Synthesis and ionic properties of nematic compounds bearing an ether-crown moiety: an NMR approach†

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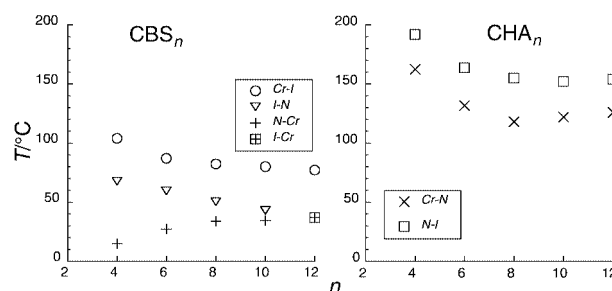[b] *Laboratoire de Physique des Solides, LA 2, Bâtiment 510, Université Paris-Sud, 91405 Orsay, France*

Thermotropic ionic nematics with moderate transition temperatures are obtained by dissolving alkali metal salts within nematogens bearing a crown ether moiety; in these media, the ions show a significant 'apparent ionic order' as measured by quadrupolar NMR spectroscopy.

Functionalized liquid crystals, which show the ordered structures of solids and the mobility of liquids, provide a combination of very innovative properties for numerous applications.[1] It is with this intent that grafting of poly(ethylene oxide)[2–6] or crown ether moieties has been already researched.[6–10] These segments are intriguing because they can dissolve organic molecules and ionic compounds.[11] However, when these polar units are linked to nematogen cores, microsegregation occurs between the different segments and leads to highly ordered self-organized phases.[12] The nematic phase is most suitable for NMR studies owing to its easy orientation in the magnetic field.

In this work we show that liquid crystals CBS_n, CHA_n and CRA_6 containing lateral chains and terminal crown ethers display a nematic phase at moderate temperatures over a wide temperature range, even when significant amounts of salt are dissolved within the phase. The cation binding ability of these new nematogens was analysed by thermal analysis and NMR studies. The three series of compounds were synthesized following standard steps which have already been reported.[4,13]
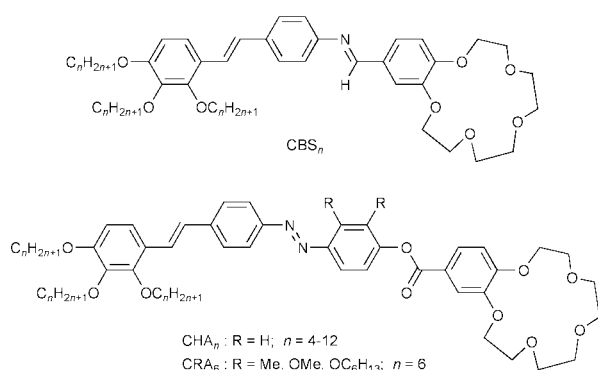
The transition temperatures of the compounds CBS_n and CHA_n are plotted in Fig. 1. The CBS_n compounds show monotropic behaviour while all compounds in the CHA_n and CRA_6 families show an enantiotropic nematophase over a wide temperature range. As expected, the mesogenic behaviour is very sensitive to the properties of the rigid core. The CBS_n series is based on three conjugated aromatic units. The balance between the mobility induced by the three alkoxy chains, the rigidity of the conjugated core and the relative rigidity of the crown ether leads to compounds presenting monotropic behaviour with a large temperature difference between the melting

† Electronic supplementary information (ESI) available: synthesis of CBS_n and CRA_6. See http://www.rsc.org/suppdata/cc/b0/b000501k/

Fig. 1 Nematic range for CBS_n and CHA_n; transition temperatures measured by DSC (10 °C min⁻¹) (Cr: crystalline, N: nematic, I: isotropic).

and the isotropic–nematic transitions.[13] Lengthening of the rigid core in the CHA_n series leads to the formation of enantiotropic nematophases at fairly high temperatures relative to the CBS_n series.

To our knowledge, molecules of the CHA_n series are the first nematogens containing a crown ether moiety which show a large liquid crystalline range and reasonably low transition temperatures. This can be explained by the presence of three alkyl chains which increases the fraction of the mobile components which perturb the molecular cooperative packing by decreasing the segregation between aromatic, polyether and aliphatic fragments.[13] This effect has been also observed in polycatenar compounds.[14] In order to decrease the transition temperatures we have introduced lateral substituents. The liquid-crystalline properties of the CRA_6 compounds are listed in Table 1. As expected, the presence of lateral substituents substantially decreases the transition temperatures.

Crown ether derivatives are widely studied for their ability to dissolve salts by complexing cations leading to 'host–guest' entities.[11] Consequently, Li^+ and Na^+ salts were introduced inside the CHA_4 compound. Measured quantities of salt and nematogen were dissolved in $CHCl_3$–THF and heated for 1 h. Then the solvents were removed *in vacuo* and further dried (0.1 mm Hg, 70 °C, 3 h). The mixtures were then studied by DSC and polarizing microscopy. The phase diagrams are shown in Fig. 2 as a function of the molar ratio x (x = cation/crown ether moiety). CHA_4 mixed with $LiBF_4$ or $NaCF_3SO_3$ behave similarly with a nematic phase observed for x up to 0.5, and a more ordered smectic phase for higher values of x.

