

**Bi-continuous orthorhombic soft matter phase made of polycatenar molecules**

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Bi-continuous orthorhombic soft matter phase made of polycatenar molecules

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We report an observation of a new type of a continuous soft matter phase with an orthorhombic symmetry made of polycatenar molecules. The bi-continuous orthorhombic structure with the $Pcab$ symmetry appears by deformation of a double gyroid cubic structure of a with the $Ia\bar{3}d$ symmetry.

In soft matter, structures having flat layers, straight columns or micelles are very common. Less frequent are 'continuous' phases having a 3D periodic organization of channels. Such phases have an intriguing complexity that has triggered a lot of scientific curiosity, especially because they also have an application potential, for example, for the production of cheap solar cells [1], photonic devices [2] or as drug delivery agents [3]. Such phases have been discovered in very different materials such as lyotropic liquid crystals [4,5], block copolymers [6], as well as inorganic mesoporous and macroporous materials [7,8]. They are also found among thermotropic mesogenic materials, where their formation is attributed to a mismatch between the volumes necessary to accommodate chemically incompatible molecular parts: alkyl chains and aromatic cores [9]. In liquid crystalline continuous phases the aromatic molecular parts usually form channels, separated by an interspace filled with alkyl chains [10]. The mid-surface between the channels is a minimal surface, with a hyperbolic saddle-shaped geometry [11]. The most commonly encountered continuous phase is a gyroid phase with two systems of endless channels, each made of linear units interconnected through flat three-fold junctions (nodes), the planes of adjacent nodes being twisted by ~ 70 degrees, with

the sense of the twist preserved along each channel. The two chiral networks are related to each other by an inversion operation [12,13]. The whole gyroid structure is thus achiral and belongs to the space group $Ia\bar{3}d$. Another type of a cubic structure, at first identified to have the $Im\bar{3}m$ symmetry, is also often observed at temperatures below the double gyroid phase. This phase was discovered in several materials [14,15] and was proposed either to have a tri-continuous grid structure [16] or a single continuous grid into which micelles are embedded [17]. Because the phase shows some optical activity [18], it is, in fact, of the symmetry $I432$ or $I43m$ and below we refer to it as a chiral cubic (CC) phase. Apart from continuous phases with a cubic symmetry, phases with an orthorhombic [19], hexagonal [20] or tetragonal symmetry [21-24] have been found, mainly among lyotropic liquid crystals or polymers. Surprisingly, in thermotropic mesogenic materials the existence of non-cubic continuous phases is very rare; so far only tetragonal phases belonging to space groups $I4_122$ or $I4_1acd$ (known also as $S4$ phase) were documented [21-26].

In this communication we show that the $Ia\bar{3}d$ phase can undergo transition to an orthorhombic $Pcab$ phase, driven by a tendency to form a system of helical pillars. We also show that the orthorhombic phase is metastable and observed only upon cooling, on heating, the $Ia\bar{3}d$ phase is formed from the chiral cubic phase.

Molecules of the studied materials (Fig. 1) have the same mesogenic core and they differ in the length of the terminal chain at the biphenyl unit. Most of the studied compounds exhibit quite a complex phase sequence except for the longest studied homologue with a linear chain, $n = 11$, which formed only columnar hexagonal phase (Tab. 1). Branching of the tail resulted in a significant reduction of a clearing point (~ 80 K) and formation of the Col_h phase in a broad temperature range. For all the studied materials, the X-ray diffraction (XRD) patterns were recorded as a function of temperature. In both, heating and cooling scans, a sequence of 3D-ordered liquid crystalline

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Table 1. Transition temperatures (in °C) and enthalpy changes (in brackets in Jg^{-1}) observed in heating and cooling scans for studied homologues. The $Ia\bar{3}d - Pcab$ and $CC - Ia\bar{3}d$ transitions are not accompanied by a measurable thermal effect (the enthalpy change is below 0.005 Jg^{-1}), the transition temperatures were obtained from the XRD studies.

