Cyclic ureas as novel building blocks for bent-core liquid crystals†

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Cyclic ureas represent a new class of bent-core liquid crystals which, depending on the ring size and other structural parameters, can form a series of polar (ferroelectric and antiferroelectric), as well as non-polar, tilted and non-tilted smectic and undulated smectic phases.

Currently there is great scientific interest in bent-core liquid crystals (LCs), as these materials show special properties not achievable with other liquid crystalline materials.[1] Smectic and columnar phases of these molecules can, for example, show polar order, which leads to antiferroelectric and ferroelectric switching. This is of significant interest for numerous applications, such as fast electrooptical switches, phase modulators and non-linear optic (NLO) materials.[2] The polar order in these mesophases is due to the restricted rotation of the molecules around their long axes because of the bend in their rigid aromatic cores. There is also the potential that biaxial nematic phases can be formed by these molecules.[3] If the molecules adopt a tilted organisation in polar layers ($\mathrm{SmCP_{A/FE}}$ phases), these layers possess an inherent chirality, as layer-normal, tilt-direction and polar direction describe either a right- or left-handed system (see Fig. S1 in the ESI†).[1,4] The occurrence of chiral superstructures in these mesophases, formed by achiral molecules, and the possibility of switching this chirality by electric fields are additional unusual properties of significant general scientific interest.[1]

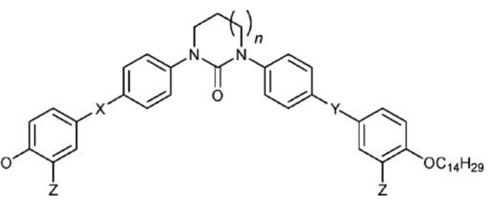
From the point of view of molecular design, bent-core LCs are obtained by introducing a bend angle in the range *ca.* 110 to 140° between two rod-like moieties (wings) by using 1,3-disubstituted benzenes, 2,5-disubstituted pyridines, 2,7-disubstituted naphthalenes or 1,3-disubstituted five-membered aromatic heterocycles (oxadiazoles, oxazoles), or by joining two rod-like molecules by non-cyclic spacers with an odd number of atoms (carbonyl, oxo, thia, 1,*n*-dioxaalkanes, *etc.*). Non-aromatic cyclic bent units are rare and to the best of our knowledge there is only one reported example—a substituted tetrahydropyrane derivative.[5]§

For bent-core molecules, it is also of significant interest to have polar substituents that can contribute to the magnitude of polarization and significantly modify the phase structures. The so-called B7 phases, for example formed by 2-nitro-substituted resorcinol derivatives, are characterized by helical superstructures.[6]

Herein we report that cyclic ureas represent new useful bent building blocks for the design of bent-core LCs (see the structure in Table 1). In comparison to other central units, the bending angle can be easily tailored by changing the ring size. Moreover, the polar carbonyl group is fixed in a defined direction in the bay region of the bent core. This is important for the systematic investigation of the effects of polar groups on phase behaviour.

Synthesis (Scheme 1) was achieved by a double Pd^0-catalyzed C–N cross coupling reaction[7] between the cyclic ureas **1/*n*** (*n* = 0, 1, 2) and ethyl 4-bromobenzoate or 4-bromobenzaldehyde to yield the diesters **2/*n*** and the dialdehydes **3/*n***, respectively. Compounds

Table 1 Mesophases, transition temperatures (*T*/°C) and associated enthalpy values (Δ*H*/kJ mol^{-1}, lower lines) of the bent-core molecules **6/*n***, **7/*n*** and **8/*n***[a]



No.	X, Y	Z	*n*	*T*/°C								
6/0	OOC, COO	H	0	Cr	189 36.8	SmC	314 —[b]	SmA	329 6.7	Iso		
6/1	OOC, COO	H	1	Cr	198 38.9[c]	($\mathrm{M_1}$	186)	$\mathrm{SmCP_A}$	200 7.3	SmA	208 10.6	Iso
6/2	OOC, COO	H	2	Cr	107 71.1	($\mathrm{SmAP_A}$	98) 0.2	SmA	159 8.0	Iso		
7/1	COO, OOC	H	1	Cr	119 52.6	$\mathrm{M_2}$	143 9.2	$\mathrm{SmCP_A}$	174 18.3	Iso		
8/1	COO, OOC	F	1	Cr	86 54.9	B5″	107 6.8[d]	$\mathrm{B5'P_{FE}}$	119 0.2[d]	$\mathrm{B5P_{FE}}$		
				$\mathrm{B5P_{FE}}$	138 3.2	USm- $\mathrm{CP_{FE}}$	165 —[e]	USmC	187 23.2	Iso		