This molecule shows an unexpected nematic phase for a wide range of x, whereas molecules described elsewhere in the literature always show very ordered phases, even for low values of x. These ordered phases are generally explained by the

Table 1 Nematic range for CRA_6 compounds

R	Cr		N		I	
H	131.7	•	163.9	•	158.8	•	65
Me	137.5	•	159.8	•	157.5	•	119
OMe	120.7	•	129.3	•	126.1	•	< 30
OC_6H_{13}	75.9	•	88.4	•	83.7	•	< 30
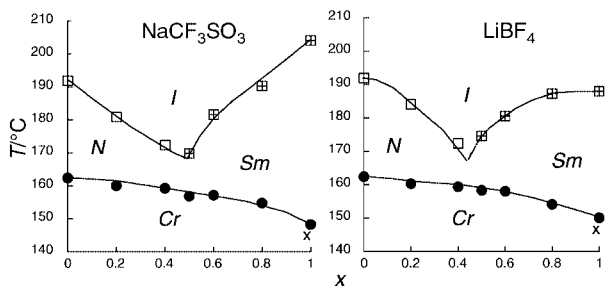
Fig. 2 Phase diagrams for CHA_4 alkali salt mixtures.

Fig. 3 ^7Li and ^{11}B NMR spectra of $LiBF_4$ (0.2 mol dm^{-3}) dissolved in $CMeA_6$, in the isotropic and nematic state. Spectra are shown to an absolute scale.

stacking of two molecules sharing one cation or by the segregation of the ionic motives in columnar mesostructures.[6] In these new systems, the observation of nematic phases over a large compositional range (x) can be explained by the three alkyl chains which prevent ionic interactions between cations, counter anions and molecules. The size of the crown cavity is larger than Li^+ but fits Na^+ ions well, while larger cations such as Cs^+ do not fit[11] and attempts to obtain mesogenic phases with this ion failed.

NMR of quadrupolar nuclei (*i.e.* with nuclear spin $I > \frac{1}{2}$) is a very sensitive method for probing the local anisotropy inside oriented media.[15] In isotropic solvents the averaged electric field gradient (*efg*) is zero and each non-equivalent nucleus gives a single line in the fast reorientation regime. In contrast, when ions are dissolved in anisotropic media, host–guest interactions may lead to the partial orientation of the dissolved entities and to a polarization of the electronic cloud, leading to a partially ordered *efg* of the cation which leads to $2I$ equally spaced lines. The existence of a quadrupolar splitting indicates that ions are effectively distorted and oriented inside anisotropic media. The measured quadrupolar splitting, $\Delta \nu_Q^{(ion)}$, represents the so-called 'apparent ionic order'.[16]

^7Li and ^{11}B ($I = \frac{3}{2}$) NMR spectra obtained for CRA_6 (R = Me) mixed with 0.2 equivalents of $LiBF_4$ [nematic range 136.6–152.4 °C (heating cycle) and down to 85 °C (cooling step)] are shown in Fig. 3. At 433 K, single lines are observed, thus showing the isotropy of the medium. Narrow linewidths were measured for both ions (*ca.* 20 Hz) which indicates their high mobility inside the fluid system. In the nematic state (400 K), triplets (intensities 3:4:3) were observed for both nuclei, indicating that both cations and anions experience the anisotropy of the media. The quadrupolar splittings, $\Delta \nu_Q^{(Li)}$ and $\Delta \nu_Q^{(B)}$ are ten times larger than those measured in swollen oriented DNA fibers[17] or lyotropic liquid crystals.[18] An enlargement of the ^{11}B central signal also indicates a quintet structure, which corresponds to the dipolar splitting $T_{B-F}^1 = 66$ Hz. An 'apparent ionic order' $S = 5 \times 10^{-3}$ was calculated for the anion inside these structures. This low value may be attributed to anisotropic tumbling and distortion of the anion from its initial T_d symmetry.[18]
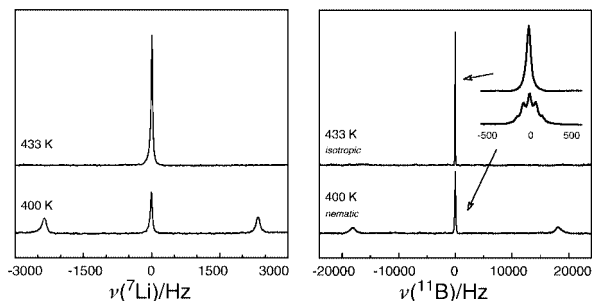
Further studies are in progress to understand the orientation inside these systems and to correlate these values with ion-crown complexation and ion-pairing.

Notes and references

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