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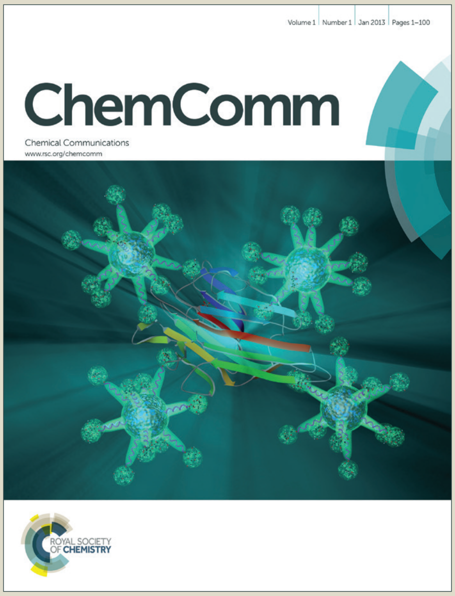

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1D, 2D and 3D liquid crystalline phases formed by bent-core mesogens

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The type of the mesophase is altered by small change in the molecular architecture, i.e. increasing number of alkyl chains attached to mesogenic core at terminal positions. A lamellar (1D) and columnar (2D) phases are formed, for molecules with one and three terminal chains, respectively. For those with two chains 3D phases are observed with either cubic or monoclinic symmetry structure.

The molecular architecture – phase structure – material properties relation has always governed liquid crystal (LC) research.[1] It is well established that the type of the mesophase, and thus material properties, are determined to large extent by the shape of mesogenic molecule, that generally can be described as the rod-like, disc-like or bent-like. The bent-core (or 'banana') mesogens, were discovered several years ago.[2] Although so far of very limited practical use, they are fascinating subject of basic research. They form versatile phases: nematic and smectic phases, typical for rod-like molecules, columnar phases typical for disc-like molecules but also large number of specific structures not observed for other groups of mesogens. Bent-core molecules, even if non chiral have ability to organize into chiral structures,[3] they also form sponge phases,[4] phases build of nanofilaments[5] or twisted nematic phases with extremely short pitch.[6] Rarely, bent-core molecules can form also phases with complex, three-dimensional (3D) structure, with cubic[7] or tetragonal[8] symmetry. Most of the studied bent-core materials are made of two linear parts connected by aromatic unit, with the angle between arms ~120 degree. In this contribution we show that the type of the phase is also largely determined by the number of alkyl terminal substituents, for the same core structure one can easily drive the structure between nematic, smectic, cubic, and columnar phases depending on the number of terminal chains. Formation of different type of phases is, similarly as for disc[9] or dendritic mesogens[10] driven by tendency to curve the mesogenic core - alkyl chain interface. Moreover, we also show that introduction of strongly interacting hydroxyl group into molecule central unit can change dramatically ordering of molecules, formation of non-cubic 3D LC phase was observed.

Two types of mesogenic bent core molecules were tested, having at resorcinol central unit either benzyloxy (**1a-d**) or hydroxyl moiety (**2a-d**). The studied systems were modified by changing the number of peripheral alkyl chains at each banana arm (Fig. 1). The synthesis of material and analytical data are de-scribed in ESI. The identification of the phases was based mainly on x-ray diffraction (xrd) studies and microscopic observation of the textures. The phase transition temperatures and enthalpy changes are collected in Table 1.

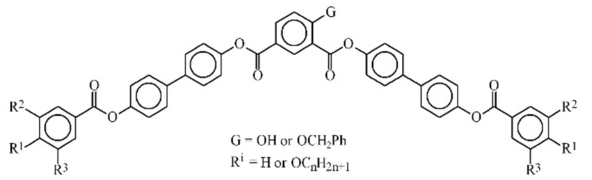

Fig. 1 Molecular structure of studied compounds

For materials **1a** and **1b**, with single terminal chain, only phases typical for rod-like molecules: non-polar nematic and SmC phases, were observed; elongation of terminal chain resulted in destabilization of nematic phase on behave of the smectic phase. In the nematic phase, for the sample placed in capillary and aligned by magnetic field, the x-ray pattern with azimuthal split of low angle signals, characteristic for the presence of cybotactic groups (SmC-like fluctuations)[11] was registered (see ESI). The presence of three aliphatic chains at each terminal phenyl ring (**1d**, **1e**) resulted in formation of columnar phase with hexagonal arrangement of columns, Col_h. The cross section of the column, with diameter changing with temperature (see ESI) in the range 50.7 – 53.0 A for **1d** and 54.5 – 57.0 A for **1e**, is made of 3-4 molecules.

