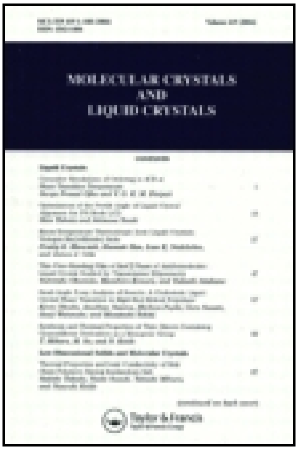

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

^{2}H NMR Study of the Cyclopalladated 4,4′-Bis (Hexyloxy)-Azoxybenzene, a Complex Showing a Nematic Phase

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To cite this article: Lucia Calucci , Donata Catalano , Mauro Ghedini , Nicola L. Jones , Daniela Pucci & Carlo A. Veracini (1996): ^{2}H NMR Study of the Cyclopalladated 4,4′-Bis (Hexyloxy)-Azoxybenzene, a Complex Showing a Nematic Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 290:1, 87-98

To link to this article: http://dx.doi.org/10.1080/10587259608031894

Mol. Cryst. Liq. Cryst., 1996, Vol. 290, pp. 87–98
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^{2}H NMR STUDY OF THE CYCLOPALLADATED 4,4'-BIS (HEXYLOXY)-AZOXYBENZENE, A COMPLEX SHOWING A NEMATIC PHASE

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Abstract The Pd complex **Azpac**, synthesised from the 4,4'-bis(hexyloxy) azoxybenzene mesogen, shows a nematic phase between 90° and 105 °C. The present work concerns the study of the orientational ordering of the ligand and complex molecules in their respective nematic phases, by ^{2}H NMR spectroscopy. To this aim, 4,4'-bis(hexyloxy)azoxybenzene, **HL**, has been specifically deuterated in the positions 3 and 5 of both the rings and the complex **Azpac**-d_4 synthesised from it. Complex **Azpac**-d_{26} was also synthesised starting from the ligand fully deuterated in the alkoxy chains. The morphism of **Azpac**-d_4 and **Azpac**-d_{26} was investigated by optical microscopy and differential scanning calorimetry. ^{2}H NMR spectra were recorded on samples of **HL**-d_4, **Azpac**-d_4 and **Azpac**-d_{26} in their mesophases as a function of temperature. By a procedure of best fitting of the experimental quadrupolar and dipolar splittings the order parameters and some structural data of the metallomesogen molecules were determined. The results are discussed with reference to the ligand.

INTRODUCTION

Interest in "unconventional" liquid crystals such as those containing metals, *metallomesogens*, is currently increasing because of their potential to open new fields of technical applications.[1] Nevertheless, since most of these liquid crystalline materials exhibit high transition temperatures, poor thermal stability and high viscosities[2], their full characterization is hardly accessible and data concerning physical properties, other than mere mesomorphism, are scarce in the literature.

We have recently reported[3] the synthesis of the metal complex [LPd(acac)], **Azpac**, which is the acetylacetonate derivative of the cyclopalladated 4,4'-bis-(hexyloxy)azoxybenzene, **HL**. **Azpac** is a liquid crystalline compound which, showing a nematic phase between 90 °C and 105 °C, displays a mesomorphic behaviour comparable with that of the unmetallated **HL**, nematic between 80 °C and 126 °C. Thus, taking advantage of both the reasonably low transition temperatures and the good thermal stability, **Azpac** has been extensively investigated and refractive indices[4], elastic constants[5], coefficients of viscosity[5], dielectric permittivities[6] and flexoelectric coefficients[7] have been determined.

Herein, we report on the structural and orientational properties of the palladium-mesogen **Azpac** as they emerge from ^{2}H-NMR studies performed on differently deuterium labelled **Azpac** complexes, namely **Azpac-d_4** and **Azpac-d_{26}**, and on the corresponding **HL-d_4** ligand (Figure 1).

