

# Average Orientation and Location of Benzyl Alcohol- $d_5$ and Alkyl Benzyl- $d_5$ Ethers in Anionic Nematic Lyotropic Liquid Crystals

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Deuterium quadrupole splittings of benzyl alcohol- $d_5$  and a series of alkyl benzyl- $d_5$  ethers, with linear aliphatic chains from 1 to 12 carbon atoms, were measured using  $^2\text{H}$  NMR spectroscopy. These molecules were dissolved in  $\text{N}_\text{D}$  anionic nematic lyotropic liquid crystals prepared with sodium decyl sulfate (NaDS) and cesium decyl sulfate (CsDS). Using the quadrupole splittings, the two order parameters that completely describe the average orientation of the aromatic ring were calculated. From these values, we have inferred the mechanism of incorporation of the guest molecules into the superstructure of the aggregate. The effect of the added molecules on the integrity of the aggregate seems to depend on the electrostatic characteristics of the surface as well as the hydrophobic properties of the guest molecule. The quadrupole splittings suggest that benzyl alcohol is positioned near the interface, possibly hydrogen bonding with the interfacial water. This disrupts the integrity of the interface, particularly in the CsDS system with the more hydrophobic derivatives decreasing the mobility of the CsDS aggregate components.

## Introduction

The motivation to study delivery sites and orientational dynamics of molecules dissolved in bilayer membranes, as well as the effect that this incorporation has on the dynamics of the lipid components of the assembly, arises in most cases from the interest in understanding the different physical forces that govern biological functions.<sup>1–3</sup> Different spectroscopic techniques and theoretical formulations are currently used for this purpose.<sup>4–10</sup> The use of order parameters, derived from nuclear quadrupole splittings measured from the NMR spectra in anisotropic solvents, is probably one of the most direct and simplest techniques to study the average orientation of molecules

partially oriented in magnetic fields.<sup>11–13</sup> In particular,  $\text{N}_\text{D}$  nematic lyotropic liquid crystals<sup>14</sup> (also known as type II<sup>15</sup>) formed from disklike fragmented lamellae may constitute a good model system of organized molecular assemblies found in nature.<sup>16</sup>

We have recently studied the location and average orientation of two series of molecules, *N*-alkylpyridinium- $d_5$  ions and alkyl benzyl- $d_5$  ethers, dissolved in  $\text{N}_\text{D}$  lyotropic nematic liquid crystals. Deuterium quadrupole splittings from the aromatic rings were measured, and the two order parameters that describe their average orientations were calculated. The lyomesophases were prepared from cationic and anionic amphiphilic molecules, namely, tetradecyltrimethylammonium bromide (TDTMABr), hexadecylpyridinium chloride (HDPyCl), sodium decyl sulfate (NaDS), and cesium decyl sulfate (CsDS). We found that at least five carbon atoms were necessary in the chain of *N*-alkylpyridinium ions for them to start to be incorporated into cationic lyomesophases prepared from TDTMABr and HDPyCl.<sup>17</sup> As expected, the same ions are significantly more attracted to the micelles of anionic liquid crystals of NaDS and CsDS, probably because of strong electrostatic interactions with the surface.<sup>18</sup> In both cases, the symmetry axis of the ring is perpendicular to the bilayer

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surface. In addition, a nonionic aromatic ring, such as that found in benzyl methyl ether, appears to interact strongly in cationic liquid crystals formed from TDTMABr and seems to be oriented with the aromatic ring plane lying on the micellar surface,<sup>19</sup> evidencing the existence of cation- $\pi$  interaction.<sup>20</sup>

In this work we have used  $^2\text{H}$  NMR spectroscopy to measure deuterium quadrupole splittings from benzyl alcohol, frequently used as an anesthetic in surgery, and from a series of alkyl benzyl ethers, each with a 20% fully deuterated aromatic ring. The ether series, with linear alkyl chains from 1 to 12 carbon atoms, as well as benzyl alcohol, were dissolved in  $\text{N}_\text{D}$  anionic nematic lyomesophases prepared from NaDS or CsDS. From the measured quadrupole splittings and assuming  $C_{2v}$  local symmetry, we have obtained the two order parameters that completely characterize the orientational order of the aromatic ring. From this information we have inferred the mechanism of incorporation of these molecules into the superstructure of the aggregate. The effect of the added guest molecule on the integrity of the aggregate is monitored using the quadrupole splittings from partially deuterated water, DHO, and decanol- $\alpha$ - $d_2$ .

