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Core-to-core dimers forming switchable mesophase

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We report structurally new type of dimers composed of bent-core molecules connected through their central cores by an alkylene spacer. Various self-assembling structures are discovered when prolonging the terminal alkyl chains in arms. Among diverse mesophases, the antiferroelectric type of switching under applied electric field is observed.

Liquid crystals (LCs) represent unique state of matter, which links anisotropy of the solid state and fluidity of the liquids. Bent-core mesogens are fascinating part of LCs due to their unusual physical properties. Until the discovery of polar switching for bent-core (BC) compounds in 1996,[1] polar properties: ferro- or antiferroelectric were exclusively reported for chiral mesogenic molecules (rod- or disc-like). The unique nature of polar order of BC mesogens is due to the strong steric hindering of close-packed molecules within smectic layers.

Most of the polar BC mesophases are tilted smectic phases (denoted as SmCP) with four distinct substructures, classified according to the tilt and/or the polarity in consecutive layers. Notation C_S means synclinic, C_A anticlinic orientation of the molecules, P_F stands for ferroelectric and P_A for antiferroelectric (A) state in consecutive layers.[2] Another distinctive feature of bent-core compounds is that they easily form modulated structures. For example, there are columnar phases (denoted as B_1) made of layer polar fragments with 2D density modulation parallel to the polarization vector.[3] Contrary to polar smectics, the B_1 phases usually do not reveal optical response and polar switching under application of electric field.

Liquid crystalline dimers and oligomers are of contemporary interest, because they frequently exhibit rich mesomorphic properties, different from those of monomers and can also serve as models to predict liquid crystalline properties of polymers.[4] Calamitic[5], discotic[6] and bent-core dimers[7] of versatile topology have been investigated. The molecular structure of a LC dimer usually consists of two monomeric units linked by a flexible spacer. Of the previously designed bent-core dimers,[7] the vast majority of materials are based on end-to-end arrangement of cores (Fig. 1a).[7a-e] Just a few dimers with other geometries were prepared, among them side-to-end type dimers (Fig. 1b).[7f] It was shown that the character of the linking group strongly influences the type of the phases formed.[7a] Bent-core dimers having W-shaped geometry with an additional inner bend unit (Fig. 1c) have been synthesized and studied.[8] BC-dimers based on core-to-core interconnection (Fig.1d) have been rarely reported.[7e]

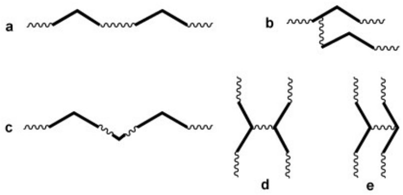

Fig. 1 Representation of different types of connections in bent-core dimers: a) end-to-end, b) side-to-end, c) W-shaped, d) and e) core-to-core

Herein, we present a new type of bent-core dimers (Fig. 1e) in which the central units are connected top-to-bottom. The molecular structure of the synthesized dimers denoted as **D3-*n*** (Fig 2) is derived from substituted resorcinol cores joined with an propylene-1,3-dioxy linking unit (3 stands for the number of carbons in the spacer and n corresponds to the length of terminal alkyl chains). The terminal chains are the same in all arms and vary from C_2H_5 (*n*=2) to $C_{12}H_{25}$ (*n*=12). All synthesised compounds exhibited mesomorphic properties. Phase transition temperatures and corresponding phase transition enthalpies are collected in Table 1. DSC thermographs are presented in ESI, see Fig.S1.

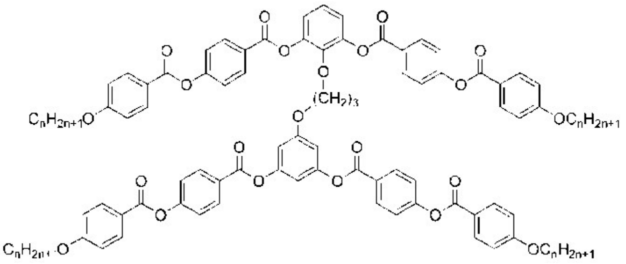

Fig. 2 Structure of the studied dimers (denoted as **D3-*n***).

