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A new room temperature dark conglomerate mesophase formed by bent-core molecules combining 4-iodoresorcinol with azobenzene units[†]

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The first bent-core molecules comprising 4-iodoresorcinol as the central core unit and incorporating azobenzene units have been synthesized. A new type of dark conglomerate phase (DC phase) is observed, which remains over a wide temperature range down to room temperature without crystallization.

Chirality has been one of the most attractive themes in chemistry since Pasteur's famous resolution experiment showing the handedness of tartaric acid.1 Since that time spontaneous formation of chiral phases by the self-assembly of achiral molecules or selfresolution of racemic conglomerates has been a well known phenomenon, often observed in the crystalline solid state.² However, with bent-core molecules this phenomenon was also found in soft crystals and even in liquid crystals.³ Spontaneous macroscopic optical activity has been observed for these achiral molecules in the soft crystalline helical nano-filament phases (assigned as HNF phases or B₄ phases)⁴ and in fluid polar smectic phases (B₂ phases).⁵ These optically nearly isotropic mesophases are composed of conglomerates of macroscopic chiral domains, which can easily be distinguished under a polarizing microscope (dark conglomerate phases, DC phases). Conglomerates of chiral domains were also found in the recently reported birefringent SmC_sP_R phase⁶ and in nematic phases formed by some bent-core mesogens,⁷ however in these cases their formation is dependent on surface interactions which are required to stabilize the chiral domains. The B₄ phase is the best investigated of the DC phases. In these mesophases the chirality arises from a crystalline packing of the aromatic cores in left- or right-handed helical nano-filaments. The packing of the terminal alkyl chains is frustrated and therefore these chains remain in a disordered liquid state.⁴ Another characteristic feature of these soft crystalline phases is that the chirality is retained upon

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dilution with a large excess of an achiral nematic phase.⁸ In contrast to the soft crystalline B_4 phase the formation of the completely fluid DC phases without crystalline nano-filaments is more difficult to understand.⁵ A common way to distinguish both types of DC phases is by XRD where the soft crystalline B_4 phases are characterized by the presence of sharp wide angle reflections, whereas only one diffuse halo around d = 0.45 nm is found for the fluid DC phases.

Herein we report a new subtype of DC phases which appears to be intermediate between these two types. Moreover, the reported compounds forming this phase are the first examples of bent-core liquid crystals (BCLCs) containing a 4-iodoresorcinol unit as the central core structure. These materials also contain photoisomerizable azobenzene groups which can be exploited for optical and optoelectronic devices.⁹ To the best of our knowledge, the compounds reported herein are the first examples of azo functionalized BCLCs showing DC phases.[‡]

The synthetic pathway leading to the bent core compounds A12 and B*n* is given in Scheme 1. The detailed synthetic procedures, purification and analytical data are reported in the ESI.[†]

Compound A12 without any lateral substituent on the outer benzene rings (X = H) was found to be non-mesomorphic, having a melting point at T = 112 °C and crystallizing at T = 77 °C. Replacing the hydrogen atoms next to the alkoxy chain by fluorine led to compounds **B***n*, (X = F, n = 8-14), which all give optically isotropic mesophases composed of a conglomerate of chiral domains (DC phases, see Fig. 2).



Scheme 1 Synthetic route to the bent core molecules An and Bn.^{10,11}

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Table 1 Phase transition temperatures ($T/^{\circ}C$), mesophase types, and transition enthalpies [$\Delta H/kJ$ mol⁻¹] of compounds A12 and B n^{a}

Compd n		1st heating	1st cooling	2nd heating		
A12	12	Cr 112 [35.1] I	I 77 [33.7] Cr	Cr 112 [34.9] I		
B8	8	DC 116 [31.5] I	I 107 [27.9] DC	DC 116 [30.6] I		
B10	10	DC 116 [25.0] I	I 102 [29.3] DC	DC 115 [23.9] I		
B12	12	DC 114 [25.8] I	I 103 [23.7] DC	DC 111 [25.3] I		
B14	14	DC 114 [30.2] I	I 109 [32.0] DC	DC 116 [30.1] I		

а	Peal	k temperatui	es from DSC	at a rate of	f 10 K m	in ⁻¹ ; abbi	reviati	ons: C]r =
с	rysta	lline solid; I	DC = dark co	nglomerate	phase;	I = isotro	pic lic	uid.	