Tab. 1 Phase transition temperatures (in °C) and enthalpy changes (in parentheses, J g^{-1}) for studied compounds.

	G	R^1	R^2	R^3	Phase sequence
1a	OCH_2Ph	$OC_{12}H_{25}$	H	H	Cr 166.0 (36.3) SmC 169.4 (0.7) N 188.9 (1.4) Iso
1b	OCH_2Ph	$OC_{16}H_{33}$	H	H	Cr 140.4 (38.1) SmC 187.1 ^{a} N 188.5 (4.7^a) Iso
1c	OCH_2Ph	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	Cr 103.7 (25.4) Cub_{Ia3d} (135.5 (1.7) Iso
1d	OCH_2Ph	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	Cr 47.8 (8.6) Col_h 108.2 (1.2) Iso
1e	OCH_2Ph	$OC_{16}H_{33}$	$OC_{16}H_{33}$	$OC_{16}H_{33}$	Cr 54.2 (58.2) Col_h 108.8 (1.5) Iso
2a	OH	$OC_{12}H_{25}$	H	H	Cr 162.1 (37.7) B_7 226.0 (24.0) Iso
2b	OH	$OC_{16}H_{33}$	H	H	Cr 152.3 (32.8) B_7 223.4 (19.8) Iso
2c	OH	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	Cr 106.9 (22.9) B_{1rev} 116.5 (0.9) B_{3D} 130.0 (4.0) Col_h 134.8 (1.2) Iso
2d	OH	$OC_{16}H_{33}$	$OC_{16}H_{33}$	$OC_{16}H_{33}$	Cr 59.2 (76.9) Col_h 80.7 (0.73) Iso

[a] total enthalpy change

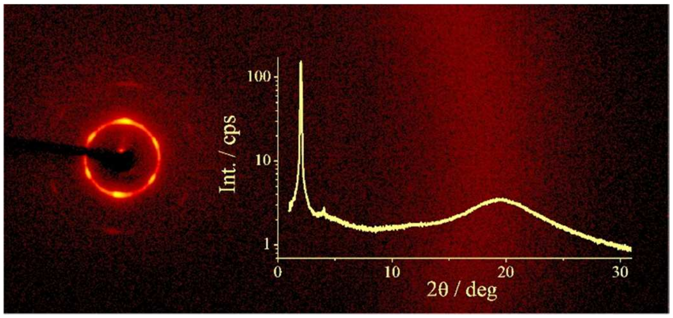

Fig. 2 XRD pattern of Col_h phase of compound **1d** at T = 90 °C. Six-fold symmetry of low angle signals indicates hexagonal arrangements of columns.

The phase shows only short range positional order inside the columns evidenced by diffused high angle xrd signal at the distance corresponding to 4.5A (Fig. 2).Columns that are characterized by highly curved interface between alkyl chains and aromatic core regions, are formed, instead of flat layers, to accumulate large number of terminal chains per molecular core. The dielectric studies showed a weak dielectric mode with relaxation frequency strongly temperature dependent (for compound **1e** the activation energy E_a = 158 kJ mol^{-1}) and the mode strength increasing with decreasing temperature ($\Delta\varepsilon$ up to 6), such a mode is characteristic for axially polar columnar phases having antiferroelectric arrangement of columns.[12] Polar structure requires that columns are made of conical objects rather that flat discs. However, contrary to analogues bent core compounds described previously[12] no electric switching was detected for Col_h phase when the electric field up to 40 $V_{pp}/\mu m$ is applied, suggesting that either antiferroelectric interactions between columns are strong enough to prevent the switching or the spontaneous electric polarization of the columns is very weak due to only small conical distortion of objects forming the columns. For molecules having two terminal chains at each banana arm, **1c**, the cubic phase, stable in a broad temperature range was found by xrd studies. Formation of the cubic phase is confirmed also by its optical texture with zero birefringence. The best fit of x-ray signal positions is obtained assuming the Ia3d symmetry[13] of the phase (Fig. 3), so this structure can be seen as double gyroid one, made of curved columns. Apparently the gyroid structure requires smaller curvature of the interface between rigid cores and terminal chains.

