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^{14}N nuclear quadrupole double resonance at zero magnetic field in the smectic *C* and nematic mesophases of HpAB

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Pure nuclear-quadrupole-resonance spectra have been measured in both nematic and smectic *C* liquid crystalline mesophases of 4-4′-bis-heptyloxy-azoxy-benzene (HpAB). The experiment involves fast-field-cycling NMR of protons and irradiation of the quadrupole ^{14}N nuclei by means of a second radio-frequency pulse during the zero-magnetic-field period. The obtained spectra show the presence of three inequivalent nitrogen nuclei in the smectic mesophase and four resolved chemically inequivalent nitrogens in the nematic. A local microstructure composed of bimolecular units explains the results. [S0163-1829(97)06229-2]

Liquid crystalline materials flow like liquids, but simultaneously present both macro- and microscopic anisotropy. The smectic *C* (Sm*C*) mesophase has biaxial symmetry of monoclinic class,[1] which originates in the coupling between the molecular tilt angle and the layer thickness. On the contrary, the nematic (Nm) phase is in general reported to be optically uniaxial.

Nuclear quadrupole resonance (NQR) is a useful experimental technique to study local order and molecular-dynamical properties.[2] Due to the averaging of the electric-field gradient tensor (efg tensor) and the relatively poor abundance of quadrupole nuclei in liquid crystal molecules, conventional NQR spectroscopy becomes unrealizable with the actual technological facilities in existence. However, indirect detection of the quadrupole interaction in liquid crystals can be achieved using proton Zeeman-quadrupole nuclei cross relaxation techniques.[3–8] From the NQR point of view, local order biaxiality in liquid crystals is observed by an effective asymmetry of the efg tensor ($\eta \neq 0$).[9–11]

In a recent work[8] we have discussed the microscopic structure of 4-4′-bis-heptyloxy-azoxy-benzene (HpAB) in the Sm*C* mesophase. We concluded that the elemental ‘‘building block’’ of the fluid mesophase is composed of two molecules. The evidence arises from measurements of the quadrupole dip (QD) structure observed on the spin-lattice relaxation dispersion $T_1(\nu_L)$. Eight quadrupole dips were measured in the Larmor frequency range from 300 kHz to 4 MHz. This fact can only be explained by assuming three inequivalent ^{14}N nuclei. As the HpAB molecule has only two nitrogens, a bimolecular elemental unit must be considered in describing the local liquid crystalline microstructure. This seems to be a characteristic legacy from the solid state, since in that situation the same inequivalences between the ^{14}N were also found for PAA.[12]

In this work we present evidence by using a zero-field nuclear-quadrupole-double-resonance (NQDOR) technique.[13,14] This technique allows us to measure the *pure* ^{14}N NQR spectra, i.e., at *zero external magnetic field*.

These results of the Sm*C* mesophase agree completely with the previous ones.[8] In addition, the study was extended to the Nm mesophase. Within the Nm temperature range, a clear local order biaxiality is present at low temperatures, just over the Sm*C*-Nm critical point. Moreover, four inequivalent nitrogens are resolved, indicating that bimolecular structure is also present in the Nm mesophase. Approaching the Nm-isotropic phase transition, resonances become noticeably broadened.

The experimental technique combines electronically fast-field cycling and two different radio-frequency excitations of the sample. The experiment consists of three different steps: polarization of the sample, irradiation of quadrupole transitions at zero field, and detection of the proton nuclear-magnetic-resonance (NMR) signal. During polarization the spin system is allowed to reach thermal equilibrium with the high magnetic field (4.2 kG) at the lattice temperature. In a second step, the external field is adiabatically switched off, and an allowed ^{14}N quadrupole transition is irradiated by a radio-frequency (rf) pulse. If the strong rf pulse frequency is nearly coincident with the quadrupole transition one, the spin quenching between protons and nitrogens at zero external static magnetic field[15] could be partially removed (‘‘solid-state effect’’[13]), and thermal contact between the spin systems takes place. The irradiation period must be of course shorter than proton T_1 at zero field. At the end of this step, the rf pulse is switched off and the Zeeman magnetic field is switched on again. During the raising and lowering of the external field, all ^{14}N quadrupole transitions are ‘‘level crossed’’ by the Zeeman splitting, and an additional thermal contact between the different spin systems takes place. During thermal contact, polarization is transferred from one spin system to another. If a quadrupole transition is saturated, proton spin polarization is partially destroyed when switching on the field, and in consequence, the proton NMR signal at high field during the detection step will be smaller than without quadrupole level saturation. A constant magnetic field of 0.7 kG was applied to the sample between measuring periods in order to externally preserve the macroscopic molecular order through the liquid crystalline sample.

