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Duncan W. Bruce^a; Gordon J. T. Tiddy^b; Jonathan M. Watkins^a

^a Centre for Molecular Materials and Department of Chemistry, The University, Sheffield, England ^b Department of Chemistry and Applied Chemistry, University of Salford, Salford, England

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The mesomorphism of 4-dodecyloxy-2-hydroxybenzoic acid and its sodium salt

by DUNCAN W. BRUCE*‡, GORDON J. T. TIDDY†
and JONATHAN M. WATKINS

Centre for Molecular Materials and Department of Chemistry, The University,
Sheffield, S3 7HF, England

† Department of Chemistry and Applied Chemistry, University of Salford,
Salford, M5 4WT, England

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The thermotropic and lyotropic mesomorphism of 4-dodecyloxy-2-hydroxybenzoic acid and sodium 4-dodecyloxy-2-hydroxybenzoate have been determined by a combination of optical microscopy, differential scanning calorimetry and NMR methods. While the free acid shows thermotropic N and S_C mesophases, its sodium salt shows lyotropic hexagonal (H₁), lamellar (L_a) and intermediate phases.

1. Introduction

In the study of mesomorphic transition metal complexes [1], one of the most interesting aspects is the comparison between the mesomorphism of the ligand(s) and that of the metal complex. While this is something which is quite well developed in thermotropic systems, it is certainly not well developed for lyotropic metal complexes, which are themselves not extensively studied. Lyotropic metal complexes may be grouped into three main classes. First, are the rigid-rod metal/acetylene polymers (see figure 1) which form nematic phases in chlorinated solvents [2]. Here, there is no real notion of the PBU₃ or acetylene ligands having some lyotropic mesomorphism in their own right.

Second are the columnar phases formed by peripherally sulphonated (or carboxylated) metallophthalocyanines [3] (see figure 2). Here, the metal is known to have an effect on the mesomorphism; for example, the inclusion of certain tripositive ions is found to suppress mesomorphism due to the formation of dimeric species.

Finally, there are the more conventional amphiphilic structures in which the metal forms part of the polar head

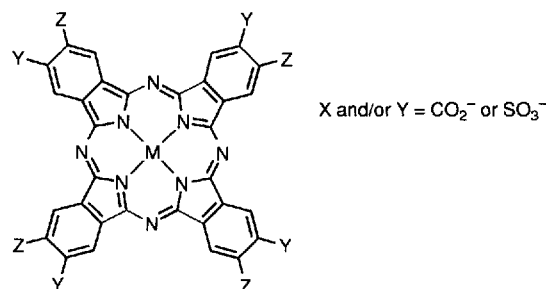


Figure 2. Laterally substituted phthalocyanines.

group; few examples are known where the lyotropic mesomorphism of such systems has been studied. We have become interested in this last area and have recently described mesomorphism in amphiphilic Fe(II) [4], Cr(III), Co(III) [5] and Ru(II) [6] systems. In the case of the iron complexes, the lamellar (L_a) phase shown by the alkylamine ligand is replaced by a hexagonal (H₁) phase of complex, while in the case of the Ru(II) complexes (see figure 3 (a)), there is no lyotropic mesomorphism of the 4-methyl-4'-alkyl-2,2'-bipyridine ligand.

The Cr(III) and Co(III) systems (see figure 3 (b)) are

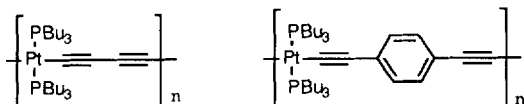


Figure 1. Mesomorphic, polymeric platinum acetylides.

* Author for correspondence.

‡ D.W.B. is the Sir Edward Frankland Fellow of the Royal Society of Chemistry 1994/95.