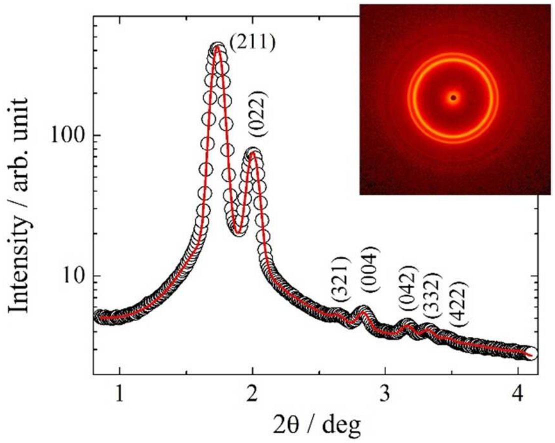

Fig. 3 Intensity of the xrd signals vs. diffraction angle for cubic phase of compound **1c** at T = 110 °C. Red line is a fit obtained assuming Ia3d symmetry with unit cell parameter a = 124.8 A. In the inset related 2D pattern is presented.

Assuming density of the material 1 g cm^{-3}, it can be estimated that the single crystallographic unit cell of the cubic phase (*a*=125 A) contains around 750 molecules. The diameter of the gyroid channels, that is approximately equal molecular length suggests that the channels are made of molecular aggregates with aromatic part in the centre surrounded by flexible alkyl chains.

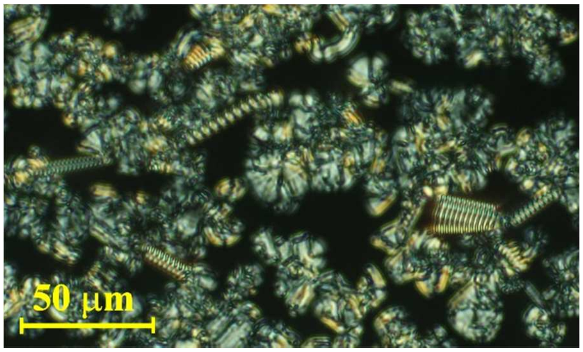

Fig. 4 Optical texture of the B7 phase growing on cooling the isotropic liquid for compound **2a**, T = 225 °C.

Studies made for banana molecules **2a-d**, in which bulky substituent at the central ring is exchanged by hydroxyl group, showed more complex behaviour. For compounds with single terminal chains, **2a** and **2b**, the optical textures with spiralling filaments were observed on cooling from isotropic liquid (Fig. 4), that are characteristic for B_7 phase.[14] The xrd studies performed for compound **2a** revealed presence of two mesophases: the upper temperature phase having a modulated lamellar structure and the lower temperature phase having simple lamellar structure (Fig. 5). The phase transition between this phases is visible only by x-ray, no optical changes or transition enthalpy is registered at transition temperature. The upper phase can be considered as made of weakly deformed layers;[15] the wavelength of modulations along layers is ~150 A. Optical textures suggest that both: modulated and non-modulated layers, have low elasticity and can be easily deformed into twisted filaments with micron periodicities. For compound **2d** with three terminal chains columnar hexagonal phase, Col_h, was observed, similarly as for compounds **1e**, however with slightly smaller column diameter, 54.0 – 56.0 A. Lack of dielectric mode in the kHz regime and no electrooptic switching show that the Col_h phase of compound **2d** is non-polar, apparently the column cross-section is made of 3-4 molecules forming stiff, flat discs as expected for molecules interacting by hydrogen bonds.