The double-resonance spectrometer is a modified version of our homemade fast-field cycling relaxometer.[8] In order to improve the heating of the quadrupole system during irradiation process, phase reversal at each 500 μs was used in the rf pulse. The hardware will be described elsewhere. Sample purification and thermal control were set with the same care

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TABLE I. NQR spectral parameter obtained from the NQDOR experiment of HpAB in the Sm*C* at $T = 82$ °C. In this case, the ν_0 lines of N_1 and N_2 are interchanged respect to the frequency assignment of Ref. 8, because $\nu_+ - \nu_-$ is greater for N_2. As can be seen, this fact has no important consequence on the final results of κ and η. ν_0 of N_3 is taken as 30 kHz from previous QD data (this transition is not affected by the presence or not of the magnetic field).

	N_1	N_2	$N_{3,4}$
ν_+ [kHz]	2738	3806	837
ν_- [kHz]	2399	3301	800
ν_0 [kHz]	471	543	30
κ [kHz]	3425	4738	1091
η	0.275	0.23	0.055

as described in Ref. 8. The same thermal treatment was used for both mesophases: i.e., cooling from the isotropic liquid state under a constant magnetic field of 0.7 kG. A 0.4 Ω resistor was connected between ground and the rf coil in order to monitor and control the rf power during the irradiation step. The same coil is used for quadrupole nuclei irradiation and detection of the high-magnetic-field NMR proton signal. A lead relay bank switches it between the corresponding tuning networks and rf power suppliers. No resonances were found in a sample of water from 300 to 5000 kHz.

The polarization time was 1300 ms for the Sm*C* mesophase and 1500 ms for the Nm. The external magnetic field was switched off to zero during 15 ms, and the rf pulse length was 9 ms in all cases. The rf magnetic-field amplitude was 0.4 G (peak to peak).

At zero external magnetic field spin $I = 1$ quadrupole spectra consist of three lines at frequencies ν_+, ν_-, and ν_0 given by the expressions

$$\nu_+ = \frac{3}{4}\kappa\left(1 + \frac{\eta}{3}\right), \tag{1}$$

$$\nu_- = \frac{3}{4}\kappa\left(1 - \frac{\eta}{3}\right), \tag{2}$$

$$\nu_0 = \nu_+ - \nu_- = \frac{\kappa\eta}{2}, \tag{3}$$

where κ is the quadrupole coupling constant and η is the asymmetry parameter of the efg tensor at the nuclear site. From these expressions κ and η can be calculated.

Table I contains frequency assignations and the values of κ and η for the different ^{14}N nuclei of the bimolecular unit cell at $T = 82$ °C (see Fig. 1). Results agree with previous analysis of quadrupole dips found in the $T_1(\nu_L)$ dispersion, and frequency assignations of the present work are adopted from the previous one. Both QD's and the present resonance frequency dispersions are closely similar. Slightly different frequency positions–calculated to be between 1% and 4%—are expected from the fact that NQDOR spectra are measured at zero field. Resonances at 800 and 837 kHz are strong enough to destroy completely the proton magnetization **M** (signal amplitude). This may be associated with the fact that two nonresolved nitrogens absorb energy from the rf field at these frequencies. Measured values of ν_0 are not equal to $\nu_+ - \nu_-$ (see Table I). This difference is associated with experimental uncertainties. In fact, if the high-frequency quadruplet lines are determined, an uncertainty of 5–200 kHz between $\nu_+ - \nu_-$ and ν_0 could arise.