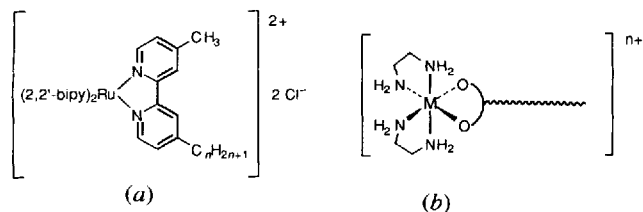


Figure 3. Lyotropic complex of Ru^{II} (a) and Co^{III} and Cr^{III} (b).

very similar and are based upon a *cis*-[(M(en)₂]³⁺ (en = 1,2-diaminoethane) unit. Depending on the other ligand (alkanoate, alkoxysalicylaldehyde or alkoxysalicylic acid) and the anion used, different lyotropic mesophases were observed. In order that some comparison be made between the mesomorphism of the ligand and that of the metal complexes, we have studied the thermotropic and lyotropic mesomorphism of one of the ligands, 4-dodecyloxy-2-hydroxybenzoic acid, HDOBA, (see figure 4) which we now report.

2. Results and discussion

4-Dodecyloxy-2-hydroxybenzoic acid (see figure 4) was prepared via reaction of methyl 2,4-dihydroxybenzoate and 1-bromododecane under basic conditions to give methyl 4-dodecyloxy-2-hydroxybenzoate which was then hydrolysed to the free acid.

2.1. Mesomorphism of 4-dodecyloxy-2-hydroxybenzoic acid (HDOBA)

The acid was insoluble in water and standard Lawrence penetration experiments [7] showed that it possessed no lyotropic mesomorphism. The thermotropic behaviour of the free acid was characterized by optical textures, observed between crossed polarizer on a hot stage optical microscope, and by differential scanning calorimetry

Table 1. Phase transition data for the acids.

Compound	Transition	<i>T</i> /°C	ΔH /kJ mol ⁻¹
HDOBA	Cr → S _C	99.4	30.9
	S _C → N	106.8	2.9
	N → I	109.9	3.3
DOBA	Cr → S _C	90.5	35.6
	S _C → N	132	1.8
	N → I	140	2.0

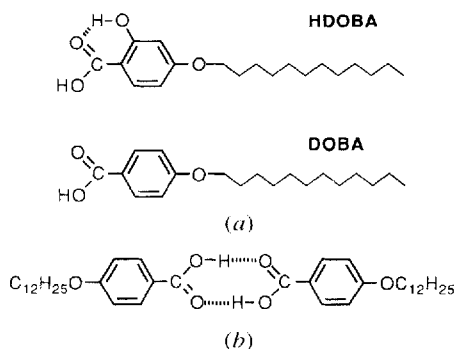


Figure 4. (a) 4-Dodecyloxy-2-hydroxybenzoic acid (HDOBA) compared to the simpler 4-dodecyloxybenzoic acid (DOBA), and (b) the hydrogen bonded dimer of DOBA.

(DSC). The optical textures clearly showed two mesophases—a smectic C phase and a nematic phase. The DSC data are consistent with this assignment. Data concerning these phase transitions are collected in table 1.

The above data are comparable to those previously determined for the structurally simpler analogue, 4-dodecyloxybenzoic acid (**2**; DOBA); the phase transition data for this material are also collected in table 1 [8].

Benzoic acid and its derivatives are known to form hydrogen bonded dimers which persist from the crystalline state through to the isotropic liquid state [4] (i.e. the intermolecular hydrogen-bonding is very strong). This is the reason why 4-dodecyloxybenzoic acid forms liquid crystalline phases; the dimerization (see figure 4) provides the necessary 'rod-like' structure. Hence, from the similarity between the mesomorphic behaviour of (**1**) and (**2**), it can be assumed that the hydroxy acid also forms hydrogen-bonded dimers, although the fact that the S_C and N phase are destabilized relative to those of (**2**) is of interest. Whether this arises from some broadening effect on the introduction of a 2-hydroxy group, or whether it depends on the fact that the hydrogen bonding situation is more complicated is not clear.

2.2. Mesomorphism of sodium 4-dodecyloxy-2-hydroxybenzoate (HDOB)

As an intermediate in the preparation of amphiphilic cobalt(III) complexes, the sodium salt is of interest in order to compare the mesomorphism of both the ligand and its complexes.

The thermotropic mesomorphism of the sodium salt was studied using optical microscopy and DSC. By optical microscopy, the sodium salt showed no phase changes until 194°C, when it adopted a non-geometric texture, often typical of a hexagonal phase. However, it also began to decompose at this temperature (confirmed by the DSC trace) and hence little information was obtained.