R	Phase sequence
C_4H_9	Heat: Cr 106.5 (19.0) CC 175 $Ia\bar{3}d$ 181 Col_h 185.1 (1.1) Iso Cool: Iso 181.4 (0.6) Col_h 172.1 (0.26) $Pcab$ 80 Cr
C_5H_{11}	Heat: Cr 100.7 (32.3) Cr_2 117.1 (1.0) CC 161 $Ia\bar{3}d$ 171 Col_h 180.7 (0.9) Iso Cool: Iso 179.8 (0.8) Col_h 165.8 (0.1) $Ia\bar{3}d$ 121 $Pcab$ 95 Cr
C_6H_{13}	Heat: Cr 108.8 (29.8) CC 176 $Ia\bar{3}d$ 179 Col_h 185.9 (1.4) Iso Cool: Iso 183.9 (0.8) Col_h 166.2 (0.1) $Ia\bar{3}d$ 123 $Pcab$ 60 Cr
C_8H_{17}	Heat: Cr 83.3 (23.2) Cr_2 96.5 (8.1) CC 160.5 (0.1) $Ia\bar{3}d$ 174.0 (0.02) Col_h 183.8 (1.1) Iso Cool: Iso 182.0 (0.8) Col_h 153 $Ia\bar{3}d$ 125 $Pcab$ 75 Cr
$C_{11}H_{23}$	Heat: Cr 113.6 (21.5) Col_h 163.0 (0.3) Iso
$CH(C_2H_5)_2C_5H_{11}$	Heat: Cr 91.0 (50.05) Col_h 105.6 (0.8) Iso

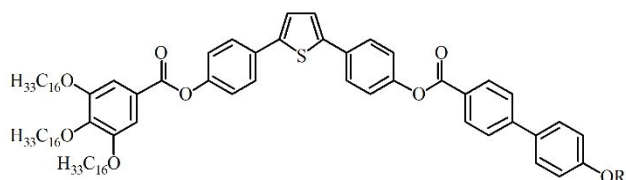


Figure 1. Molecular structure of the studied compounds.

phases was revealed (Fig. 2); all of them having only short-range positional correlation between neighbouring molecules as evidenced by broad diffraction signal at high diffraction angle range (Fig. S1). DSC studies showed no or very small enthalpy changes accompanying some of the phase transitions (Fig. S2). Upon melting the crystal, the consecutive phases in the heating scans are: $CC \rightarrow Ia\bar{3}d \rightarrow Col_h \rightarrow Iso$. In the hexagonal columnar phase, the crystallographic unit cell parameter (column diameter) is consistent with a molecular length and in the gyroid and CC phases it corresponds to 2 and 3 molecular lengths, respectively. Both cubic phases have zero optical birefringence and the CC phase exhibit domains with a low optical activity, ~ 0.5 degree/ μm (Fig. S3). Different phase sequence was observed upon cooling from the isotropic phase: $Iso \rightarrow Col_h \rightarrow Ia\bar{3}d \rightarrow Pcab$ (Fig. 3). Below the $Ia\bar{3}d$ phase, instead of the CC phase, a 3D phase with a non-cubic symmetry, $Pcab$, appears. At the $Ia\bar{3}d \rightarrow Pcab$ phase transition, diffraction signals of the gyroid phase split, but the relative intensities among them remain approximately the same, which shows that the cubic structure becomes only weakly deformed. The symmetry of the new phase was determined by a gradual reduction of symmetry of a 'parent' $Ia\bar{3}d$ phase, using a sequence of maximal subgroups: $Ia\bar{3}d \rightarrow I4_1cad \rightarrow Icab \rightarrow Pcab$. The space group was also confirmed by checking the extinction rules for several possible symmetries belonging to the orthorhombic class, and the group $Pcab$ seems to be the most probable.