The transition temperatures of the synthesized compounds are summarized in Table 1. All compounds Bn exhibit only one mesophase (the DC phase), and the phase transition temperatures are almost the same irrespective of the terminal chain length. Compound B14, as a representative example, was investigated in more detail. Upon cooling B14 under the polarizing microscope the isotropic liquid becomes highly viscous with glass-like appearance at 109 °C but no birefringence is observed between crossed polarizers (Fig. 2b). Fig. 1 shows the heating and the cooling differential scanning calorimetry (DSC) curves obtained for compound B14. The formation of this phase is associated with a relatively high transition enthalpy of $\Delta H \sim 30$ kJ mol⁻¹, which is a value similar to typical transition enthalpies of the B₄ to isotropic liquid transition.⁴ The onset temperatures of the transition peaks upon heating and cooling are approximately the same (\sim 111 °C) indicating the absence of a hysteresis. Also the transition peaks upon heating and cooling have approximately the same enthalpy values in the first and all following heating-cooling cycles.

Upon further cooling no crystallization occurs down to room temperature (Fig. 1). Even after storage of the sample at room temperature for 6 weeks the same transition temperatures and enthalpies were obtained and there was no indication of any crystallization (see Fig. S1 in the ESI⁺), even the samples obtained



Fig. 2 Textures of the DC phase of compound **B**14 at T = 80 °C: (b) between crossed polarizers and (a) after rotating one polarizer by 7° from the crossed position in the clock-wise direction and (c) in the anticlockwise direction, showing dark and bright domains, indicating the presence of areas with opposite chirality sense.

by "crystallization" from solvents appear to be in the mesomorphic state. Uncrossing the polarizers by a small angle leads to the appearance of dark and bright domains with a maximum contrast at an angle of *ca*. 7° . Uncrossing the polarizer in the other direction reverses the dark and bright domains (Fig. 2a and c). Rotating the sample between crossed polarizers does not lead to any change and this indicates that the distinct regions represent chiral domains with opposite handedness.

No current peak could be observed for compound **B**14 in electrooptical investigations of the mesophase and no birefringent mesophase is induced under an applied triangular wave voltage of up to 200 Vpp in a 6 μ m ITO cell. These features are also very similar to those of the soft crystalline B₄ type DC phases (helical nanofilament phases).

However the XRD pattern (see Fig. 3 and Fig. S2, ESI[†]) is different from those of the B₄ phases. For compound **B**14 an intense small angle reflection is observed, corresponding to a distance of d = 4.63 nm (90 °C). From this *d*-value and the molecular length L = 6.1 nm (in a 120° V-shaped conformation and all-*trans* alkyl chains) a d/L ratio of 0.76 results, which allows a tilt angle of the molecules up to $\beta = 41^{\circ}$ (cos $\beta = d/L$). Whether there is a tilt of the molecules or whether the difference between *d* and *L* is only due to chain folding and chain interdigitation cannot be decided at present. The reasons are that aligned samples cannot be obtained for DC phases due to their locally distorted structure (see Fig. S2a, ESI[†]) and that optical methods cannot be used for tilt angle determination of these isotropic mesophases.

With the exception of the intense small angle scattering all other scatterings have only very low intensity and are more or less diffuse. The low intensity could, at least partly, be due to the absorption by the heavy atom iodine incorporated in the molecular structure. A broad scattering is found at about $2\theta = 9.3^{\circ}$, corresponding to a mean distance of 1.0 nm and in the wide angle region there are two additional even weaker diffuse scattering maxima corresponding to *d*-values of 0.52 and 0.43 nm. So the majority of intensity of the diffuse scattering is found in the medium angle region. This kind of XRD pattern is distinct from the B₄ phases, which show three or more sharp wide angle reflections at larger angles in the 2θ range of 18° - 28° . However, it is also distinct from the fluid DC phases showing only one diffuse halo in the wide angle region at $2\theta \sim 20^{\circ}$ besides the small angle layer reflection.^{5a}

Though the precise origin of this diffraction pattern is still unclear, in a tentative model it can be assumed that the individual bent-core molecules form densely packed crystalline nano-clusters