### Experimental Section

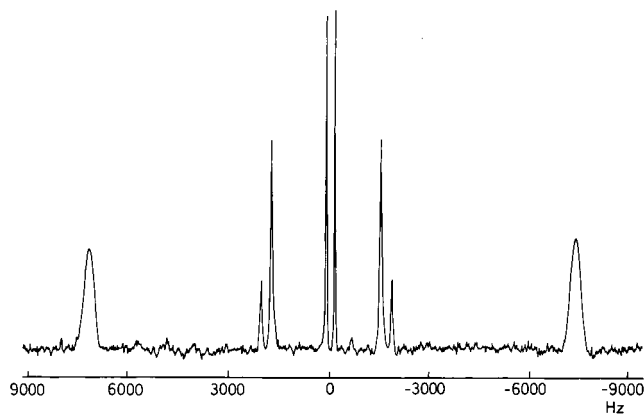
**Synthesis of Alkyl Benzyl- $d_5$  Ethers.** The ether series, 20%  $d_5$ , was synthesized starting from a mixture of 80% benzyl alcohol and 20% benzyl alcohol- $d_5$  (99%), both commercially available reagents. More details of the procedure were described in a previous paper.<sup>19</sup>

**Preparation of Samples.** The NaDS and CsDS employed in the preparation of the liquid crystals were synthesized using the reaction between decyl alcohol and sulfuric acid. The acid sulfate was neutralized using either NaOH or CsOH. Details of the methodology were described in a previous paper.<sup>18</sup> CsDS samples were prepared by dissolving 363 mg of detergent and 19 mg of  $\text{K}_2\text{SO}_4$  in a mixture of 440  $\mu\text{L}$  of  $\text{H}_2\text{O}$ , 0.05% v/v  $\text{D}_2\text{O}$ , and 44  $\mu\text{L}$  of decyl alcohol, 10% v/v enriched with decyl alcohol- $\alpha$ - $d_2$ . Between 6 and 12  $\mu\text{L}$  of guest molecule was added to this homogeneous mixture, increasing the amount with the molecular weight of the ether. The NaDS mesophase was prepared by mixing 475 mg of NaDS, 41 mg of  $\text{Na}_2\text{SO}_4$ , 97  $\mu\text{L}$  of decanol, and 600  $\mu\text{L}$  of water. Between 6 and 12  $\mu\text{L}$  of guest molecule was also added to each sample, depending on molecular weight.

**NMR Experiments.** All NMR spectra were recorded using a Bruker Avance-300 spectrometer, at a constant temperature of 300 K.  $^1\text{H}$  and  $^2\text{H}$  NMR spectra of each sample were obtained using a 5 mm inverse detection broad band probe. In the case of deuterium spectra, between 30 000 and 90 000 transients were accumulated in 32 kB files. The spectral window was 30 kHz.

### Results and Discussion

Figure 1 shows the  $^2\text{H}$  NMR spectrum of benzyl- $d_5$  ethyl ether dissolved in the CsDS mesophase. First-order deuterium quadrupole splittings from decanol- $\alpha$ - $d_2$ , from DHO, and from the aromatic ring can be measured directly from the spectra. Table 1 summarizes the values of these parameters (Hz) for all the studied molecules. The nomenclature used to identify the different molecules is related to the number of carbons in the aliphatic chain: for instance,  $C_0$  corresponds to benzyl alcohol,  $C_1$  to benzyl methyl ether,  $C_2$  to benzyl ethyl ether, and so on. Table 1 also includes entries for the deuterium quadrupole splittings of decanol- $\alpha$ - $d_2$  and DHO in the absence of added guest molecule, in both mesophases.



**Figure 1.**  $^2\text{H}$  NMR spectrum of benzyl ethyl ether dissolved in the CsDS mesophase. The splittings assignment is as follows: the central doublet comes from DHO, the next external doublet arises from the *ortho* and *meta* positions of the aromatic ring, the smallest signal comes from the *para* position of the ring, and the largest splitting is from decanol- $\alpha$ - $d_2$ .

