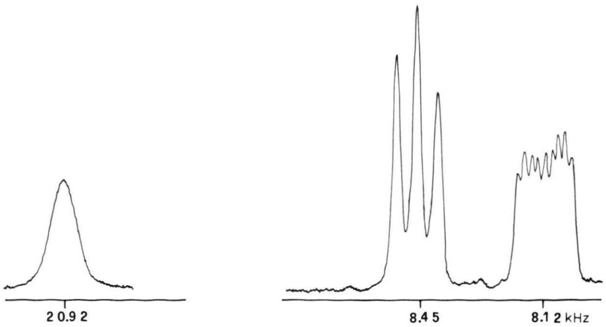

Fig. 1. 61.4 MHz ^{2}H NMR spectrum (low field half spectrum) of deuterated chlorobenzene partially oriented in PCH liquid crystal at 28 °C.

Table 1. Order parameters and quadrupolar splittings (kHz) for pyridine-d_5, benzonitrile-d_5 and chlorobenzene-d_5. Quadrupolar coupling constants (DQCC, kHz) and asymmetry parameters (η).

	Pyridine-d_5			Benzonitrile-d_5			Chlorobenzene-d_5		
	ZLI 1167	PCH	EBBA	ZLI 1167	PCH	EBBA	ZLI 1167	PCH	EBBA
S_{xx}	0.0622(2)	0.1171(4)	0.0233(4)	0.0128(1)	−0.0147(1)	−0.0369(1)	− 0.0139(1)	−0.0237(1)	−0.0384(2)
S_{yy}	− 0.0137(2)	0.0446(4)	0.0477(4)	− 0.1242(5)	0.1972(5)	−0.1192(4)	0.0961(4)	0.1493(4)	0.1635(5)
$\Delta\nu^{\text{ortho}}$	−13.47(3)	21.13(3)	8.62(2)	− 6.74(1)	12.35(2)	1.85(1)	−10.61(1)	16.90(1)	5.21(2)
$\Delta\nu^{\text{meta}}$	−14.57(3)	22.53(3)	8.27(2)	− 6.37(1)	11.79(2)	1.42(1)	−10.18(1)	16.23(1)	4.35(2)
$\Delta\nu^{\text{para}}$	− 4.13(2)	9.63(2)	13.52(5)	−34.00(3)	53.51(4)	31.92(3)	−26.96(3)	41.84(4)	45.10(20)
$\text{DQCC}^{\text{ortho}}$		183(1)			171(12)			180(2)	
η^{ortho}		0.030(5)			0.07(3)			0.06(1)	
$\text{DQCC}^{\text{meta}}$		185(1)			175(12)			174(2)	
η^{meta}		0.030(10)			0.05(3)			0.09(1)	
$\text{DQCC}^{\text{para}}$		188(6)			176(5)			182(4)	
η^{para}		0.01(5)			0.10(7)			0.06(4)	

valence force fields for Py [14], CNB [19] and ClB [20] known from the literature.

By means of the SHAPE computer program, the order parameters for the unlabelled solute in each solution were extracted from the corrected dipolar couplings. The order parameters are collected in Table 1. If it is assumed that the isotopic effect on the orientation of Py, CNB and ClB in the nematic solution is negligible, the order parameters so determined can be used to describe also the ordering of the deuterated solute in every solution.

Each of the deuterium quadrupolar splittings, $\Delta\nu$, obtained from the ^{2}H-NMR spectra can be expressed as [21]

$$\Delta\nu = (3/2)\, q_{aa}\{S_{aa} + \eta(S_{bb} - S_{cc})/3\}, \qquad (1)$$

where $S_{\alpha\beta}$ are the elements of the Saupe ordering matrix, a, b, c denote the principal axes of the e.f.g. tensor, a being the axis of maximum e.f.g. (see Figure 2). q_{aa}, the component of the e.f.g. tensor along axis a, is the deuterium quadrupolar coupling constant DQCC and η is the asymmetry parameter $(q_{bb} - q_{cc})/q_{aa}$.

The elements of the order tensor in the a, b, c frame can easily be obtained from those in the x, y, z frame using the transformation between two coordinate systems of a second rank cartesian tensor [21]. To do this it is necessary to locate the a, b, c reference frame with respect to the x, y, z one; as is usually assumed, the a axis was taken along the C−D bond direction (see Figure 2). The c axis was chosen perpendicular to the molecular plane.

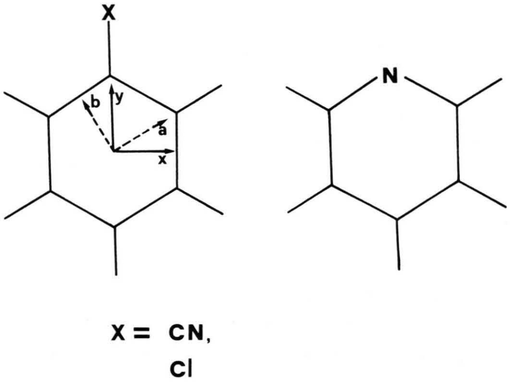

Fig. 2. Reference frames used: (x, y, z), where the molecular ordering matrix is diagonal and (a, b, c), where the e.f.g. tensor on the *ortho* deuteron is diagonal.

DQCC and η, supposed to be independent of solvent effects, could eventually be determined for each of the three different deuterons in Py-d_5, CNB-d_5 and ClB-d_5 by solving a set of three independent equations of the type of (1) (the three equations refer to the same solute in the three different solvents). The results thus obtained are shown in Table 1.