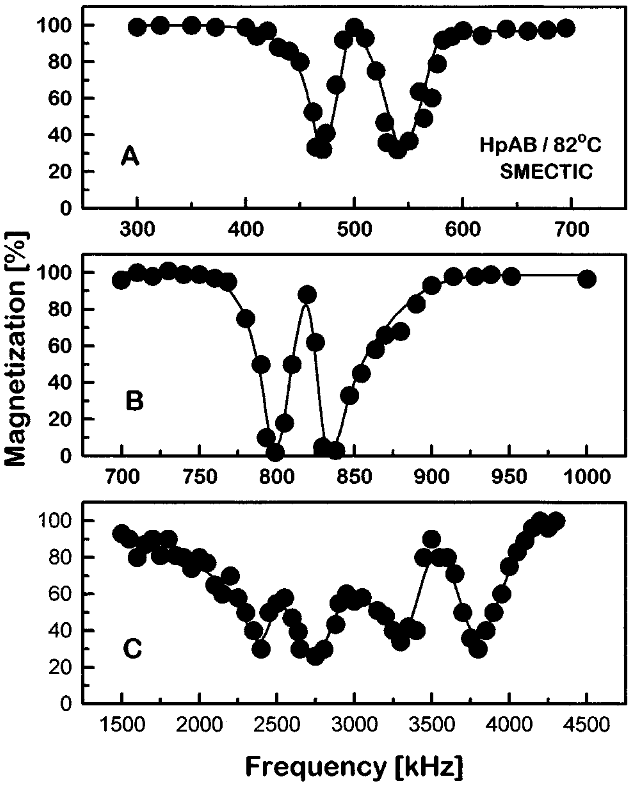

FIG. 1. NQDOR spectra of HpAB at $T = 82$ °C. ^{14}N resonances were found to be in close agreement with previous data of QD's found in the spin-lattice relaxation time experiment reported in Ref. 8. Solid line was built up by successive smoothing and fast Fourier transform (FFT) filtering of data just to guide the eye.

Experimental results obtained in the Nm phase at $T = 98$ °C are depicted in Fig. 2. The spectral structure is similar to that of the Sm*C* phase. It is clear that the NQR spectrum consists of a low-frequency doublet [Fig. 2(a)], a pair of frequency doublets at medium frequencies [Fig. 2(b)], and a high-frequency quadruplet [Fig. 2(c)]. Table II includes frequency assignations and quadrupole parameters calculated from them. Assignations were made by simple comparison with the Sm*C* spectra; i.e., the strongest resonances of the unresolved nitrogens at the Sm*C* are now split into two weaker doublets with similar intensity.

TABLE II. Frequency assignations and NQR parameters corresponding to data obtained at $T = 98$ °C in the nematic mesophase. An asterisk indicates the value speculated from a NQR dip analysis of the nematic mesophase of HpAB at $T = 110$ °C (Ref. 6).

	N_1	N_2	N_3	N_4
ν_+ [kHz]	1915	2898	587	671
ν_- [kHz]	1706	2463	560	640
ν_0 [kHz]	349	382	10*	10*
κ [kHz]	2414	3574	765	874
η	0.29	0.21	0.026	0.023