[a] Determined in the first DSC heating run (10 K min^{-1}). Abbreviations: Cr = crystalline solid (Cr–Cr transitions occurring below the melting temperature are included in the enthalpy value), SmC = tilted smectic phase with uniform (synclinic) tilt direction, SmA = non-tilted smectic phase, Iso = isotropic liquid, $\mathrm{SmAP_A}$ = antiferroelectric (AF) switching non-tilted smectic phase, $\mathrm{SmCP_A}$ = AF switching tilted smectic phase, B5″ = non-switching smectic low temperature phase with in-plane order, $\mathrm{B5P_{FE}}$ and $\mathrm{B5'P_{FE}}$ = ferroelectric (FE) switching smectic phases with in-plane order, USmC = undulated (wavy deformed) smectic phase, $\mathrm{USmCP_{FE}}$ = FE switching undulated smectic phase, $\mathrm{M_1}$ and $\mathrm{M_2}$ = mesophases with unknown structures. [b] Second order phase transition. [c] Not resolved due to rapid crystallization. [d] Peak splits only in the cooling run; in the heating run there is only one peak at 119 °C for both transitions. [e] Transition between USmC and $\mathrm{USmCP_{FE}}$ is not associated with an enthalpy change (see Fig. S5).

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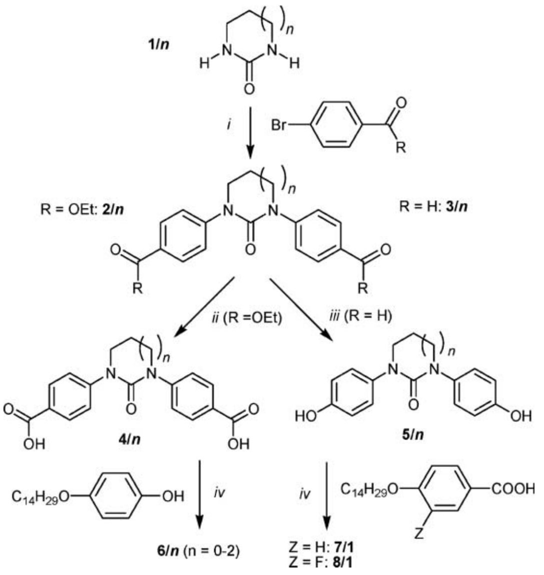

Scheme 1 Synthesis of compounds **6/n–8/n**. *Reagents and conditions*: (i) $Pd_2(dba)_3$, XANTphos®, Cs_2CO_3, dioxane; (ii) 1: KOH, EtOH, H_2O, 2: H^+, H_2O; (iii) m-CPBA, $CHCl_3$; (iv) 1: $SOCl_2$, 2: phenolic component, DMAP, Et_3N, CH_2Cl_2.

2/*n* were hydrolyzed to the dicarboxylic acids **4/*n***, whereas the diphenols **5/*n*** were obtained by the Bayer–Villiger oxidation[8] of aldehydes **3/*n***. Esterification reactions of **5/*n*** with benzoic acids or **4/*n*** with 4-alkoxyphenols lead to the bent-core molecules **6/*n***, **7/*n*** and **8/*n***, which were purified by crystallization (see ESI†).

Preliminary investigations of the mesomorphic properties of bent-core ureas **6/*n***, **7/1** and **8/1** are based on polarized light microscopy on a hot stage (Mettler FP 82 HAT), differential scanning calorimetry (DSC-7, Perkin-Elmer), X-ray diffraction, as well as on electrooptical experiments.

The mesophases and transition temperatures of the synthesized compounds are collated in Table 1. Though all compounds show LC phases, the mesophase stability and the mesophase type strongly depend on the size of the central ring, on the direction of the COO linking units and on the substitution at the aromatic core (H, F). Attention is first focused on the effect of the size of the cyclic urea. Compound **6/0**, with a five-membered ring, has extremely high transition temperatures and exclusively non-polar smectic A (SmA) and smectic C (SmC) phases. These are LC phases, as typically observed for rod-like molecules. This indicates that the five-membered heterocyclic unit provides a nearly linear molecular shape and therefore this compound behaves like a rod-like molecule. The transition temperatures can be significantly reduced by enlarging this ring.

For compound **6/1**, with a six-membered ring, there is also a non-polar SmA phase at high temperature, but a polar-tilted smectic phase is observed at lower temperature. The transition can be seen optically by the occurrence of a dense stripe pattern in the fan texture of the original SmA phase, as shown in Fig. 1a (bottom). This mesophase shows antiferroelectric switching behaviour (P_s = 950 nC cm^{-2} at T = 190 °C) and is therefore assigned as $SmCP_A$ (B2 phase).¶ Hence, this compound behaves more like a bent-core molecule, and the phase structure can be changed from a non-polar to a polar smectic phase by a reduction of temperature.