Discussion

All our results are in good or fairly good agreement with the values found by previous studies for ^{2}H in aromatic compounds (DQCC = 175−185 kHz, with $\eta = 0.04-0.06$ [4, 5, 14, 22-30]. Other determinations of the quadrupolar parameters are reported in refs. [4, 14, 23, 30] for Py and in [25 and 27] for ClB). This seems to indicate that none of our assumptions is dramatically inadequate. Anyway, some difficulties which cannot be overlooked appear to put limits to the precision and applicability of the method.

First of all, in order to have an overdetermined system of equations for each deuteron, it is necessary to collect data in many solvents; moreover, the orientation of the solute in the different solvents must be described by uncorrelated sets of order parameters. On the other hand, as already stated, a necessary condition for a meaningful determination of DQCC and η is the use of non-distorting solvents. If we consider the graphic solution of (1) shown in Fig. 3 for the *meta* and *para* deuterons of CNB-d$_5$, it clearly appears that the curves (DQCC as a function of η) relative to ZLI 1167 and PCH are almost superimposed, owing to the strong correlation between the order parameters of CNB in this couple of solvents. A similar situation is found for all the different deuterons considered. This unfortunately precludes the possibility of obtaining a good solution for DQCC and η using only these solvents, which have been shown not to give significant distorting effects on many solutes and, in particular, on Py [14, 15], CNB [11] and ClB [16]. Therefore, we also used the data from EBBA, even if this solvent is known as prone to give multi-site exchange, vibration-rotation correlation or "solvent effects" not clearly defined on small solute molecules [6, 31-33]. In the case of our solutes in EBBA, however, we have found no evidence of such effects, since the dipolar couplings of the ^{1}H spectra were well fitted using the r^α structures determined in ZLI 1167 or PCH.

Another critical point lies in the fact that the values of quadrupolar parameters obtained for the *ortho* and *meta* deuterons depend strongly on the direction chosen for the axis of maximum electric field gradient. In fact, in previous works, the abnormal values found for the *ortho* and *meta* deuterons in pyridine-d$_5$ [4] and for the *ortho* deuterons in nitrobenzene-d$_5$ [5] could be easily corrected by rotating this direction by only some tenths of a degree in the case of pyridine and by 2° in the other case. As already stated, the *a* axis is assumed to be collinear with the C-D bond direction, which in turn is taken coincident with the C-H direction in the unlabelled molecule. Either one or both of these assumptions might be incorrect. In particular, the isotopic effect on the structure of the deuterated molecule or on the vibrational correction could be significant. Moreover, the mentioned solute-solvent interaction effects, even when not clearly revealed and recognized, can be present in the nematic solution and cause a false determination of the order parameters and geometry.

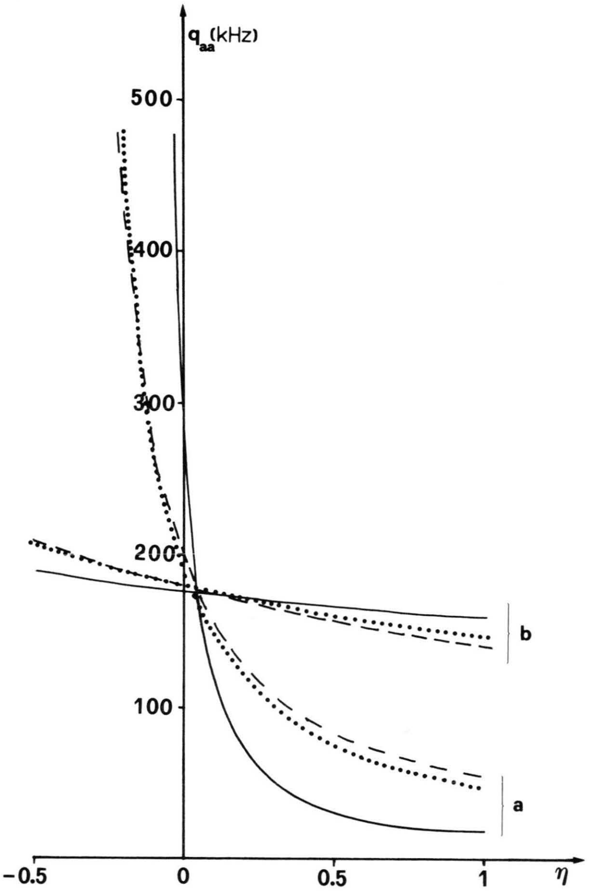

Fig. 3. q_{aa} versus η (see Eq. (1)) for the *meta* (a) and *para* (b) deuterons of benzonitrile-d$_5$ dissolved in PCH (- - -), ZLI (· · · ·) and EBBA (——).

A third difficulty originates from the assumption of equal orientation for the deuterated and the unlabelled molecule in the liquid crystal phase. An isotopic effect on the order parameters has been hypothesized elsewhere [28] and cannot be excluded. Furthermore, the ^{1}H and ^{2}H spectra of the same solution are recorded at different times, and even a small variation of the temperature at which the two spectra are recorded can cause a significant change of the order parameters. An error of more than 2% on the S values, which in our cases can correspond to a temperature variation of 2 °C, yields unacceptable results.

All these facts prevent in practice a detailed comparison of the results and a discussion of small differences between values of the parameters for *ortho*, *meta* and *para* deuterons.

In conclusion, up to now the liquid crystal method has revealed to be the most reliable and promising for the determination of DQCC and η for the various deuterons in molecules in the fluid phase, but a series of problems remains. Perhaps the most serious is the problem of accounting properly for the solvent effects. Some of these effects, however, have been tackled recently for simple and symmetric cases [7, 34, 35] and there is hope that the extension to bigger non-symmetric molecules will be possible in the near future.

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