Trigonal columnar self-assembly of bent phasmid mesogens†

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Three compounds with a bent rod-like aromatic core and with three alkoxy chains at each end were synthesised by click reaction. The compounds form a columnar liquid crystal phase with non-centrosymmetric trigonal $p31m$ symmetry, the columns having a 3-arm star-like cross-section.

The term “phasmid” mesogen is used to describe rod-like molecules with three flexible chains, usually alky1, at each end, and the name refers to the similarity with the six-legged insects known by the same name. Usually such mesogens form the hexagonal columnar (Colhex) liquid crystal (LC) phase, where typically three aromatic rods lie parallel to each other and perpendicular to the column axis, forming a stratum of the column; the alky1s fill the space between the columns. Phasmids are a subclass of a wider class of rod-like mesogens. Columnar phases, particularly the most commonly observed hexagonal phase, are normally assembled from disk-like or fan-shaped molecules. Alternatively a variety of “honeycomb” columnar phases are seen in rod-like amphiphiles with flexible side-chains. One may ask why phasmidic columns, with elongated rods lying normal to the column axis, pack on a lattice with hexagonal symmetry, when such packing is normally reserved for round cylinders or hexagonal prisms. The answer may be in that the successive strata in a column are rotated, forming a helix, making the averaged cross-section circular. Such helical twist of polycatenar segments.10 Columns made up of more circular strata, containing discotic or fan-shaped mesogens, are also understood to feature helical twist.11–14

The question we address here is whether a trigonal columnar LC phase can be formed, with three-fold rather than six-fold symmetry and with non-cylindrical columns. In honeycomb-like inverted columnar phases of side-chain-containing rod-like amphiphiles, in some cases the cross-section of the prismatic channels with aromatic walls is hexagonal; thus although the columns are not circular, naturally the symmetry is still hexagonal, plane group $p6mm$. However, in two cases amphiphiles of that kind were reported to form honeycombs with only three-fold symmetry (see below).15,16 Such non-centrosymmetric structures are rare in liquid crystals but are of interest for their potential ferroelectric, pyroelectric or nonlinear optical properties. The question remains whether such three-fold symmetry is possible in the more conventional columnar phases where the hard aromatic moieties occupy the centre, rather than the periphery of the column. Here we show that columns with a three-arm star cross-section and trigonal symmetry can form from bent-core, or banana-shaped phasmids. While the crystallographic plane group belongs to the hexagonal system, the phase symmetry is actually trigonal.

The aromatic rod-like core in the compounds described here have a bend of $109^\circ$ in the centre due to the $sp^3$-hybridized methylene group – see Scheme 1. The compounds are labelled IC$^3/n$, with $n = 10, 12, 14$ the number of carbon atoms in each of the six terminal alkyl chains. They were synthesized by a Cu(i)-catalyzed click reaction. All three compounds display a liquid crystal phase, with the texture recorded by polarized optical microscopy (POM) featuring clear developable domains (“spherulites”), typical of a columnar LC phase – see Fig. 1. The transition temperatures and heats of transition on 1st heating, cooling and 2nd heating, determined by DSC in combination with X-ray diffraction and nonlinear optical

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of the diazonium salt and subsequent substitution with sodium azide.

4 was esterified with the appropriate 3,4,5-trialkylbenzoic acids 2′/n to 4-azidophenyl-3,4,5-trialkylbenzoates 5′/n.21 Finally click reaction between bisacetylene 8 and aromatic azides 5′/n produced the target compounds IC3/n. All of the target compounds were purified by column chromatography. For more details, see ESL†.

X-ray scattering at small and wide angles (SAXS and WAXS) experiments were performed to characterize the LC phases. Grazing incidence SAXS (GISAXS) on well oriented thin films on silicon facilitated indexing of X-ray reflections.