**Table 1. Deuterium Quadrupole Splittings from Decanol- $\alpha$ - $d_2$ , from DHO and from the *ortho*, *meta*, and *para* Positions of the Aromatic Ring of the Studied Molecules Dissolved in NaDS and CsDS<sup>a</sup>**

added molecule	DeOH- $\alpha$ - $d_2$	HDO	<i>ortho</i>	<i>meta</i>	<i>para</i>
NaDS Mesophase					
$C_0$	15 940	434	912	1004	-13654
$C_1$	15 973	444	4415	4498	-8850
$C_2$	15 995	443	5346	5404	-5594
$C_3$	14 800	395	5326	5326	-5044
$C_4$	15 125	420	5906	5906	-4995
$C_5$	15 487	403	6202	6202	-4882
$C_6$	16 010	452	6741	6741	-5359
$C_7$	17 721	520	7800	7800	-5885
$C_8$	15 760	447	6946	6946	-5001
$C_9$	15 395	433	6862	6862	-4863
$C_{10}$	15 850	446	7206	7206	-4981
$C_{11}$	15 850	440	7080	7080	-4950
$C_{12}$	15 757	439	7175	7175	-4881
no added molecule	16 327	442			
CsDS Mesophase					
$C_0$	13 542	224	258	273	-8557
$C_1$	14 604	244	2607	2675	-6369
$C_2$	14 599	234	3299	3299	-4181
$C_3$	15 316	278	3991	3991	-3991
$C_4$	15 930	312	4522	4522	-4171
$C_5$	15 763	266	4690	4690	-4520
$C_6$	17 609	296	5527	5527	-4771
$C_7$	16 854	284	5341	5341	-4379
$C_8$	17 163	296	5427	5427	-4181
$C_9$	16 986	266	5341	5341	-4102
$C_{10}$	17 907	340	5699	5699	-4114
$C_{11}$	19 661	359	6326	6326	-4460
$C_{12}$	18 344	315	5874	5874	-4076
no added molecule	16 271	226			

<sup>a</sup> All values are in hertz. The errors are  $\pm 2$  Hz for DHO,  $\pm 10$  Hz for  $C_0$  to  $C_8$  derivatives, and  $\pm 25$  Hz for the others.

The first CMC and the ratio between the dissociation degrees of spherical micelles of CsDS and NaDS were previously measured<sup>18</sup> using the method of Evans.<sup>21</sup> The values of  $\text{CMC}_{\text{NaDS}} = 3.3 \times 10^{-2}$ ,  $\text{CMC}_{\text{CsDS}} = 2.3 \times 10^{-2}$ , and  $\alpha_{\text{NaDS}}/\alpha_{\text{CsDS}} = 1.48$  suggest that the NaDS surface is significantly more charged than the surface of CsDS. The data for the two samples with no added guest molecule suggest that the interaction of water molecules with the more neutral surface of CsDS is weaker than the interaction with the more negatively charged surface of NaDS. Moreover, the value of the quadrupole splitting of HDO

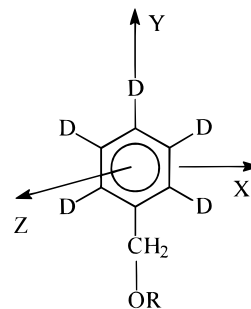
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in the NaDS mesophase seems to be constant along the series of samples, about 400 Hz, including the sample without added guest molecule. A different situation is observed for the quadrupole splitting of HDO in the CsDS mesophase. In this case the splitting is a function of the length of the aliphatic chain of the added guest molecule, and the value ranges from about 224 Hz, for the sample with benzyl alcohol or no guest molecule added, to about 350 Hz for samples containing long alkyl chain ethers. A similar behavior is observed for the quadrupole splitting of decanol- $\alpha$ - $d_2$ . This parameter represents the degree of order in the internal region of the bilayer, near the interface. It remains constant for all the NaDS samples, about 16 kHz, and it is a function of the added guest molecule in the case of the CsDS mesophase. This indicates that the inclusion of the guest molecules into the NaDS liquid crystal solution does not significantly modify the integrity and dynamics of the surface of the aggregates. More surprising is the fact that the first few additives ( $C_0$  to  $C_3$ ) seem to disrupt the integrity of the CsDS interface, since the splitting of decanol- $\alpha$ - $d_2$  decreases significantly for these samples. Further increase in the aliphatic chain length of the ether increases the magnitude of the decanol splitting to values close to 19 kHz, indicating a decrease in the mobility of the bilayer interface. This effect of the added guest molecule on the dynamics of the interface of the CsDS mesophase was observed before for the incorporation of *N*-alkylpyridinium ions in the same mesophase, but with greater intensity. It was attributed to the difference in the surface charge between both aggregates.<sup>18</sup>