It has long been known that anhydrous soaps [9] and other anhydrous amphiphiles [10] exhibit various different phases between the crystalline and the isotropic liquid phases. It is now known [11] that one of these transitions often occurs when the hydrocarbon moieties of the amphiphile go from being crystalline (i.e. in the all-*trans* conformation) to being 'molten' (i.e. conformationally disordered), while the polar portions of the amphiphile remain in a crystalline state. This process is called conformational [11] or chain [12] melting. The DSC trace of anhydrous HDOB shows two small transitions at 40°C and 44°C with heats of transition being 5.2 kJ mol⁻¹ and 0.9 kJ mol⁻¹, respectively. Both transitions are assigned as partial conformational melting transitions (cf. the partial conformational melting transition of dodecylammonium chloride at 74°C with an enthalpy of transition of

2.91 kJ mol⁻¹) [10], because disordering of the ionic head groups occurs at much higher temperatures, [9, 12].

The lyotropic mesomorphic behaviour of this material was initially studied using standard Lawrence penetration experiments [7] followed by more detailed study by optical microscopy and ²H and ²³Na NMR spectroscopy, using samples of known composition.

The penetration experiment showed the formation of a hexagonal (H₁) mesophase with a non-geometric texture at 33.8°C between the micellar solution (L₁) and the crystalline state (S). As the temperature was increased, the phase became more mobile, until at 57.2°C, a more geometric texture with homeotropic areas appeared (between the H₁ and S); this intermediate mesophase was less viscous than the preceding phase (see figure 5). At 59.2°C, a lamellar (L_α) phase appeared (between the intermediate phase and S) and all three mesophases persisted up to the point the water evaporated. An outline phase diagram (see figure 6) was constructed by observation of the optical



Figure 5. Penetration scan for HDOB (70°C). (Top -H₁; middle-intermediate; lower-L_α. Sample size c. 0.4 × 0.5 mm).

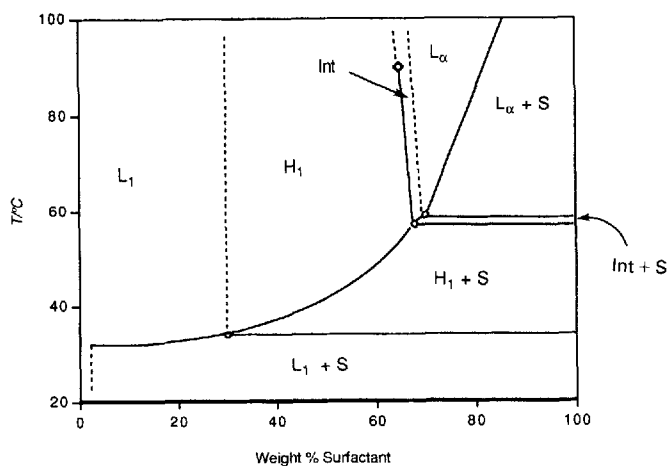


Figure 6. Phase diagram for the sodium 4-dodecyloxy-2-hydroxybenzoate/water system.

textures of samples of known composition and confirmed by the use of ²H and ²³Na NMR spectroscopy (see below). This phase diagram shows fairly unremarkable mesomorphic behaviour, although more samples (of different composition to those already studied) would need to be examined in order to establish the phase boundaries with accuracy; those given are only approximate and are based on data from optical microscopy. One unusual feature is the occurrence of the intermediate phase between H₁ and L_α, rather than a bicontinuous cubic (V₁) phase. These phases occur with long chain surfactants while V₁ phases are formed with short chain homologues [13]. Typically, the change in behaviour occurs at chain lengths of C₁₀-C₁₆. Clearly, the V₁ phase occurs with chain lengths below C₁₂ for the hydroxybenzoate series, if it forms at all.

Several points about the outline phase diagram should be noted. Firstly, in general two-phase regions have not been shown due to difficulties in observing them under the microscope. Secondly, the boundary between the micellar solution (L₁) and the hexagonal phase (H₁) was not accurately determined, and this is also true for the intermediate (Int) phase/lamellar (L_α) phase boundary. The upper limit of measurement is due to water loss, and the lower line (open squares) is the Krafft boundary below which pure solid (S) and almost pure water (W) coexist. Finally, the H₁/Int boundary is represented by open diamonds. The observation of L_α at the highest surfactant concentrations suggest that it is unlikely that the thermotropic mesophase is hexagonal.