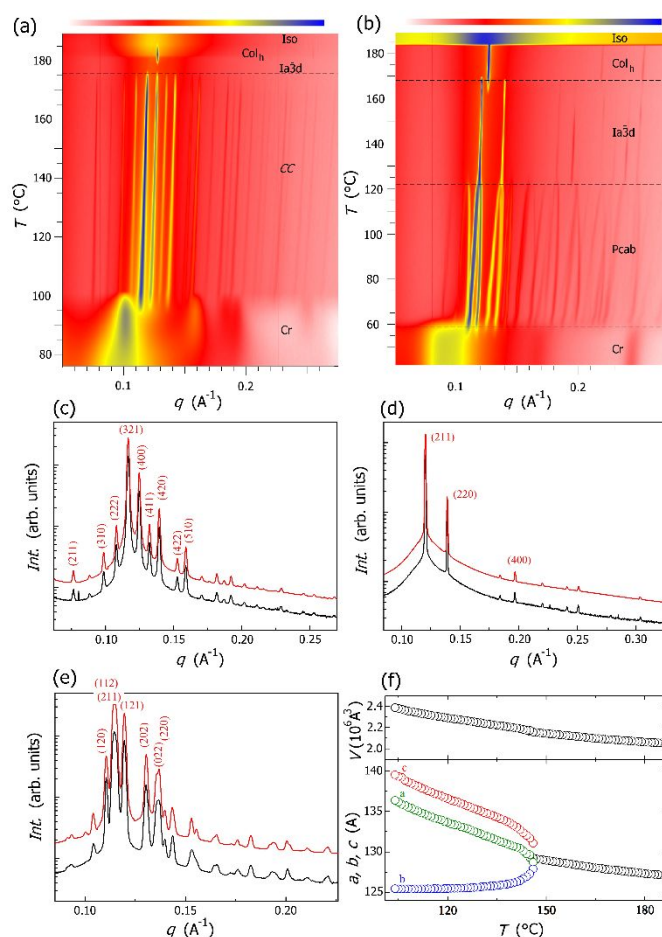


Figure 2. Temperature evolution of the low angle X-ray diffraction signals in (a) heating and (b) cooling scans for compound with $n = 6$. X-ray diffraction patterns in the (c) CC , (d) $Ia\bar{3}d$ and (e) $Pcab$ phases. Black lines show experimental and the red ones simulated patterns. Detailed information on signal positions is given in Tabs S1-S3 in

ESI. (f) Temperature evolution of the crystallographic lattice parameters (a , b , c) and the unit cell volume across the $Ia\bar{3}d - Pcab$ phase transition, detected in a cooling run.

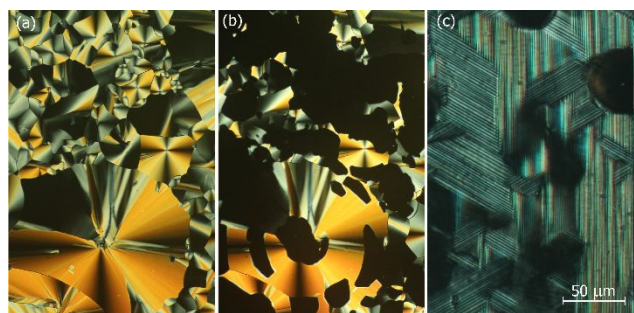


Figure 3. Optical textures taken for compound with $n = 6$: (a) columnar hexagonal phase, (b) optically isotropic cubic $Ia\bar{3}d$ phase growing on cooling of the Col_h phase, (c) the $Pcab$ phase.

The best indexing of the X-ray pattern is obtained assuming a crystallographic lattice with the unit cell parameters being $a = 13.16$ nm, $b = 12.59$ nm, $c = 13.41$ nm (10 K below phase transition, for $n = 6$), which can be considered as a slightly distorted cubic unit cell of the $Ia\bar{3}d$ phase ($a = 12.92$ nm at the transition temperature, for $n = 6$).

The $Pcab$ phase is weakly birefringent ($\Delta n < 0.003$) and optical textures with striped domains are observed (Fig. 3c) as opposed to the plate like textures reported for tetragonal phases ($I4_122$ or $I4_1acd$ [21–26]). Although the different phase sequence observed on heating and cooling is a well reproducible effect, the ranges in which particular phases exist were found to depend on the temperature scan rate. Sometimes, the $Ia\bar{3}d$ phase coexisted with the $Pcab$ or CC phase in a broad temperature range. Although the transition $Ia\bar{3}d \rightarrow Pcab$ seems to be continuous (Fig. 2f), we thus conclude, that it must be of a weakly first order and that $Pcab$ is a metastable phase.