The most interesting phase sequence is observed for compound **2c** with two terminal chains at the outer phenyl rings. The sequence of three mesophases, all with liquid like positional order of neighbouring molecules, was observed on cooling the isotropic phase (Fig. 6a). The phase transitions are easily detected in DSC scans (see ESI).

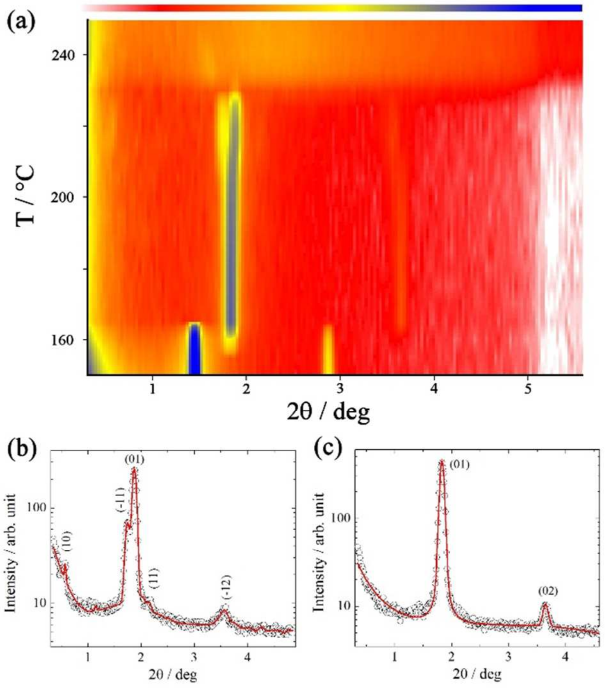

Fig. 5 (a) Temperature evolution of xrd pattern for compound **2a**, showing a transition between modulated lamellar and simple lamellar phases. (b) and (c) 2θ dependence of diffracted intensity at T = 220 °C and 190 °C, respectively. Fits to the patterns were obtained assuming 2D structure with oblique unit cell with parameters a = 167.2 A, c = 50.75 A and β = 111.5 deg, for (b) and a lamellar structure with d = 48.3 A for (c).

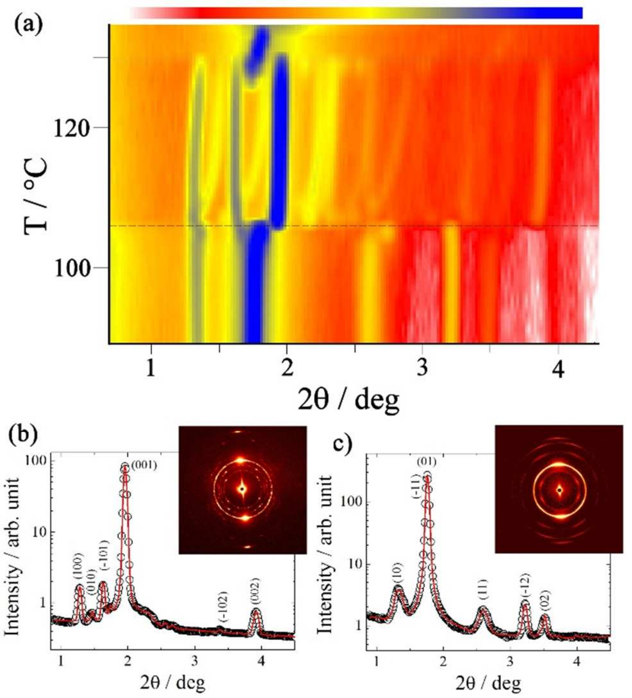

Fig. 6 (a) Temperature evolution of xrd pattern for compound **2c**, showing 3 distinct LC phases between isotropic liquid and crystalline phase. (b) and (c) 2θ dependence of diffracted intensity at T = 120 °C and 95 °C, respectively. Fits to the patterns were obtained assuming 3D structure of P1 symmetry with unit cell with parameters: a = 83.7 A, b = 61.8 A, c = 54.7 A, α = 95.7 deg, β = 122.8 deg and γ = 96.7 deg for (b) and oblique 2D (B_{1rev}) structure with unit cell parameters: a = 72.5 A, c = 54.8 A and β = 113.7 deg for (c).