The quadrupole splittings from the deuteriums of the *ortho*, *meta*, and *para* positions of the aromatic ring also appear in Table 1. These values show that the molecules are tightly attached to the aggregates, which is expected from the hydrophobic character of these structures. A closer inspection of Table 1 reveals an important increase in the splitting from the *ortho* and *meta* positions and a decrease in the absolute value of the splitting from the *para* position of the ring, on going from  $C_0$  to  $C_1$ . In fact, the values of the splitting from the *ortho* and *meta* positions increase several times. This important change of the quadrupole splittings reveals differences in the way that  $C_0$  interacts with the aggregate, as compared with the ether molecules. For the molecules in the ether series, it is seen that the splittings from the *ortho* and *meta* positions increase with the alkyl chain length, in both mesophases, whereas the absolute value of the splitting from the *para* position decreases with increasing length of the aliphatic chain. With these experimental splittings it is possible to calculate the two order parameters that completely characterize the average orientation of the aromatic ring. We have observed that there is an appreciable dependence of the integrity of the aggregate of CsDS on the hydrophobic characteristics of the added guest molecule. To obtain information that properly reflects the average orientation of the aromatic ring, independent of modifications induced in the aggregate, we have normalized the quadrupole splittings before calculating the order parameters. The quadrupole splitting of decanol- $\alpha$ - $d_2$  is indicative of the modifications of the aggregate and most likely changes in size with incorporation of additives. Therefore, we have divided the observed quadrupole splittings of the aromatic ring by this value, and multiplied the result by 15 000. These normalized quadrupole splittings will be independent of the particular effect of each added guest molecule on the integrity of the aggregate. Using previously reported values for the aromatic deuterium quadrupole coupling constant, electric field asymmetry parameter, and geometrical parameters,<sup>19</sup> the two order



**Figure 2.** Basic structure of the studied molecules and designation of the symmetry coordinates of the aromatic ring. In the calculation of the order parameters, it is assumed that the principal axis of the electric field gradient tensor is along the C–D bond.

**Table 2.** Normalized Order Parameters,  $S_{xx}$  and  $S_{yy}$ , of Benzyl Alcohol and the Series of Alkyl Benzyl Ethers<sup>a</sup>

added molecule	$S_{xx}$	$S_{yy}$	$S_{zz}$	$S_{yy}/S_{xx}$
NaDS Mesophase				
$C_0$	0.0208	-0.0462	0.0254	-2.22
$C_1$	0.0304	-0.0305	0.0001	-1.00
$C_2$	0.0305	-0.0196	-0.0109	-0.64
$C_3$	0.0322	-0.0192	-0.0130	-0.60
$C_4$	0.0341	-0.0187	-0.0154	-0.55
$C_5$	0.0346	-0.0179	-0.0167	-0.52
$C_6$	0.0364	-0.0190	-0.0174	-0.52
$C_7$	0.0377	-0.0189	-0.0188	-0.50
$C_8$	0.0381	-0.0181	-0.0200	-0.48
$C_9$	0.0378	-0.0180	-0.0198	-0.48
$C_{10}$	0.0383	-0.0179	-0.0204	-0.47
$C_{11}$	0.0378	-0.0178	-0.0200	-0.47
$C_{12}$	0.0383	-0.0177	-0.0206	-0.46
CsDS Mesophase				
$C_0$	0.0137	-0.0340	0.0203	-2.48
$C_1$	0.0212	-0.0239	0.0026	-1.13
$C_2$	0.0216	-0.0159	-0.0057	-0.74
$C_3$	0.0236	-0.0146	-0.0097	-0.62
$C_4$	0.0252	-0.0148	-0.0104	-0.59
$C_5$	0.0264	-0.0152	-0.0112	-0.58
$C_6$	0.0276	-0.0153	-0.0123	-0.55
$C_7$	0.0276	-0.0147	-0.0129	-0.53
$C_8$	0.0272	-0.0138	-0.0134	-0.51
$C_9$	0.0270	-0.0137	-0.0133	-0.51
$C_{10}$	0.0271	-0.0131	-0.0140	-0.48
$C_{11}$	0.0273	-0.0130	-0.0143	-0.48
$C_{12}$	0.0271	-0.0127	-0.0144	-0.47