Furthermore, for any potential future application of such materials in electronic or optical devices, orientation in thin film needs to be understood. Fig. 2 shows a transmission powder SAXS and a GISAXS pattern of the main liquid crystal phase, on the example of IC3/12. Equivalent patterns for compounds IC3/10 and IC3/14 are shown in ESL† Fig. S4–S6. The measured and calculated d-spacings for all three compounds are listed in Tables S1–S3 in ESL†. The d2 values of the three peaks in the SAXS pattern are in the ratio 1 : 3 : 4, which is typical of a two-dimensional hexagonal lattice, with the respective Miller indices (10), (11) and (20). The GISAXS patterns confirm this indexing, as seen in Fig. 2b and Fig. S4a, S5a (ESI†). The fact that the reflections are not confined to the equatorial plane means that the columns are oriented parallel to the substrate surface (planar anchoring), rather than perpendicular to it. This is consistent with the appearance of the optical micrographs in Fig. 1 and Fig. S3 (ESI†). As the real space unit cell is related to the reciprocal cell by 90° rotation, the fact that reflections (10) and (20) are on the meridian means that the real hexagonal cell lies on one of its sides on the substrate. That implies that the (10) plane is parallel to the substrate, suggesting in turn that it is the most densely packed plane (see Fig. S9, ESI†).

The X-ray scattering in the XY plane is 2D due to structural fluctuations along the Z axis, which is perpendicular to the film surface and below the detectable X-ray scattering angle. As the real space unit cell is related to the reciprocal cell by 90° rotation, the fact that reflections (10) and (20) are on the meridian means that the real hexagonal cell lies on one of its sides on the substrate. That implies that the (10) plane is parallel to the substrate, suggesting in turn that it is the most densely packed plane (see Fig. S9, ESI†).

In compounds IC3/12 and IC3/14 another metastable mesophase (M-phase) has been observed in rapidly cooled samples. The GISAXS pattern is presented in Fig. S7 (ESI†). The structure of this complex phase is not clear at present, and is the subject of further investigations.

Fig. 2 (a) Powder SAXS curve of IC3/12 recorded at 80 °C at station I22 at Diamond. (b) GISAXS diffraction pattern of IC3/12 recorded at 80 °C on beamline B28 at ESRF.
The lattice parameters of IC3/10, IC3/12 and IC3/14 at different temperatures are listed in Table 2. As expected, the value of lattice parameter \( a \) is seen to increase with increasing end-chain length. The continuous trend suggests that the basic phase structure is the same in all three compounds. It is also seen in Table 2 that \( a \) decreases with increasing temperature, a common trend observed in columnar phases, particularly those containing a large aliphatic fraction.\(^{13}\)

In order to determine the molecular arrangement in the columnar phase, we first need to establish the orientation of the molecular cores relative to the column axis and then determine the number of molecules in the unit cell. Using the \( \lambda \) retardation plate (Fig. 1b and S3b, d, f, ESI\(^{\ddagger} \)) we confirm that the slow axis, hence the long axis of the aromatic core, is perpendicular to the column axis (see ESI\(^{\ddagger} \)). For the calculation of the number of molecules refer to Table S4 in ESI\(^{\ddagger} \). To estimate molecular volume in the LC phase the molecule is split in two parts. The volume of the rigid aromatic part is estimated using the methods of crystalline volume increments.\(^{32}\) For the aliphatic part the density of 0.8 g cm\(^{-3}\) is assumed, being in between the values for liquid \( n \)-alkanes and amorphous polyethylene. From the measured area of the unit cell and an assumed intermolecular spacing along the column axis \( c \) in the usual range between 0.4 and 0.45 nm, we obtain close to 3 as the number of molecules per unit cell. As we don’t know the actual value of \( c \) (no sharp feature is observed in the 0.3–0.5 nm WAXS range), in Table S4 (ESI\(^{\ddagger} \)) we give the calculated value of \( c \) assuming that the number of molecules, which must be an integer, is exactly 3. As can be seen, the value of \( c \) is in the range between 0.407 and 0.433, increasing slightly with the length of the terminal chains.

With the above in mind, we consider two alternative models of molecular packing. In both models three molecules cluster together in one stratum, with their aromatic cores back-to-back, forming a three-arm star. The models differ in the arrangement of the star-profiled columns. In model A the centres of the stars are situated at apices of hexagons, producing a hexagonal honeycomb with aromatic walls where the central methylene groups occupy alternative corners of the hexagon. This packing model resembles that found in anchor-shaped mesogens consisting of a bent-rod aromatic core with a flexible chain attached to the inside of the bend point.\(^{15}\) However, while in the case of anchor mesogens the ends of the aromatic arms were linked via hydrogen-bonding terminal groups, the present compounds do not. In fact the bulky end-chains on adjacent molecules would face each other and clash, having to bend sharply in order to fill the interior of the hexagonal channel. Even rotating the star-like columns by 60° about their axis does not solve the packing problem as tested by molecular simulation.