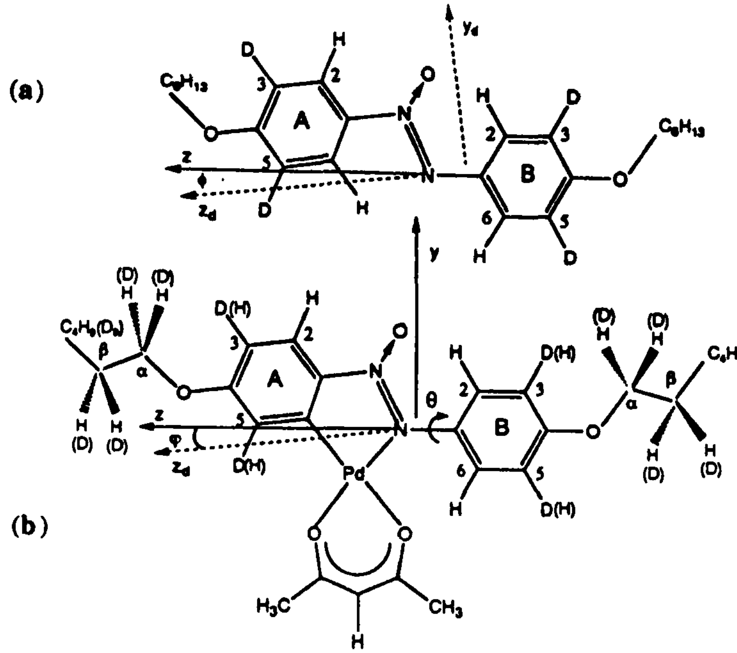

FIGURE 1 Molecular structure and labelling of atoms and groups for HL-d_4 (**a**), Azpac-d_4 and Azpac-d_{26} (**b**). Location of the relevant axes y, z and y_d, z_d.

To our knowledge, no NMR studies of the orientational order have been performed until now on metallomesogens in general and on Pd(II) complexes in particular. This is in spite of the fact that NMR spectroscopy could be very useful for clarifying some hypotheses concerning the structure of these complexes in the liquid crystalline phases and that ^{2}H-NMR spectroscopy in particular is a very powerful technique for studying the molecular orientational order and dynamics in such phases[8].

EXPERIMENTAL

Syntheses

Ligands were synthesised by procedures described in the literature[9], starting from [2,5-$^{2}H_2$]phenol prepared as reported by Zimmermann[10] in the case of **HL**-d_4 and using perdeuterated 1-Br-hexane in the case of **HL**-d_{26}. **Azpac**-d_4 and **Azpac**-d_{26} were synthesised as follows. To a suspension of 0.26 mmol of the ligand in methanol (10 ml) 0.26 mmol of $[Pd(PhCN)_2Cl_2]$ dissolved in benzene (10 ml) were added and the mixture was stirred at room temperature for 3 days. A yellow solid, $\{Pd[L(\mu\text{-}Cl)\}_2$, was filtered off and washed with fresh methanol. To a suspension of $\{Pd[L(\mu\text{-}Cl)\}_2$ (0.08 mmol or 0.05 mmol in the two cases) in absolute ethanol (10 ml), K-acetylacetonate (0.24 mmol or 0.15 mmol) was added. The mixture was heated under reflux for 2.5 h and filtered while hot. Slow cooling of the yellow solution afforded a solid which was filtered, washed with water and ethanol and then recrystallized from diethyl ether. Yellow solids, whose elemental analysis accounts for the expected products **Azpac**-d_4 (60% yield) and **Azpac**-d_{26} (38% yield), were obtained.

Thermal analysis

The recognition of the mesophases was performed by optical observations with a Zeiss Axioskop polarizing microscope equipped with a Linkam CO 600 heating stage and temperature control. Transition temperatures and enthalpies were measured on a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating and cooling rate of 10°/min. The apparatus was calibrated with indium (156.6 °C, 28.5 J/g) and tin (232.1 °C, 60.5 J/g).

NMR measurements

The deuterium NMR measurements were performed at 46.07 MHz on a Bruker AMX300 spectrometer equipped with a variable temperature control unit. Two series of spectra of **HL**-d_4 were recorded with decreasing temperature in the ranges 110 °C ÷ 74 °C and 128 °C ÷ 74 °C, respectively. In the first case (*nem*) the middle of the nematic phase was reached heating the crystalline sample in the NMR spectrometer; then the sample was cooled and the spectra recorded. In the second case (*iso*), the isotropic phase was reached before starting the cooling cycle. Two series of spectra were also performed on samples of **Azpac**-d_4 and **Azpac**-d_{26}, respectively, between the temperature corresponding to the nematic-isotropic transition (≈102 °C) and 90 °C. In the cases of **HL**-d_4 and **Azpac**-d_4, ^{2}H spectra were also recorded under proton decoupling conditions at each temperature.