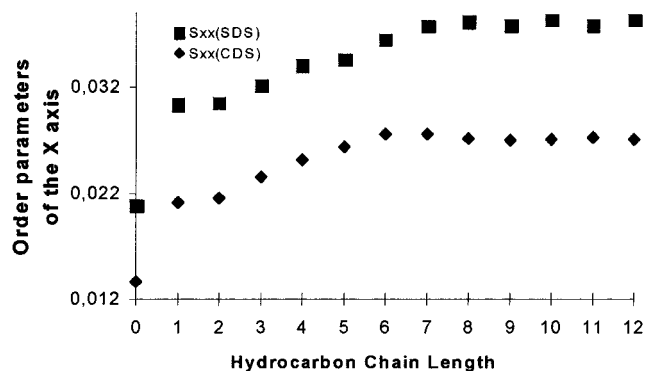
<sup>a</sup> The molecules were dissolved in NaDS and CsDS  $N_D$  lyomesophases.

parameters,  $S_{xx}$  and  $S_{yy}$ , which completely describe the average orientation of the aromatic ring, were calculated.<sup>22,23</sup> Figure 2 shows the structure of the studied molecules and the labels of the molecular symmetry axes. The values of  $S_{xx}$  and  $S_{yy}$  appear in Table 2, while Figures 3 and 4 provide a graphical representation of these normalized order parameters for both NaDS and CsDS.

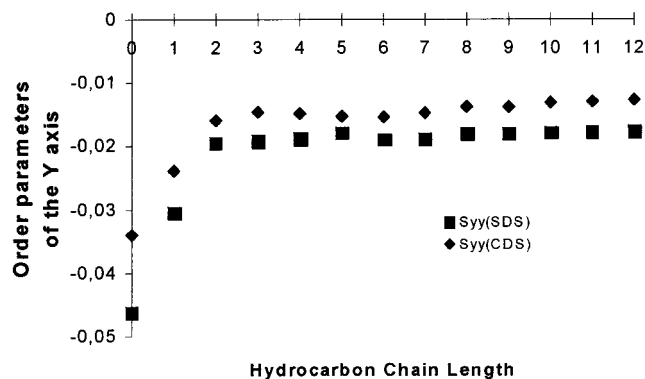
The order parameters allow a detailed picture of the orientational properties of these molecules to be drawn. The values of the ratio  $S_{yy}/S_{xx}$  (Table 2) reveal a systematic change in the average orientation of the phenyl ring with an increase in alkyl chain length. Perhaps the critical clue comes from the orientation parameters for the methylated derivative. Since  $S_{xx} + S_{yy} + S_{zz} = 0$ , it is evident that, for this solute,  $S_{zz}$  is very close to zero. This

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**Figure 3.** Normalized order parameters along the  $X$  molecular symmetry axis of the aromatic ring of benzyl alcohol and alkyl benzyl ethers, dissolved in  $N_D$  lyomesophases made from NaDS (■) and CsDS (◆), as a function of the alkyl chain length.



**Figure 4.** Normalized order parameters along the  $Y$  molecular symmetry axis of the aromatic ring of benzyl alcohol and alkyl benzyl ethers, dissolved in  $N_D$  lyomesophases made from NaDS (■) and CsDS (◆), as a function of the alkyl chain length.

means either that the  $Z$  axis is aligned along an axis corresponding to the “magic” angle for this axis or it is undergoing an averaging process. It seems most likely that the zero value derives from an averaging of two, or possibly more, orientations where the sign of  $S_{zz}$  is opposite so that the sum is close to 0. It certainly is not a case of a small overall degree of alignment of this particular molecule because the alignment throughout the series of molecules remains relatively constant, as can be judged from Table 2.