Fig. 3 XRD pattern of the DC phase of compound **B**14 at T = 90 °C; the inset shows the magnified (~40 fold) wide angle region after baseline correction.

incorporating around 4-6 molecules. The mean distance between these nano-crystallites is assumed to give rise to the weak diffuse scattering with a maximum around 1.0 nm. The further growth of these clusters is obviously inhibited. This might be caused by the packing of helical conformers, which leads to a twist and inhibits the further growth to larger nano-filaments or crystalline layers. Nano-crystallites with identical twist sense arrange in layers with only short range order in the layers. As packing of nano-crystallites with identical chirality is favorable macroscopic chirality develops. The chirality induces twist and bend of the layers which, together with the effects of steric and packing frustrations,⁵ gives rise to a strong non-regular deformation or fragmentation of these layers. The correlation length of uniformly oriented domains is in the range of 35 nm (as estimated from the full width at half-maximum of the layer reflection peak) which is below the wavelength of light, thus leading to an optically isotropic appearance of the phase. Some parts of the alkyl chains seem to remain in a disordered state and contribute to the diffuse wide angle scatterings (see Fig. 3).

As it is known that B₄ phases can be diluted by nematic LC hosts to a high degree (>95%) without loss of the chirality⁸ we investigated a 1:1 mixture and a 1:9 mixture of B14 with 4'-pentyl-4-cyanobiphenyl (5-CB). In the 1:1 mixture the DC-Iso transition is reduced to 60 °C, but the chiral domains are still clearly visible (see Fig. S3a-c, ESI[†]). This DC phase rapidly crystallizes at 46 °C (Fig. S3d, ESI[†]) and upon heating the crystalline material melts at 86 °C to an isotropic liquid. In the 1:9 mixture no DC phase is formed, again compound B14 crystallizes from the nematic phase at T = 35 °C and these crystals melt at 52 °C. So, in contrast to B_4 phases there is a clear destabilizing effect of 5-CB on the DC phase. Simultaneously, formation of a crystalline phase is strongly enhanced. It seems that the 5-CB molecules can reduce the frustration of the packing of the molecules and allow the growth of the small nano-crystallites to a macroscopic crystalline phase. It is however not clear if pure B14 crystallizes or if these crystals involve additional 5-CB molecules.

It appears that the presence of the relatively large and highly polarizability of iodine in the 4-position of the resorcinol unit provides bent-core mesogens with new interesting phase structures. The observed kind of DC phase is not reported for related molecules with chlorine at the same position.¹¹ Bromine seems to be a bit more favorable for the formation of DC phases,¹¹ § whereas iodine seems to have a much stronger DC-promoting effect. The bulky iodine might lead to strongly twisted helical molecular conformations by twisting the adjacent COO group out of the planes of the adjacent benzene rings,¹² thus favouring layer distortion and formation of chiral superstructures. Iodine–iodine interactions or weak halogen bonding interactions¹³ could also contribute to this effect.

In summary, we report herein the first bent-core liquid crystalline materials containing 4-iodine substitution in the central core unit. These compounds exhibit a new type of DC phase¶ occurring in broad temperature ranges including room temperature. Moreover, these are the first examples of azobenzene-based BCLC showing DC phases.‡ The DC phase formed by this kind of molecules is different from the previously reported types and could contribute to an improved understanding of these phases and the occurrence of spontaneous achiral symmetry breaking in soft matter in general. Moreover, the possibilities provided by the photoisomerizable azobenzene units could lead to interesting perspectives for chirality switching and phase modulation by interaction with circularly polarized light.^{9,14}

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Notes and references

 \ddagger B₄-type DC phases have been reported for bent shaped mesogenic dimers combining two rod-like azobenzene units. 15 A B₄-like DC phase was found recently for one homologue in a series based on a 4-bromoresorcinol core with rod-like azobenzene units upon cooling from a nematic phase, but with a very short range before crystallization. 11

§ Besides the B_4 -type helical filament phases a soft crystalline dark conglomerate phase with a 2D lattice¹⁷ and for the fluid DC phases, which usually have a single layer structure, an intercalated B_6 -like version was also reported recently,¹⁸ moreover an achiral cubic phase composed of vesicular layer aggregates has been reported.¹⁹

 \P Dark conglomerate phases were also observed for some 4-bromores orcinol esters with Schiff base wings. 16

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