2.3. NMR quadrupole splitting measurements

Nuclei with a spin quantum number, $I \geq 1$, possess an electric quadrupole moment and the interaction of this moment with an electric field gradient splits the NMR absorption line into $2I$ bands. Hence, a ²H nucleus ($I = 1$) has two bands, and a ²³Na nucleus ($I = 3/2$) shows three bands, when in an anisotropic phase (in isotropic phases, the interaction is averaged to zero). This splitting is known as the quadrupole splitting, Δ , and is dependent on the order parameter, S (a measure of the molecular ordering within the phase); for a uniaxial mesophase these parameters are related as shown in the following equation [14]:

$$\Delta = \frac{3}{2I(I-1)} \chi S$$

where χ is the quadrupole coupling constant and I is the spin quantum number. The quantity χ is determined by the magnitude and direction of the electric field gradient at the nuclei, while S is dependent on the time-average angle between the electric field gradient and the mesophase uniaxial (θ_{DM}) given by [10]

$$S = \frac{1}{2}(3 \cos^2 \theta_{DM} - 1).$$

Note that alignment at the micelle surface has $\theta_{DM} = 0^\circ$ and 90° for lamellar and hexagonal phases, respectively; hence for identical molecular orientations, $S(\text{hex}) = -0.5 S(\text{lam})$.

For deuteriated water molecules in a mesophase, the quadrupole splitting, Δ^w , is determined by the fraction of water molecules 'bound' to the water/surfactant interface. These water molecules undergo rapid exchange with the unbound or 'free' water molecules (for which $\Delta^w = 0$). Thus Δ^w is given by [15]

$$\Delta^w = p_b^w \Delta_b^w = p_b^w \frac{3}{4} \chi_b^w S_b^w$$

where p_b^w is the fraction of bound water and the subscript b refers to the properties of bound water molecules.

Often, the concentration of bound water is directly proportional to the surfactant concentration (C_s) because the surfactant head groups (and counter-ions) have a specific number of water molecules bound to them. Thus, we can write [15]

$$\Delta = K \frac{C_s}{C_w} \Delta_b^w$$

where C_w is the total (bound and free) water concentration and K is a constant.

Counter-ion quadrupole splittings in a mesophase again arise from 'bound' ions, i.e. those with *c.* 3 Å of the surfactant aggregate [16]. For many binary ionic surfactant/water systems, the fraction of counter-ions in this region is fairly constant (the 'ion-condensation' approximation [17]) and is almost independent of surfactant concentration or temperature. So the quadrupole splitting for sodium counter-ions, Δ^{Na} , is again related to the fraction of bound molecules (p_b^{Na}) [15]:

$$\Delta^{\text{Na}} = p_b^{\text{Na}} \Delta_b^{\text{Na}} = p_b^{\text{Na}} \frac{3}{4} \chi_b^{\text{Na}} S_b^{\text{Na}}$$

Using these equations, the results from the sodium 4-dodecyloxy-2-hydroxybenzoate/water system were interpreted.

Figure 7 shows the dependence of Δ^{Na} on composition at both 70 and 80°C. All of the spectra observed gave

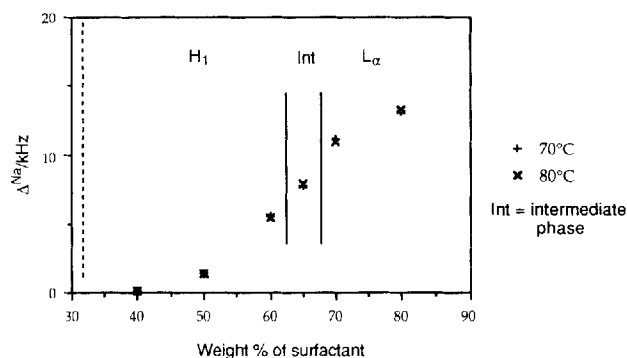


Figure 7. Sodium NMR quadrupole splittings (Δ^{Na}).