The upper temperature phase is a columnar hexagonal one, as evidenced by 6-fold symmetry of low angle x-ray signal. The phase shows very weak ($\Delta\varepsilon$~1) dielectric mode in kHz regime, that suggests antiferroelectric arrangement of axially polarized columns. The optical texture is typical for columnar hexagonal phase, with pale smooth fans and large non-birefringent areas in which column axes are oriented along light propagation direction (see ESI). In the lowest temperature mesophase the x-ray signals can be fitted to B_{1rev} structure[15] that is made of smectic layer fragments, infinitive along one direction, and laterally shifted to give structure with the oblique 2D primitive cell with parameters: a = 72.5 A, c = 54.8 A and β = 113.7 deg. The parameter c corresponds to molecular length, the parameter a is the width of the layer fragment. The situation that the same material forms in upper temperature range columnar phase and in lower temperature range layer type (broken layer) structure is rare; it was observed for example for molecules with intermediate shape and associated with the change of molecular conformation from disc to rod.[16] Alternatively, such a change of the type of the structure can be driven by entropy effect; as the terminal chains fluctuate more abruptly at high temperature, they require more space and destroy the layers.[17] It was found that the transition from hexagonal to lamellar phase can be direct or through the intermediate structure: cubic[18] or iso-tropic.[16] For material **2c** between columnar hexagonal and broken layer type phase another type of intermediate phase was found (B_{3D}), its x-ray pattern (Fig. 6) cannot be fitted to any 2D type structure, nor to the 3D cubic or tetragonal one. The best fit of x-ray data is obtained assuming that the structure of intermediate phase (B_{3D}) has P_1 symmetry, with unit cell parameters: a = 83.7 A, b = 61.8 A, c = 54.7 A, α = 95.7 deg, β

$= 122.8$ deg and $\gamma = 96.7$ deg. The transition from B_{1rev} to 3D structure is marked by appearances of few additional signals reflecting weak electron modulations along third dimension (along *b* crystallographic axis). Modulations along third direction only slightly modifies the size and positions of the molecular blocks in *ac* plane. Area of *ac* plane of the crystallographic unit cell is similar for both phases B_{1rev} and $B_{3D.}$ The structure of the 3D phase seems to be a tilted analogue of the phase recently described for anchored shaped bent-core molecules.[19] The texture of intermediate phase and B_{1rev} phase are identical, transition cannot be detected optically. Also dielectric studies did not revealed any changes at the transition temperature between B_{1rev} and B_{3D} phase, showing that the structures are similar having compensated polarization; no electric switching could be observed in any of the phases under electric field up to 20 V_{pp} μm^{-1}. The transition between B_{1rev} and B_{3D} phase is however accompanied by small transition enthalpy (see ESI).

Conclusions

The influence of terminal branching of molecular structure on the packing of bent-core molecules has been studied, a general trend was observed that for three alkyl chains at terminal position the columnar hexagonal phase was formed, while for one terminal chain lamellar-type structures appeared. Such general tendency has been observed also for other group of mesogens and explained by curving of aromatic-alkyl interface, necessary to accommodate larger number of terminal chains per single molecular core. For molecules with two chains at terminal position either cubic gyroid phase is formed, that can be viewed as made of deformed columns. For the studied here system another usual phase sequence was observed or in case of molecules that are able to form hydrogen bonds between mesogenic cores, complex 3D structure made of finite molecular blocks was found as intermediate structure between columnar phase made of discs and columnar phase made of layer fragments. The sequence of phases observed on cooling: columnar and broken-lamellar-type with intermediate phase of 3D structure between, seems to be related to thermal expansion of terminal chains with increasing temperature.

Notes and references

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