It is hard to think of a physical reason the  $Z$  axis would maintain an alignment near that of the magic angle and thus give a 0 value for the order parameter. It seems more likely that the value derives from a dynamic reordering process occurring between two or more orientations. In fact, if it is assumed that there are two sites and the order for the  $C_0$  molecule represents one such alignment and the order for  $C_{12}$  the other, then for the NaDS case, a 0.45/0.55 weighted average gives 0.0001 for  $S_{zz}$ . The critical question is whether the same average using the  $C_0$  and  $C_{12}$   $S_{yy}$  limiting values gives a value for  $S_{yy}$  corresponding to that observed. Indeed it does, the calculated value being  $-0.0305$ , which is the same as the observed value. This suggests that the  $C_1$  compound spends close to 45% of its time in a  $C_0$ -type orientation and 55% in a  $C_{12}$ -type orientation. Similar calculations for the CsDS mesophase suggest that the average population ratio is 0.49/0.51 between the two extremes. On going to  $C_2$  the corresponding weighting is about 0.21/0.79 for the NaDS mesophase and 0.25/0.75 for the CsDS system. On this basis it seems very likely that the observed alignment of the solutes with intermediate-sized alkyl chains derives

from an orientational averaging process. The smooth change in the  $S_{yy}/S_{xx}$  is in accord with such a conclusion.

These observations suggest that benzyl alcohol is very likely to be positioned near the interface, possibly oriented so that the alcoholic functional group forms a hydrogen bond with the interfacial water and the aromatic ring is directed toward the interior of the aggregate. This location is consistent with the observation that quadrupole splittings from the *ortho* and *meta* positions of the ring are differentiated only for benzyl alcohol and the short chain ethers. In effect, the H-bond introduces restrictions to the mobility of the  $Y$  axis, but allows certain freedom to the torsional motion of the ring. On going from  $C_0$  to  $C_1$ , the proposed H-bond, if it exists, is much weaker and present only in the first orientation, but not the second. The alkyl group allows the phenyl ring to reorient so that it is directed into the interface region of the micelle, while the alkyl chain extends into the interior of the micelle. The average orientation of the aromatic ring is further modified on going from  $C_1$  to  $C_2$ , but the change is smaller as the average orientation approaches its limiting value. By about  $C_4$  the torsional mobility of the ring, as suggested by the  $S_{yy}/S_{xx}$  ratio, undergoes only minor additional modifications.

These results strongly suggest that four carbon atoms in the ether alkyl chain are sufficient to incorporate the molecule fully into the superstructure of the aggregate with essentially one orientation. There appear to be some additional modifications in the ring orientation with a continuing increase in the length of the alkyl chain, but they are minor. Changes in chain length, by themselves, can influence overall motion and orientation, so it is difficult to ascribe a source to the minor changes observed in  $S_{yy}/S_{xx}$ . The orientation adopted by the aromatic ring is of some interest. For the longer  $n$ -alkyl derivatives,  $S_{yy}$  and  $S_{zz}$  are approximately equal and negative. This can only arise if the  $Y$  and  $Z$  molecular fixed axis is bisected by the director. In other words, the phenyl ring is preferentially aligned with its face at about  $45^\circ$  to the plane of the micellar surface and possibly rotating in this plane. This is quite different from the orientation of benzyl alcohol, where the ring protrudes more or less vertically into the core of the micelle.

Studies on the location and orientation of biologically active molecules in lipid bilayers are a very active field of research.<sup>1,7,8,24–28</sup> The location and orientation of benzyl alcohol, a commonly used anesthetic, in phospholipid aggregates has been recently studied experimentally and theoretically. Using  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts as well as UV spectroscopy, Okamura and Nakahara<sup>1</sup> have described the distribution of benzyl alcohol between the inner and outer interfaces of small unilamellar vesicles of egg yolk phosphatidylcholine. Our data also show that benzyl alcohol is effectively located at the interface of the NaDS or CsDS aggregate, but possibly oriented to accept an H-bond from the interfacial water. A recent molecular dynamics study<sup>8</sup> shows that benzyl alcohol, when located at the interior of a phospholipid bilayer membrane, does not significantly affect the order of the interior of the aggregate, and only a slight increase in the disorder of the core of the hydrophobic region is observed. In contrast,

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our results show that when benzyl alcohol is located at the interface of the CsDS mesophase, it significantly decreases the order of the bilayer surface.

Finally, in this work we have estimated the average location and orientation of benzyl alcohol and a series of alkyl benzyl ethers in  $N_D$  nematic lyomesophases prepared from NaDS and CsDS. In particular, benzyl alcohol seems to be positioned at the bilayer interface, possibly hydrogen-bonding with the interstitial water and disrupting the integrity of the CsDS bilayer surface. The effect of the

added guest molecule on the structure of the aggregate seems to depend on the electrostatic characteristics of the surface of the aggregate and also on the hydrophobic properties of the added guest molecule.

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