uniaxial powder patterns. There is no influence of temperature on Δ^{Na} but the change with concentration is enormous, from *c.* < 0.2 kHz at 40 per cent to 13 kHz at 80 per cent. Also, there is an apparently continuous increase in Δ^{Na} through the $H_1 \rightarrow \text{Int} \rightarrow L_\alpha$ transition region, with $\Delta^{\text{Na}}(H_1, 60 \text{ per cent}) \approx \frac{1}{2} \Delta^{\text{Na}}(L_\alpha, 70 \text{ per cent})$. Such a dramatic change with composition is not expected from the above introduction. However, Δ^{Na} values which are highly dependent on concentration have been reported for other carboxylate systems such as sodium octanoate/decanol/water mixtures [18]. There is a weak specific interaction between the sodium ions and head groups in addition to electrostatic attractions, such that the average position of the bound ions changes with concentration. At low concentrations, the ions are located between head groups, with the axes of the electric field gradient being close to normal to the interface axis. As the water content is reduced, the average axis of the electric field gradient shifts to being along the interface axis. This causes θ_{DM} to pass through the 'magic angle' where $\Delta^{\text{Na}} \approx \text{zero}$, followed by a sharp increase to a plateau value. For the present system, the value of Δ^{Na} at 40 per cent corresponds roughly to the magic angle, while given the factor of two increase expected at the $H_1 \rightarrow L_\alpha$ transition, the values at 60, 70 and 80 per cent are reasonably similar. Hence, θ_{DM} probably lies along the normal to the micelle surface. Thus, it seems likely that the same specific ion binding phenomenon found to occur with other sodium alkylcarboxylates also occurs here. Given the large size and polarizable nature of the hydroxybenzoate moiety, this is not surprising.

If the above holds true, then large changes in the Δ^{Na} values above the 60 per cent concentration reflect changes in the micellar architecture. The values for hexagonal and lamellar phases imply a structure for the intermediate phase which is uniaxial, but of intermediate curvature. Such a structure is the body-centred tetragonal phase, $T_1(L_\alpha^H)$ which occurs at a similar position in the phase diagram for a number of other surfactants [19]. This consists of a series of surfactant layers with each layer having a tetragonal array of water-filled holes. The junction zones in a given layer are located above and below the holes in neighbouring layers. Further discussion of these phases is given in [19]. We note that this phase has a strong tendency to form homeotropic regions, as we observe here (see figure 5).

When the deuterium spectra are considered (see figure 8), there are some surprises. Firstly, the major peaks rarely show well-resolved splittings, and hence most of the data for water in table 2 are the peak width at half height ($\Delta v_{1/2}$). Secondly, the quadrupole splittings (or $\Delta v_{1/2}$) are much smaller than expected above 60% w/w surfactant (see table 2), where we would expect to see an increase by at least a factor of two between samples containing the 60

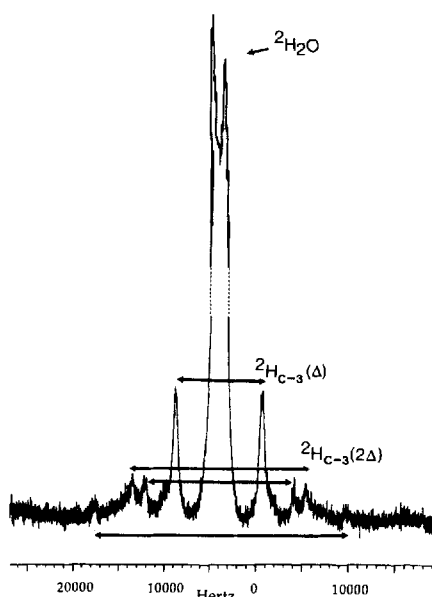


Figure 8. A deuterium NMR spectrum of 60% w/w surfactant in D_2O at $70^\circ C$. Peak assignments are shown where this is possible. The two unassigned peaks arise from $^2H_{C-5}$ and $^2H_{C-6}$.

Table 2. 2H Quadrupole splittings for sodium 2-hydroxy-4-dodecyloxybenzoate (HDOB)/water mixtures.