RESULTS AND DISCUSSION

Results of thermal analysis

4,4'-bis(hexyloxy)azoxybenzene is known to exhibit a wide enantiotropic nematic phase and a monotropic S_C one[11]. The transition temperatures (°C) and enthalpies (J/g) determined by differential scanning calorimetry on a sample of **HL**-d_4 have confirmed such mesomorphism:

$$\begin{tikzcd}
K \arrow[rr, "83\ (90.3)"] & & N \arrow[r, shift left, "129(4.0)"] \arrow[dl, "74(88.4)"] & I \arrow[l, shift left] \\
& Sc \arrow[ul, "72"] & &
\end{tikzcd}$$

The mesomorphic phase of both **Azpac**-d_4 and **Azpac**-d_{26} was identified as a nematic one by optical observations. The transition temperatures (°C) and enthalpies (J/g) are reported in the following scheme:

$$\begin{tikzcd}
K \arrow[r, "91.1(71.2)"] & N \arrow[r, shift left, "103.4(1.6)"] & I \arrow[l, shift left]
\end{tikzcd}$$

Azpac-d_4

$$\begin{tikzcd}
K \arrow[r, "89.1(66.4)"] & N \arrow[r, shift left, "101.5(1.6)"] & I \arrow[l, shift left]
\end{tikzcd}$$

Azpac-d_{26}

With decreasing the temperature, the nematic phase can be considerably supercooled and is frozen in a glassy state before slowly crystallizing.

Assignment of the Deuterium NMR spectra

HL-d_4. In the deuterium spectra recorded under proton decoupling conditions on the nematic phase of **HL**-d_4 two pairs of doublets are distinguishable. Rapid rotation of the aromatic rings about their para axes averages out the quadrupolar interactions of deuterons in positions 3 and 5. Thus each couple of deuterons D_3^A, D_5^A and D_3^B, D_5^B give rise to a doublet. The dominant dipolar coupling between the deuteron and the nearest proton further splits each component of the doublets into two signals. The partial superimposition of signals relative to the rings A and B and the line broadening due to the dipolar coupling between the deuterons and the protons on the first terms of the alkyloxy chains give rise to the spectral features shown in Figure 2. The quadrupolar splittings have been determined at each temperature from the ^{1}H decoupled spectra. The dipolar splittings have then been determined from the coupled spectra using a deconvolution procedure[12]. In the series of spectra recorded with decreasing the temperature starting from the isotropic phase (*iso*), all the splittings increase, except those relative to the two lowest temperature mesurements. In these spectra the signal intensity is dramatically reduced, indicating that the sample is partially crystallised. The dipolar splittings relative to the inner doublet range from 1230 to 1530 Hz, while those corresponding to the outer one have values between 1280 and 1730 Hz (all absolute values). The larger quadrupolar and dipolar splittings of each spectrum are attributed to the deuterons of ring A, since, based on what has been reported in the literature for analogous compounds[13], the *para* axis of ring A should be more oriented than that of ring B. In the series of spectra recorded with decreasing the temperature starting from the middle of the nematic phase (*nem*), the quadrupolar splitting trends are very similar to those found in the previous case, but the dipolar splittings have unusually high absolute values, ranging from 1580 to 1930 Hz and from 1720 to 2110 Hz for deuterons of rings B and A, respectively. This indicates that the molecular order is different in the two cases and, in particular, that the long molecular axis must be better oriented in the *nem* case; this is more fully described below.