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† Footnotes relating to the title and/or authors should appear here.
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For all compounds only a single enantiotropic liquid crystalline phase has been observed. Nevertheless, character of the phase depends strongly on the length of alkyl terminal chains (on *n* number). For homologues with the shortest chain **D3-2** and **D3-4**, a fan-shaped texture is observed under polarizing microscope for planar samples (Fig. 3a), as well as a homeotropic texture for one-surface-free samples. No electro-optical response was obtained under applied electric field up to 20 V/μm. Type of the optical textures and lack of electric response suggested an orthogonal SmA phase (SmA). The x-ray measurements confirmed a layered structure; in the small-angle region a sharp peak was detected, while in wide-angle region a broad peak was found corresponding to the mean in-plane distance between molecules about 4.5Å. (Fig.4a). The observed broad peak is interpreted as related to the mean distance between terminal alkyl chains. Similarly as for rod-like molecules, we do not see separate signals from the distance between cores. The layer thickness, *d*, was established from the small-angle peak position. We found *d*=16.5 Å and *d*=18 Å for **D3-2** and **D3-4**, resp. The *d* value corresponds to the half of calculated length of BC dimer, *l* (*l*≈33.6Å and *l*≈37.4Å for **D3-2** and **D3-4**, respectively). Therefore, we conclude that short homologues **D3-2** and **D3-4** formed an intercalated type of the SmA phase (model is presented in ESI, Fig. S2).

Table 1
Melting point, m.p., the phase transition temperatures, T_{tr}, crystallization temperature, T_{cr}, in °C and corresponding enthalpy changes, ΔH, in kJ mol^{-1} (in brackets), detected on the second temperature run at a rate of 5 Kmin^{-1}.

	n	m.p. (ΔH)	T_{cr} (ΔH)	**M**	T_{tr} (ΔH)
D3-2	2	160 (+41.9)	129 (–30.1)	SmA	201 (–25.0)
D3-4	4	146 (+21.4)	98 (–12.3)	SmA	183 (–25.3)
D3-6	6	133 (+30.4)	91 (–19.6)	B_1	157 (–31.3)
D3-8	8	136 (+38.9)	93 (–22.8)	B_1	140 (–32.7)
D3-10	10	138 (+77.6)	112 (–31.7)	SmC_AP_A	133 (–35.6)
D3-12	12	129 (+37.3)	99 (–25.3)	SmC_AP_A	139 (–39.4)

Homologues with the intermediate length of terminal alkyl chains, **D3-6** and **D3-8,** revealed a columnar phase. Textures with coloured domains were observed under polarizing microscope (Fig. 3b), and similarly to shorter homologues no electro-optical response was detected. For both compounds the x-ray diffraction studies unambiguously evidenced the B_1 type of mesophase, with the columnar phase built of smectic layer fragments. In the x-ray pattern there are few incommensurate signals in the small-angle region and a broad maximum in large-angle region (Fig. 4b). The small angle x-ray patterns could be indexed assuming centred orthorhombic crystallographic unit cell, one of the unit cell dimensions was found to be comparable to the calculated molecular length (for the cell parameters see ESI).

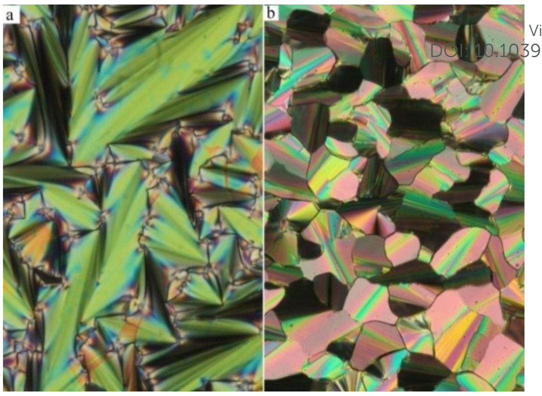

Fig. 3 Textures a) for **D3-2** in the SmA phase at temperature T=160ºC and b) for **D3-8** in the columnar B_1 phase at T=140ºC.