Conc. wt%	$T/^\circ C$	2H_2O		$3-^2H^\ddagger$	$5,6-^2H^\ddagger$	$2-OH^\ddagger$
		$\Delta\nu_{1/2}/Hz$	ΔHz	ΔkHz	ΔkHz	ΔkHz
40	70	170	—	3.30	2.2	—
	80	150	—	3.48	2.5	—
50	70	150	—	—	—	—
	80	200	—	—	—	—
60	70	—	279	9.56	16.4, 29.5	—
	80	—	282	9.58	16.0, —	—
65	70	800	—	8.61	14.64	—
	80	550	—	8.43	12.6	—
70	70	—	380	10.40	15.1	49.5
	80	540	—	13.78	23.4	—
80	70	780	—	15.4	25.03, 31.0	—
	80	800	—	14.99	23.54, 30.8	—

† Low intensity.

‡ Very low intensity.

and 70% w/w surfactant (due to the hexagonal-to-lamellar transition, cf. the Δ^{Na} in figure 7). Thirdly, there are extra, small peaks in the spectra; although there are several of these, they are all of very low intensity except for one set (see figure 8). Considering the magnitude of Δ_b^w , we expect surfactant-bound water on the CO_2^- , OH and Na^+ moieties. The sodium hydration water will have $\Delta_b \approx$ zero, since the solvation shell has high symmetry and there is rapid rotation of the ion. For the other two polar entities, we expect a finite Δ_b^w which increments by a factor of c .

5 over the concentration range 40–80 per cent. However, if the water bound to the two groups is in sites with order parameters having opposite signs, then a low averaged Δ_b^w value might occur. Since the aromatic ring appears to change its orientation with concentration (see below), the same will occur for the bound water, and this further complicates matters.

That the water signal is usually too broad for the Δ values to be measured is surprising, given that well-resolved spectra were obtained for ^{23}Na . This probably arises from partially-averaged hydrogen exchange between the water and the 2-hydroxy group. In the 70 per cent sample at $70^\circ C$, a barely-resolved water doublet ($\Delta = 380$ Hz) was observed together with a low intensity doublet ($\Delta = 49.5$ kHz). At 80° , the outer doublet was not observed and the water doublet had broadened to obscure the splitting. This behaviour is typical of proton exchange where the exchange rate is of the same order as the quadrupole splitting [20]. The Δ value observed for the 2-hydroxy group is large compared even to the largest values observed for the ring C– 2H groups. However, given the highly anisotropic environment of the 2-hydroxy moiety (hydrogen-bonded to the carboxylate group and solvated by water), the value of χ is likely to be larger than that of water, for which $\chi = 222$ kHz [20], giving unusually large Δ values.

The other minor peaks in the spectrum arise from partial replacement of the aromatic protons by deuterium. The samples used for NMR were held at 70 – $80^\circ C$ for at least a week before measurement, to ensure complete mixing. Comparison of the proton NMR spectrum of a sample of the material which had been thus held, showed that the material had become partially deuteriated at the 3-position under these experimental conditions. This was confirmed by the appearance of a single peak at δ 6.35 in the deuterium NMR spectrum (in methanol) of the partially-deuteriated material.

From the proton NMR spectra, the aromatic hydrogen atom in the 3-position was estimated to be approximately 75 per cent deuteriated. That the proton in the 3-position should have proved to be so labile is not too surprising given that it has two electron-withdrawing groups adjacent to it on either side, whereas the other hydrogens have at most only one electron-withdrawing group adjacent to them.

Some of the spectra show that significant deuteriation of other ring positions has occurred, since one or two lower intensity doublets are frequently observed (see table 2). Only in a few spectra (60 per cent HDOB at $70^\circ C$ and 80 per cent HDOB at 70 and $80^\circ C$) are three doublets observed which could be assigned to the three ring C– H groups. (The outer doublet cannot be assigned to the O– 2H group because the intensity is too low.) This might have given the opportunity to obtain all the order parameters