Azpac-d_4. One of the spectra is shown in Figure 2. Each spectrum consists of three pairs of quadrupolar doublets, the inner two of which are further split by the dipolar coupling between the deuteron and the nearest proton on the phenyl ring. These doublets are partially superimposed and a precise determination of the related quadrupolar and dipolar splittings has been done comparing, at each temperature, the ^{1}H coupled to the ^{1}H decoupled spectrum. The evolution of the spectra with decreasing the temperature consists of a progressive increasing of the quadrupolar splittings. The dipolar splittings, ranging from 1200 Hz to 1600 Hz, have been determined with an uncertainty of about 100 Hz. Considering the relative intensities of the signals (1:1:2 starting from those with the largest splitting) and the comparison between coupled and uncoupled spectra, the outer doublet is attributed to the D_5^A deuteron that has no protons in the *ortho* position, the intermediate doublet to D_3^A, and the inner and more intense one to D_5^B and D_3^B. The signals of these last deuterons are averaged out by fast rotation of ring B around its *para* axis.

Azpac-d_{26} In the spectra of **Azpac-d_{26}** eight pairs of doublets are distinguishable, whose splittings increase when decreasing the temperature (see Figure 2). By measuring the intensities of the signals, the inner doublet can be attributed to the methyl groups of both the chains. Following the literature[14], the methylene deuterons give quadrupolar doublets with decreasing splittings going from the α CD_2 group, the one closest to the aromatic core, towards the methyl group. In some cases[14b] an inversion has been found in this trend, involving the γ and δ CD_2 groups. The possible assignments of the signals in the spectrum are shown in Figure 2. It is evident that the β, γ and δ methylenes of the two chains give different splittings, but the assignment of the signals to one or to the other chain is not possible.

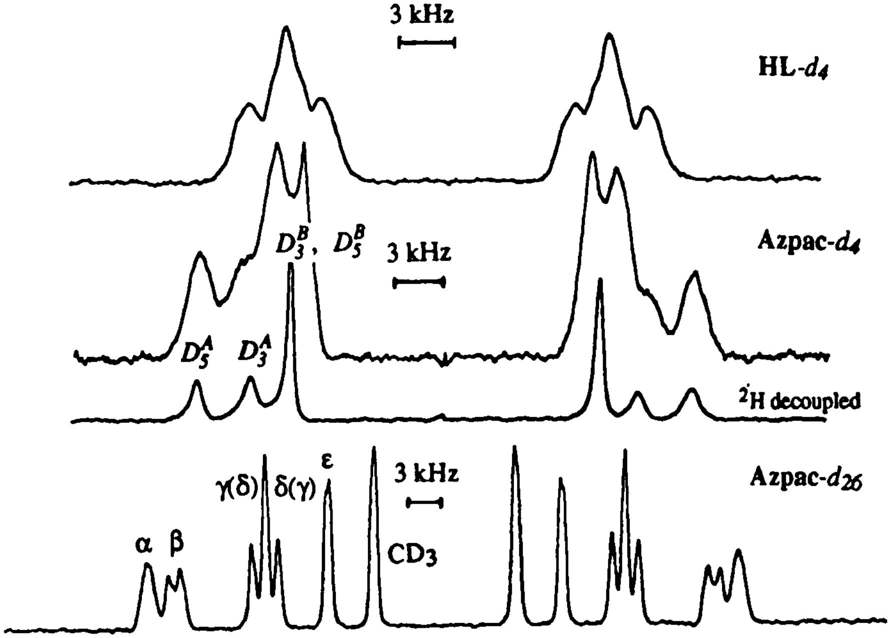

FIGURE 2 Examples of ^{2}H NMR spectra of the compounds studied at 90 °C

Orientational ordering

HL-d_4 The quadrupolar splittings can be expressed in terms of local order parameters by Equation (1):

$$\Delta\nu_q = \frac{3}{2}q[S_{aa} + \frac{\eta}{3}(S_{cc} - S_{bb})] \qquad (1)$$

where q, the quadrupolar coupling constant is 185 kHz and η, the asymmetry parameter, is 0.04[15]. The a axis of the local reference frame, where the electric field gradient tensor is diagonal, coincides with the C-D bond direction, and the b axis is perpendicular to the aromatic ring plane. The dipolar splittings are related to the order parameters relative to the internuclear D-H direction by Equation (2):