Homologues with the longest terminal alkyl chain, **D3-10** and **D3-12**, exhibit a switchable lamellar phase and the characteristic electro-optical behaviour allowed to identify the observed mesophase as the SmC_AP_A. In the ground state (SmC_AP_A) an average optical axis results from alternation of the tilt direction in neighbouring layers, being parallel to polariser and analyser at zero voltage (Fig.5a). Under the applied electric field the optical birefringence increased significantly (Fig. 5b) and the extinction brushes rotated from the position along the polarizers by the angle of ~45 degrees, which proves that the SmC_AP_A phase transforms into SmC_SP_F structure. There are three distinct states, which can be distinguished by optical investigations, confirming the AF switching. The polarization current measured under triangular electric field exhibits two sharp peaks per half-period (Fig. 6), which is characteristic for antiferroelectric phase. The similar value of electric polarization, *P*=850 nC/cm^2, has been measured for both **D3-10** and **D3-12** compounds, by integration of the switching current peaks.

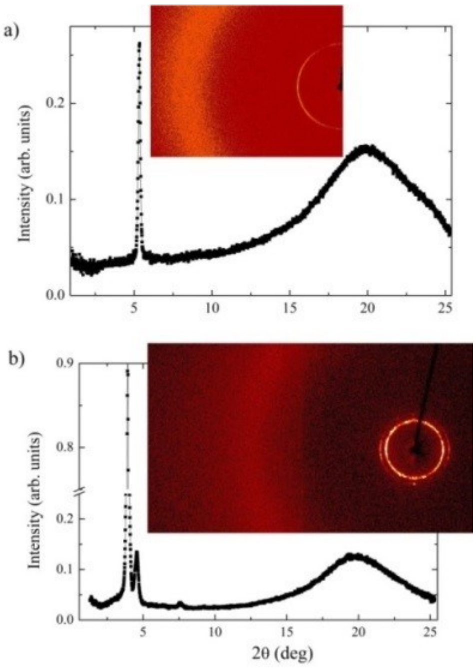

Fig. 4 The x-ray intensity profile versus the scattering angle for a) **D3-2** at T= 170°C and b) **D3-6** at T= 110°C. At insets the x-ray pattern for partially oriented sample is shown at corresponding temperature.

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The dielectric spectroscopy revealed one distinct mode in the SmC_AP_A phase. The mode disappears in the isotropic and crystalline phases and originates from polar packing in the SmC_AP_A phase rather than from reorientation along molecular axes. Imaginary part of dielectric permittivity plotted versus frequency and temperature (Fig. 7 for **D3-12)** shows that mode strength does not change with temperature and the dielectric strength, $\Delta\varepsilon$, is rather small ($\Delta\varepsilon\approx 8$, for details see ESI and Fig. S5). We can conclude that the observed mode probably corresponds to interlayer antiferroelectric interactions, which are relatively strong for studied system.

The x-ray diffraction experiments performed for **D3-10** and **D3-12** confirmed a layered structure of the mesophase (see ESI for details). The measured layer spacing, *d*=35.3 Å for **D3-10** and *d*=37.7Å for **D3-12** (only weakly dependent on temperature) was significantly smaller than *l* (*l*≈51 Å and *l*≈56 Å for **D3-10** and **D3-12**, respectively), which is consistent with strong tilting of molecules from the layer normal evidenced by the electro-optical observation (Fig. 5) i.e. rotation of the extinction position under the electric field.

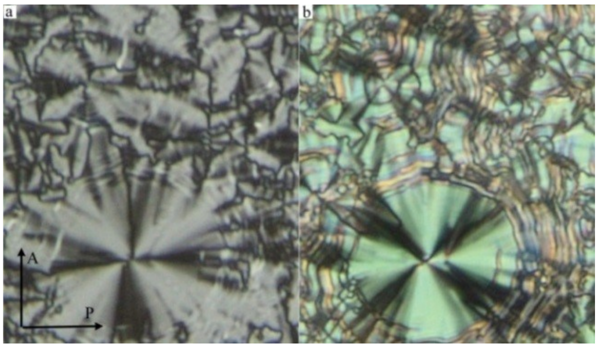

Fig. 5 Planar texture of **D3-12** at temperature T=130°C a) without the electric field and b) under the applied electric field E=+25 V/μm. The width of the microphotograph is 250 μm.