required to define the exact ring orientation. However, to a first approximation, we expect the C–H bonds in the 3- and 6-positions to be colinear, with almost identical Δ values. This clearly is not the case. Hence, it is likely that the ring substituents alter the values of $\chi(\text{C}-^2\text{H})$ from the standard quoted value of $180 \pm 5 \text{ kHz}$ [21]. Thus, we cannot distinguish between C–5 and C–6 in assigning the low intensity doublets. However, two factors are immediately obvious from table 2. Below 50 per cent HDOB, the lowest intensity splitting is smaller than that of the deuteron attached to C–3 ($^2\text{H}_{\text{C}-3}$), whilst above 50 per cent all the values are larger. This demonstrates a major alteration in the head group conformation over the concentration range 40–60 per cent HDOB, in line with the ^{23}Na NMR data. Also note that the ring ^2H Δ values generally increase with concentration and do *not* show the factor of two change at the H_1/L_z boundary. Again, this indicates that the average conformation of the head group continues to vary up to the highest concentration examined.

We observe that $\Delta(^2\text{H}_{\text{C}-3})$ for the intermediate phase sample is slightly smaller than the value of the 60 per cent HDOB hexagonal sample. This implies an aggregate with curved surfaces, again being consistent with the previously proposed tetragonal phase structure. (Note that the observation of a doublet pattern for the $^2\text{H}_{\text{C}-3}$ resonance is good evidence that the sample is uniaxial, not biaxial, as for the deformed hexagonal phase.) To summarize, the NMR behaviour of HDOB exhibits special features due to the weak, specific interaction between sodium and the polar group, and the exchange of ring protons for deuterium. The presence of the bulky substituents in the aromatic ring alters the χ values for the different $^2\text{H}_{\text{C}}$ groups, making it impossible to use ring deuterium quadrupole splittings to measure order parameters.

Our NMR measurements have confirmed the presence of the hexagonal (H_1) and lamellar (L_z) mesophases, and also provided a possible, reasonable, structure for the intermediate phase.

3. Experimental

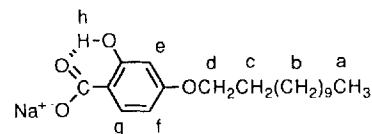
4-Dodecyloxy-2-hydroxybenzoic acid was prepared as described previously [5] and spectroscopic data were in good agreement with those previously reported. General instrumental methods are also previously described [5].

3.1. Preparation of sodium 4-dodecyloxy-2-hydroxybenzoate

4-Dodecyloxy-2-hydroxybenzoic acid (3.0 g, 9.30 mmol) was dissolved in a warm solution of sodium hydroxide (0.37 g, 9.25 mmol) in water (25 cm³) and the resulting solution was stirred for 5 min. After filtering the solution, it was cooled at 4°C for at least 1 h to precipitate the product as a colourless solid. This solid was filtered off,

washed with ice-cold water and air-dried. After thoroughly washing with ether the product was redried at 55°C under vacuum.

NMR data (250 MHz, CD₃OD):



δ ppm	Proton	No. of protons	Multiplicity	J/Hz
0.89	a	3	t	6.6
1.3	b	18	m	—
1.74	c	2	qn	6.9
3.94	d	2	t	6.3
6.29	e	1	d	2.5
6.32	f	1	dd	2.5, 8.5
7.71	g	1	d	8.8

Yield = 2.4 g (74 per cent). Microanalysis: expected; C(65.1), H(8.5), found; C(65.2), H(8.5) per cent. Expected values calculated using the molecular formula $\text{C}_{19}\text{H}_{29}\text{O}_4\text{Na} \cdot \frac{1}{3} \text{H}_2\text{O}$.

3.2. Partial deuteration of sodium 4-dodecyloxy-2-hydroxybenzoate

Deuterium oxide (*c.* 1 cm³) was added to a sample of sodium 4-dodecyloxy-2-hydroxybenzoate (*c.* 0.5 g) in a glass tube. This mixture was heated to 80°C and the glass tube was then sealed with a rubber septum. The sealed tube was maintained at 80°C for 2 weeks and then cooled to 4°C where it was kept for at least 1 h. The partially deuterated material was filtered off, washed once with ice-cold deuterium oxide and air-dried. After washing once with ether, the product was re-dried at 55°C under vacuum.

Due to broadening of the spectrum was not possible to measure any coupling constants for the aromatic protons or to determine the multiplicity of some signals.

3.2.1. ^2H NMR spectrum (61.4 MHz, CH₃OH)

Singlet at 6.35 ppm assigned to a deuteron in position e.

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