$$\Delta D_{DH} = -2K_{DH}\frac{S_{DH}}{r_{DH}^3} \tag{2}$$

where $K_{DH} = \frac{\gamma_D \gamma_H h}{4\pi^2}$ and r_{DH} is the internuclear distance. The two couples of deuterons D_3^A, D_5^A and D_3^B, D_5^B give rise to averaged quadrupolar and dipolar data. The local order parameters S_{aa}, S_{bb}, S_{cc} and S_{DH} are then expressed in terms of the order parameters S_{xx}^d, S_{yy}^d and S_{zz}^d relative to the frame x_d, y_d, z_d, fixed on the molecular core, where the Saupe matrix is diagonal[16]. The molecular structure considered, shown in Figure 1, has standard bond lengths and angles. The molecular fragment formed by the two aromatic rings and the azoxy group is assumed to be planar, in agreement with X-ray structural data for alkoxy-azoxybenzenes[17], and rigid, with the exception of a rapid 180° rotation of the rings about their *para* axes. The y_d and z_d axes will be in this plane. The available set of experimental data does not allow us to determine the orientation, in the core plane, the z_d axis of the diagonalized molecular frame and at the same time to determine the angle ϕ between the two *para* axes. The z_d axis is assumed to coincide with the most oriented direction among those experimentally sampled, that is with the D-H internuclear direction corresponding to the higher dipolar coupling. The angle ϕ is considered unknown and its value is determined by the best fit of quadrupolar and dipolar data measured in the spectra at all temperatures, together with the values of the principal order parameter, S_{zz}^d, and of the biaxiality, $S_{xx}^d - S_{yy}^d$, at each temperature.

The signs of the splittings cannot be inferred directly from the spectra, but sound assumptions can be made on the basis of their values and of the molecular structure. The dipolar couplings are certainly negative, since the related D-H internuclear directions must lie nearly parallel to the molecular long axis; moreover, the maximum positive value for ΔD_{DH}, if r_{DH}= 2.48 Å, is 1208 Hz, corresponding to the unrealistic value of S_{DH}= -0.5. The experimental ΔD_{DH} values indicate $S_{zz}^d \equiv S_{DH} \approx 0.53 \div 0.68$ and even $S_{zz}^d \equiv S_{DH} \approx 0.71 \div 0.86$ for the series of spectra recorded decreasing the temperature from the nematic phase. In these conditions, the quadrupolar splittings relative to deuterons for which the C-D direction forms an angle of about 60° with the z_d axis can be considered negative.

From these assumptions and from the global fitting of the experimental splittings with equations of the type of (1) and (2), we have found, between 74 °C and 110 °C, the couples of order parameters S^d_{zz}, and $S^d_{xx} - S^d_{yy}$ shown in Figure 3 for the two sets of data recorded, called *nem* and *iso*, respectively. It is evident that the trends of S^d_{zz} are similar, but the one relative to the *nem* series is shifted to unusually high values for the nematic phase. In the *iso* case the biaxiality practically vanishes, while it assumes small but non-vanishing values (about -0.03) in the *nem* case. The angle ϕ between the *para* axes of the aromatic rings is 10° and 9.5° in the two cases with unusual and regular order parameter S^d_{zz}, respectively, in good agreement with the data reported for various compounds of the series of 4,4'-bis(alkyloxy)azoxybenzenes[17]. Minor changes of the structural assumptions, for instance of the angles formed by the C-D^A_3 and C-D^A_5 bonds with the *para* axis of ring A, strongly influence the value of ϕ and the fitting quality generally gets worse. The choice of the standard value of 60° for the cited angles, together with 2.48 Å for the C-D distance, allows a quite good reproduction of the ratio between the dipolar splittings. Since in the spectra recorded above 110 °C (series *iso*) only the quadrupolar splittings are resolved, the computing procedure previously described is impossible. Therefore the values obtained for the lower temperature range, ϕ=9.5° and $S^d_{xx} - S^d_{yy}$ =0, have been assumed and S^d_{zz} has been computed from the quadrupolar splittings at each temperature. Altogether, the trend of S^d_{zz} from the isotropic-nematic transition to the sample crystallization agrees with those found by previous studies[18] and fits fairly well to that predicted by the Maier Saupe mean-field theory[19], also plotted in Figure 3. The only essential deviation involves the two points recorded between 78 °C and 74 °C. In this narrow range, S^d_{zz} steeply decreases with decreasing temperature, probably indicating that the S_C phase expected before the crystallization aligns with its layers perpendicular to the magnetic field of the NMR spectrometer; inside the layers, the molecular long axes are tilted, and the tilt angle increases with decreasing the temperature.