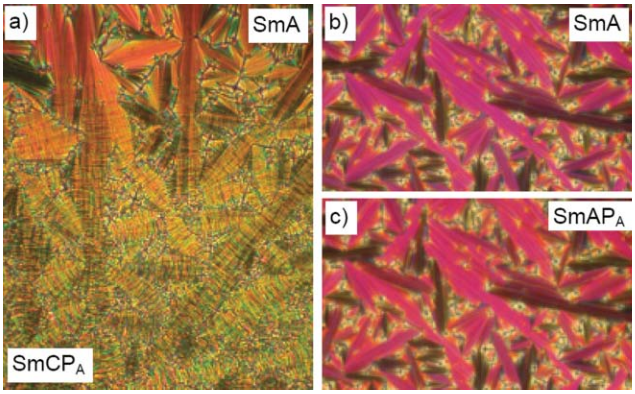

Fig. 1 Textures, as seen between crossed polarizers: (a) Compound **6/1** at 200 °C; due to a temperature gradient, the SmA phase is seen on top and the $SmCP_A$ phase at the bottom. (b) SmA phase of compound **6/2** at 110 °C. (c) $SmAP_A$ phase of **6/2** at 90 °C.

Compound **6/2**, incorporating a seven-membered ring as a bent unit, also shows a SmA phase at high temperature (Fig. 1b) and an antiferroelectric switching low temperature phase (see Fig. 1c and Fig. 2a), but the phase transition is completely different from that observed for **6/1**. Though the occurrence of a weakly birefringent schlieren texture in the homeotropically-aligned regions (see Fig. S2†) indicates a transition to a biaxial smectic phase at 98 °C, the fan shape texture is retained (see Fig. 1b,c). This means that there is no layer shrinkage at this phase transition, and therefore it is assumed that the polar smectic phase of **6/2** is a non-tilted $SmAP_A$ phase.|| This type of mesophase is extremely rare.[9] It seems that this seven-membered ring, due to its increased flexibility in comparison to the related six-membered urea, leads to a preference for non-tilted (polar and non-polar) over strongly-tilted smectic LC phases.

Inversion of the direction of the ester linkages, in the case of compound **6/1**, gives rise to a significant reduction of the phase transition temperatures. This leads to broader mesophase ranges at lower temperatures. For compound **7/1**, the SmA phase is completely removed and an antiferroelectric switching $SmCP_A$ phase (see Fig. S3†) is found, as is typical for bent-core molecules.** Below 143 °C, the $SmCP_A$ phase is replaced by a non-switchable mesophase characterized by sharp reflections, also

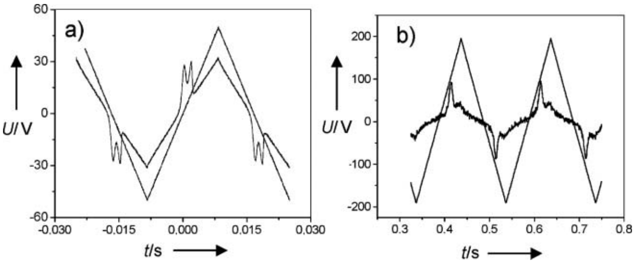

Fig. 2 Repolarisation current response curves: (a) $SmAP_A$ phase of **6/2** at T = 90 °C (V_{pp} = 100 V, f = 30 Hz, cell thickness = 5 μm, P_s = 630 nC cm^{-2}); the appearance of two peaks in each half period of the applied triangular wave voltage indicates antiferroelectric switching. (b) $B5P_{FE}$ phase of **8/1** at T = 130 °C (V_{pp} = 385 V, f = 5 Hz, cell thickness = 5 μm, P_s = 520 nC cm^{-2}); the appearance of only one peak is a first indication of a ferroelectric switching process.

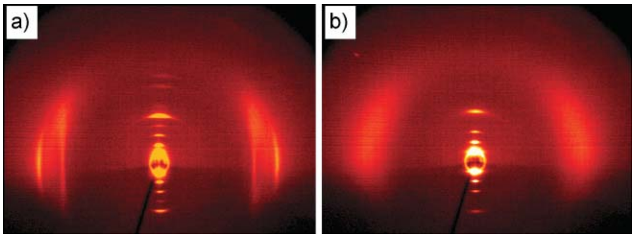

Fig. 3 X-Ray diffraction pattern of aligned samples of **8/1**: (a) $B5_{FE}$ phase at T = 120 °C. (b) $USmCP_{FE}$ phase at T = 150 °C. Alignment was achieved by surface alignment upon slow cooling on a glass substrate, where the X-ray beam was parallel to the substrate (HI-Star 2D detector (Siemens)).

in the wide angle region of the X-ray diffraction pattern (crystalline mesophase M_2).