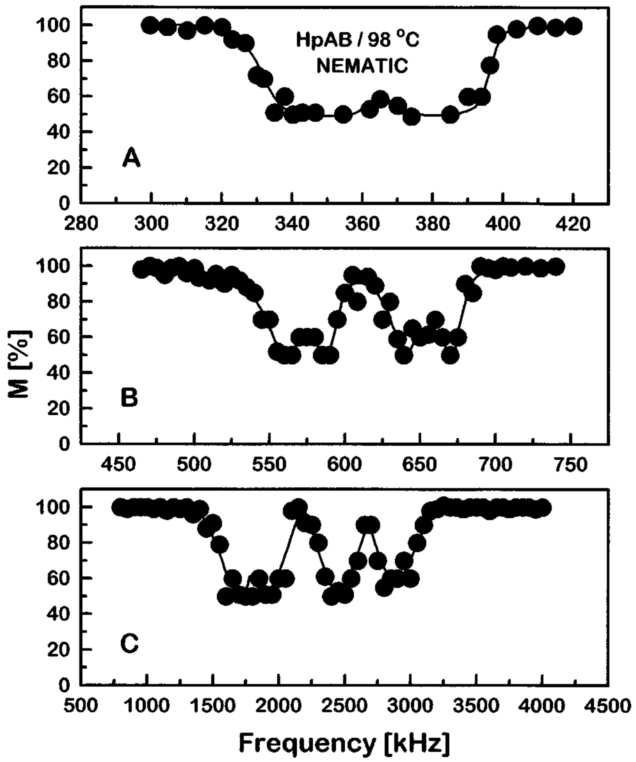

FIG. 2. NQDOR spectra in the same experimental conditions of that of Fig. 1, but at $T = 98$ °C in the Nm liquid crystalline phase. The resonances clearly indicate a bimolecular local structure. Note that as compared with the spectrum of Fig. 1, the complete resonances set was shifted to lower frequencies, as expected, because of the highly molecular mobility in the nematic structures.

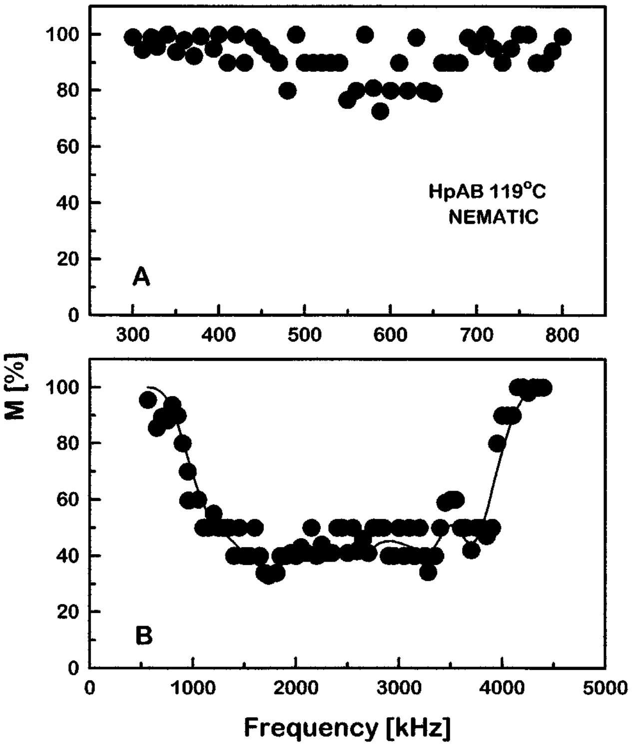

FIG. 3. Experimental spectrum at high frequencies measured with the sample at $T = 119$ °C. A broad line replaces the previous individual resonances spectrum [Fig. 2(c)]. A uniaxial local molecular organization, including individual free rotations, is deduced from the single broad NQR line.

Figure 3 shows results obtained at $T = 119$ °C near the Nm-isotropic phase transition ($T = 125$ °C). Note that only a weak absorption is detected between 400 and 700 kHz [Fig. 3(a)], while a background appears in the high-frequency quadruplet [Fig. 3(b)]. A further increment of the bimolecular unit mobility is expectable after the Sm*C*-Nm transition, affecting the average value of the efg tensor seen by each of the inequivalent ^{14}N nuclei. In fact, NQR frequencies are shifted to lower values. At $T = 119$ °C sharp resonances between 400 and 700 kHz are no longer detected. The high-frequency quadruplet becomes spread over a broad frequency range because of the dispersion on the efg tensor values. As can be clearly observed upon comparing Figs. 2(c) and 3(b), the area under the absorption spectrum at $T = 119$ °C is nearly duplicated with respect to the $T = 98$ °C spectrum. We assume that close to the nematic-isotropic phase transition, the molecular structure near the nitrogen sites is modified. In this way, the angles of the principal axis of the efg tensor with respect to the rotational axis become such that the resonance of N_3 and N_4 shifts to a higher value. Therefore, we conclude that the observed broad spectrum is composed of the ν_+ and ν_- lines of the inequivalent nitrogens. The weak resonance still present between 400 and 700 kHz may correspond to the broadened ν_0 resonances of N_1 and N_2. No resonances were detected in the isotropic phase at 130 °C.

In summary, we believe that in the light of the present study two experimental features can be highlighted: (1) The same experimental information previously obtained from the $T_1(\nu)$ study in the Sm*C*-HpAB transition is now available from the NQDOR experiment, and (2) the bimolecular structure is also present in the Nm mesophase.

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