Azpac-d_4 and **Azpac-**d_{26}. Quadrupolar and dipolar splittings measured in the spectra of **Azpac-**d_4 are described by Equations (1) and (2), respectively. The local order parameters S_{aa}, S_{bb}, S_{cc} and S_{DH} must be expressed in terms of the order parameters of an axis system fixed on a molecular fragment. We have assumed for the molecular core the geometry shown in Figure 1, with bond lengths and angles in accordance with crystallographic data of analogous solid compounds[20]. The molecular fragment formed by the Pd atom and the coordinated groups (the acetylacetonate ligand and the phenyl ring A) is planar and rigid and the angle formed by the ring *para* axes is 7°; a dihedral angle of about 41° is reported between the planar fragment and the phenyl ring B[20b]. We

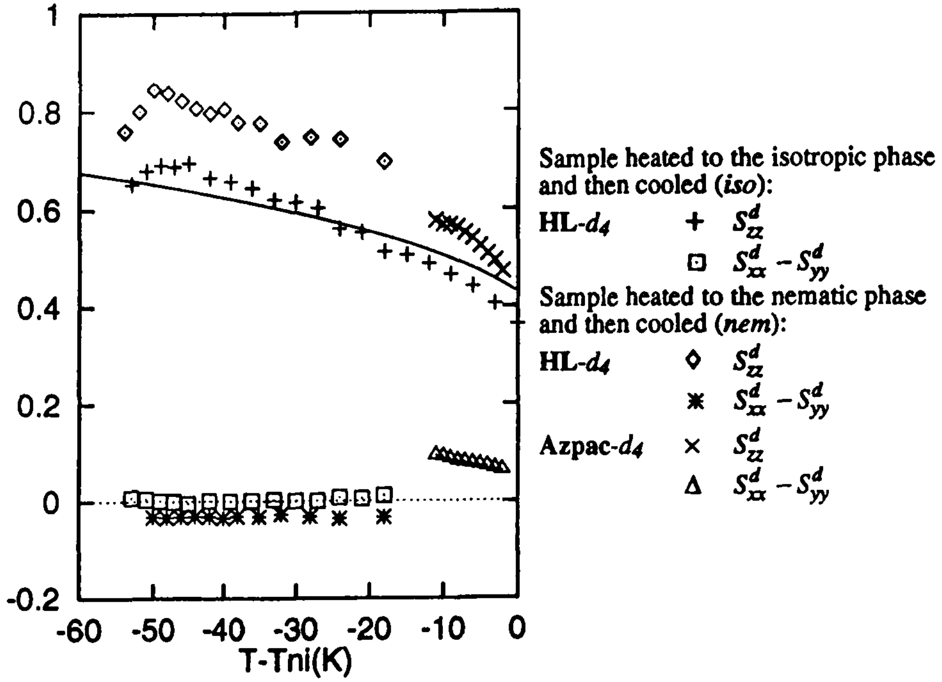

FIGURE 3 Order parameters of HL-d_4 and Azpac-d_4.

have assumed that the phenyl ring B flips between the stable conformations characterized by a dihedral angle ±θ or 180°±θ with respect to the yz plane. The angle θ is considered to be unknown, but the same at all temperatures, since it could be significantly different for different compounds and phases. The x, y, z axis system shown in Figure 1 has been chosen as a suitable intermediate one for expressing S_{aa}, S_{bb}, S_{cc} and S_{DH} [16]. Then Equations (1) and (2) for the various quadrupolar and dipolar splittings have been rewritten in terms of S^d_{zz} and S^d_{xx}-S^d_{yy}, the order parameters in the molecular frame x_d, y_d, z_d, where the Saupe matrix of the planar fragment is diagonal, and of φ, the angle between the z and z_d axes. The values of S^d_{zz} and S^d_{xx}-S^d_{yy} at each temperature are determined together with θ and φ by a fitting procedure of the whole data set.