Fluorination at the periphery of the aromatic core, adjacent to the terminal alkyl chains, gives rise to a further modification of the LC phases.[10] The melting temperature was further reduced and the antiferroelectric switching $SmCP_A$ phase of the non-fluorinated compound **7/1** was replaced by a series of different LC phases in compound **8/1**. In the temperature range 86 to 138 °C, the X-ray diffraction pattern of the aligned samples are characterized by a series of sharp layer reflections, in combination with relatively sharp and diffuse wide angle scatterings. The diffraction pattern between 120 and 138 °C (Fig. 3a) is very typical of a so-called B5 phase. This is a smectic phase with additional in-plane order, but without correlation between the layers.[11] The diffraction pattern only slightly changes at the transition to a phase assigned as B5′ at 119 °C on cooling. However, the wide angle reflections become sharper, and additional wide angle reflections appear at the next phase transition at 107 °C. This low temperature mesophase seems to be a more ordered version of the B5′ phase and is assigned as B5″. At temperatures above 138 °C, only layer reflections remain in the X-ray diffraction pattern, whereas the wide angle scattering becomes diffuse, indicating a fluid smectic phase (Fig. 3b). The first order reflection is accompanied by satellite reflections that indicate an undulation of the layers. As the texture of this high temperature phase is also similar to that of a columnar phase (see Fig S4†), it is assumed that this phase is an undulated or modulated smectic phase. In the temperature range 107 to 167 °C, these mesophases show ferroelectric switching ($B5'P_{FE}$, $B5P_{FE}$, $USmCP_{FE}$) characterized by the occurrence of only one relatively sharp polarisation current response peak in the half period of an applied triangular wave field (Fig. 2b).†† In the USmC phase above 167 °C and in the B5″ phase below 107 °C, no switching could be observed. It seems that in the non-polar USmC phase at high temperature, the rotation of the molecules is fast, and polar order is only achieved at reduced temperature ($USmCP_{FE}$ phase). The threshold voltage increases and the position of the peak changes at the transition to the $B5P_{FE}$ and $B5'P_{FE}$ phases. Below 107 °C, the relatively high order seems to inhibit molecular reorientation, and the ability of polar switching is again lost (B5″ phase).

In summary, we have reported a new universal building block for the design of novel bent-core liquid crystalline materials with ferroelectric and antiferroelectric LC phases. It can be expected that further structural modifications, for example, by introducing silyl units[12] and by combining with dendritic or polymeric structures will lead to new series of bent-core LC materials with interesting materials properties.

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Notes and references

§ 3,6-Di-*O*-[4-(4-octyloxybenzoyloxy)benzoyl]-1,5-anhydro-2-desoxy-D-arabinohexitol: This chiral compound, besides a cholesteric phase, also shows polar switching LC phases, but the spontaneous polarization is relatively low (P_s = 10–40 nC cm^{-2}), comparable with values typically observed for SmC* phases of rod-like molecules. Hence, the molecules reported herein represent the first examples of bent-core molecules with a non-aromatic and cyclic bent unit that form mesophases characterized by high polarization values in the absence of molecular chirality.

¶ Antiferroelectric switching was additionally confirmed by the observation of a tristable switching by optical investigation.

‖ Due to rapid crystallization, confirmation of the non-tilted organization was not possible by X-ray scattering. However, the presence of two-brush and four-brush disclinations in the schlieren texture confirmed a $SmAP_A$ structure. Also, in optical investigations, no rotation of the extinction crosses could be seen during the switching, as expected for $SmAP_A$ phases.

** Though there is only a single peak per half period of the applied triangular wave voltage, optical investigations clearly indicate a tristable switching characterized by a relaxation at 0 V, P_s = 200 nC cm^{-2}. The ratio of experimentally determined layer distance d (4.3 nm, X-ray) to molecular length L (5.8 nm in the most stretched conformation) is in line with a tilted organization of the molecules.

†† This single peak cannot be split by using a modified triangular wave voltage, where a pause is introduced at 0 V, thereby confirming FE switching. The switching process in all phases seems to take place by a collective rotation around the long axis, but a detailed understanding of the phase structures and switching behaviour requires further investigation. B5 phases usually show AF switching, whereas FE switching B5 phases are very rare.[11]

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