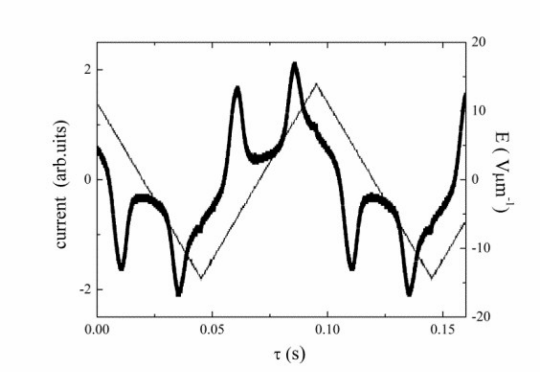

Fig. 6 The switching current at a triangular field, E, frequency of 10 Hz, for **D3-12** at T=150°C in the SmC_AP_A phase.

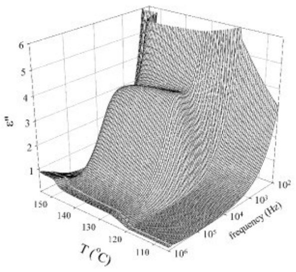

Fig. 7 Imaginary part of the permittivity, ε'', versus temperature and frequency for **D3-12**.

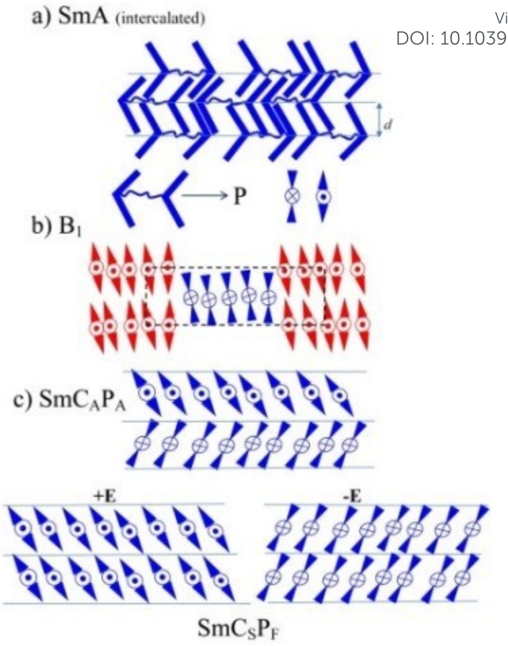

Fig. 8 Schematic organization of dimeric molecules in mesophases.

Self-organization of the studied dimers is schematically depicted in Fig. 8. In Fig. 8a the intercalated SmA phase is presented, in Fig.8b the smectic layer fragments are shown and the cell unit depicted for the B_1 phase. In Fig. 8c the orientation of dimeric molecules in neighbouring layers is described for the SmC_AP_A phase and effect of the applied electric field, ±E, is scatched.

The mesomorphic behaviour can be compared with previously reported monomeric BCs.[9] In spite of the fact we have no relevant data for the shortest terminal chains, we can conclude that studied dimers revealed the same type of mesophases as corresponding monomeric BCs. Nevertheless, for monomeric BCs the reported mesophases are only monotropic and existing in a very narrow temperature range.[9] For studied dimers we observed slight increase of the transition temperatures in comparison with monomeric BCs. We can conclude that stabilization of mesophases was confirmed in the studied dimers.

In summary, we have synthesized and characterized mesomorphic behaviour of a new type of bent-core dimers in which bent-core molecules are connected core-to-core via the propylene-1,3-dioxy chain. Interestingly, despite short linkage connecting the mesogenic cores, which should stiffen the molecular structure, the phase sequence for the dimeric homologue series is similar to thus observed for many monomeric bent-core homologue series. Dimers show different type of mesophases depending on the length of the terminal chains. The shortest studied homologues formed the intercalated smectic A phase, the longest – switchable SmC_AP_A phase, analogously as can be often observed for BCs.[2] For the dimers with intermediate terminal chains the broken-layer columnar B_1 phase appears, built of small layer fragments (blocks) arranged into body centred 2D crystallographic lattice.

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