As in the case of compound HL-d_4 , the dipolar couplings are known to be negative on the basis of their experimental values. The D-H direction is highly ordered, with S_{DH} values between 0.5 and 0.6, that is in the range expected for the order parameter of the molecular long axis in a nematic phase. However, nothing can be safely said about the signs of the quadrupolar splittings, because the core of the compound under study has an unconventional structure and the location of the principal axis of the order matrix is not obvious. Therefore, all the eight possible combinations of signs have been considered for the three quadrupolar doublets and the computation of S^d_{zz} and S^d_{xx}-S^d_{yy} has been performed for each combination. Three cases can be discarded because they completely fail to reproduce the experimental data; two other combinations give absurd values of S_{yy}, being smaller than -0.5. The three remaining cases (with all splittings negative (**a**), or with $(\Delta\nu_q)^A_3 > 0$ (**b**), or $(\Delta\nu_q)^A_5 > 0$ (**c**)) are in principle all acceptable because the data are reproduced within the experimental error at each temperature and the best fit parameters are physically sensible. In order to discriminate among the three acceptable cases, the values of the molecular core order parameters and of the dihedral angle have been used to calculate the quadrupolar splittings of the deuterons of the first methylene group, considered tetrahedral, of both chains at various temperatures. This was done assuming that the only populated conformations are those with the phenyl-O-C fragment planar and the D-D internuclear vector perpendicular to the plane. The values obtained in the three cases have then been compared with those determined from the spectra of **Azpac**-d_{26} at the corresponding temperature T-T_{NI}. In this way, cases **b** and **c** could definitely be discarded, since they produce too large, well distinct splittings for the methylenes of the two chains, while the experimental ones are always coincident within the experimental resolution. Therefore, all the quadrupolar splittings of the core deuterons are negative. The best-fit angle θ is 40°, in good agreement with literature results.[20b] The z_d axis (our best approximation to a hypothetical molecular long axis) is located in the xz plane as indicated in Figure 1, with a tilt of only 1° from the *para* axis of ring A toward the z axis. The trends of S^d_{zz} and S^d_{xx}-S^d_{yy} are reported in Figure 3. The most relevant difference with the case of **HL**-d_4 is the non vanishing molecular order biaxiality, evaluated about -0.06+-0.09. These values, however, do not exceed those estimated for other compounds in their nematic phases.[21, 22]

CONCLUSIONS

The orientational study of **HL**-d_4 in its nematic phase finds vanishing order biaxiality for this molecule; the trend of the principal order parameter with temperature fits well the prediction of the Maier Saupe mean field theory.[19] The mesophase obtained heating the crystallized sample only up to 110 °C (18 °C below the nematic-isotropic transition, *nem* case) exhibits an unusually high order parameter, revealing a sort of memory of the high crystalline order degree. We stress that the combiation of the order parameters plotted in Figure 3 produces, in the *iso* and *nem* cases, quite similar values for the quadrupolar splittings and significantly different values for the dipolar ones. All this serves as a warning: it is certainly necessary to control carefully the experimental procedure and to collect a data set as rich as possible in order to perform accurate orientational order studies. The monotropic S_C phase aligns with its layers perpendicular to the magnetic field of the NMR spectrometer; inside the layers, the molecular long axes are tilted, and the tilt angle increases with decreasing the temperature, as is typical of the so called S_{C2} phase.[23] It is interesting to observe that, in the S_C phase of the homologous compound 4,4'-bis(heptyloxy) azoxybenzene, the molecules align along the magnetic field and the layers are tilted.[24] Different orientational behaviours are also reported for two otherwise similar troponic mesogens in their S_C phases.[21, 25] It seems therefore difficult to argue by analogy the kind of alignment exhibited by a S_C mesophase in the magnetic field.

As far as the **Azpac** complex is concerned, the location of the molecular frame where the ordering matrix is diagonal and the trends of the order parameters (Figure 3) indicate that it behaves as a typical calamitic mesogen in its nematic phase. This happens in spite of the unconventional molecular structure of this mesogen. The disk-like rigid core fragment certainly tends to enhance the order biaxiality, but this effect is partially compensated by the cylindrical average structure of the rotating ring B with the bonded alkoxy chain. Finally, we stress that a bulky sample is studied in the NMR experiment: quite different results could be obtained in other experimental conditions, for instance in thin layers where surface-induced effects dominate.

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