To reveal detailed structure of the observed phases, electron density maps were calculated by the reverse Fourier transform (RFT) of the XRD patterns [27], in which a spatial distribution of the electron rich and poor regions corresponds to locations of molecular cores and alkyl chains, respectively. Diffraction peak intensities were analysed to obtain the structure factors used for RFT. The structure factor amplitudes and phases used to reconstruct the electron density maps of the $Ia\bar{3}d$ and $Pcab$ phases for the homologue with $n = 6$ are given in Table S4. Because the $Pcab$ phase seems to be only a weakly distorted version of the gyroid phase, we assumed that the main structure factors have the same phases (signs) as in the $Ia\bar{3}d$ phase. The reconstructed electron density maps of the $Ia\bar{3}d$ and $Pcab$ phases are given in Fig. 4 and in both cases two systems of interlocked channels are clearly visible. If we assume, based on the molecular structure, that $1/3$ of the crystallographic unit cell volume in the $Ia\bar{3}d$ phase is occupied by mesogenic cores, then the diameter of channels filled with the cores is approximately $0.2a_{Ia\bar{3}d}$ ($a_{Ia\bar{3}d}$ is the length of the unit cell), which is approximately 40% of the molecular length and is comparable to the length of the molecular core. The distance between two neighbouring nodes is $0.35 a_{Ia\bar{3}d}$, which

is approximately 10 widths of a molecule. The electron density map of the $Pcab$ phase is very similar to that of the gyroid phase, with an exception of some connections between nodes becoming weaker (density is lowered).

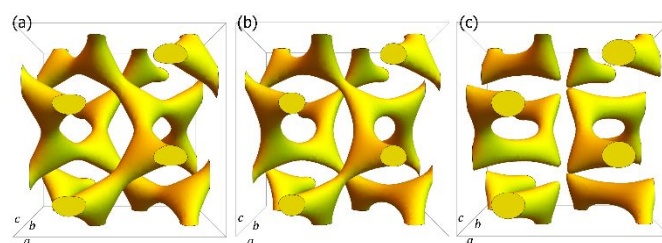


Figure 4. Electron density maps reconstructed from the XRD data for compound $n = 6$ for a (a) cubic $Ia\bar{3}d$ phase (b) orthorhombic $Pcab$ phase 10 K below the transition from the $Ia\bar{3}d$ phase and (c) 'hypothetical' $Pcab$ phase far below the transition from the $Ia\bar{3}d$ phase

In order to understand the structure of the $Pcab$ phase, we also plot a map of a 'virtual', more strongly deformed structure, for which we assumed that the peak intensities will continue to change accordingly to the changes observed close to the phase transition. We thus assumed the intensity of the diffraction peak (202) being significantly larger than the intensities of the (220) and (022) peaks (Fig. 4(c)). In this 'virtual' structure, the system of two channels is transformed into a net of separated helical pillars, with an equal amount of left and right handed pillars. Apparently, the structure observed experimentally is an intermediate state towards a development of a pillar (columnar-type) phase in which columns twist and so do the long molecular axes of the molecules forming them.

Conclusions

We have shown that for some mesogenic materials a double gyroid phase deforms into an orthorhombic phase upon cooling. Some connections between helical channels of the double gyroid phase weaken due to the tendency to develop separated helical pillars. This drives the double gyroid structure with the symmetry $Ia\bar{3}d$ into an orthorhombic phase with the $Pcab$ symmetry, a rare example of a liquid crystalline bicontinuous phase with a non-cubic symmetry. One can expect that $Pcab$ phase could be applied as conducting medium in photovoltaic or photonic devices, that require anisotropic conducting properties. Presence of a weak connections between helical unidirectional channels should make the conducting properties less sensitive to defects in the structure, discontinuities of single channels.

Conflicts of interest

There are no conflicts to declare.

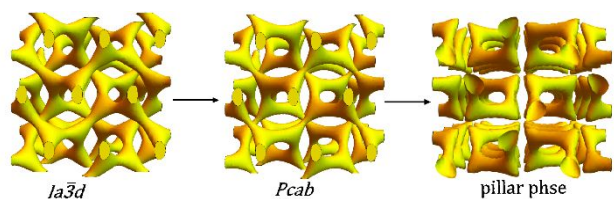
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Graphical and textual abstract for the contents pages



New type of a continuous-type liquid crystalline phase made of polycatenar molecules is reported, having an orthorhombic $Pcab$ symmetry. The phase is formed by slight deformation of a double gyroid structure of a cubic $Ia\bar{3}d$ phase. The reported structure can be considered as an intermediate state toward formation of a columnar phase made of helical pillars.