In the alternative model (B) the self-assembled stars are located on a triangular lattice all with the same orientation – see the models in Fig. 3b–d. This arrangement is favoured for steric reasons, as the bunch of six allys emanating from the end of a star arm faces the empty concave “armpit” of the adjacent column. To test the viability of the two arrangements and their variants, molecular models of crystals were built with the experimental unit cell parameter \( a \) and with \( c \) from Table S4 (ESI\(^{\ddagger} \)). These were then subjected to molecular dynamics annealing. Space could not be filled uniformly with model A, while a very satisfactory density distribution was achieved with model B – see snapshot in Fig. 3c. A short video of the dynamics of model B is available from the ESL\(^{\ddagger} \).

The columnar structure in Fig. 3 has 3-fold rather than 6-fold symmetry, and the plane group is \( p31m \) rather than the usual \( p6mm \) symmetry of the \( \text{Col}_{\text{hex}} \) phase. While the \( p6mm \) plane group has a centre of inversion, \( p31m \) has not. To distinguish between them, we performed second harmonic generation (SHG) experiments. Fig. 3a shows a large increase in SHG signal above the background level on cooling from Iso to \( \text{Col}_{\text{hex}} \) phase, showing clearly that the latter phase lacks centre of symmetry and is thus a trigonal phase (see also ESI\(^{\ddagger} \)).

The lack of centre of symmetry causes a problem when reconstructing the electron density (ED) map from X-ray diffraction intensities. That is, the phase \( \phi \) of the structure factor of one of the three reflections, the (11), is not limited to 0° or 180°, a condition that applies to all reflections in centrosymmetric space groups. A value of \( \phi \) different from 0° or 180° breaks the hexagonal symmetry. Choosing an arbitrary angle \( \phi = 120° \) we obtain the ED map in Fig. 3b, onto which the schematic molecules of an IC3/m compound are superimposed. The high density regions (purple) represent the aromatic moieties, and the blur comes from the time
and space averaging in the liquid crystal. We note that choosing a
different value of $\phi$ merely changes the extent of deviation from
circularity of the high-density maxima – see Fig. S8 (ESI†).

We consider that the efficient back-to-back packing of the
three bent cores in this structure is facilitated by a degree of
flexibility in the core, particularly around the oxymethylene
linkage. The long-range polarity, on the other hand, is believed
to be secured by the high barrier for uncorrelated rotation
around the column axis.

It is interesting to compare the present structure with that of
a bent-core phasmid compound also having six terminal $C_6H_{12}$
chains but with longer arms and a pyridine ring as the bend
point.\textsuperscript{23} The model proposed for the hexagonal phase had four
rather than three molecules in a stratum resulting in a 4-arm star. $p6mm$ symmetry was assumed. Interestingly, at lower
temperatures a phase transition to a polar columnar phases
took place but unlike in the current case, the poling was
parallel rather than perpendicular to the column axis. Longitu-
dinal poling was explained by an out-of-plane distortion of
the stars.

It is also appropriate to compare the present structure with
those of a number of mesogens with 3-fold ($C_3$) symmetry in
their chemical structure. In the columnar phase of the 3-arm star
molecules by Lehmann et al.\textsuperscript{24} the molecules are actually
thought to be distorted into an E-shaped conformation, making
them effectively fan-shaped and thus assembling as other
fan-shaped mesogens such as dendrons. In other cases the fact
that the non-centrosymmetric 3-arm star molecules of $C_3$ symmetry
formed the Colhex phases was thought to be the result of rotational
averaging.\textsuperscript{25} However, even though the diffraction pattern has
hexagonal symmetry, this does not preclude the real-space structure
having only trigonal symmetry. One has to remember that the Laue
symmetry (i.e. the symmetry of the diffraction pattern) is hexagonal
even if the crystal symmetry is trigonal. Indeed the columnar phase
of compounds described in ref. 26 showed strong second harmonic
generation (SHG), characteristic of non-centrosymmetric structures.
In other reported cases of $C_3$ star-like mesogens only 6-fold sym-
metry was claimed for the columnar LC phase.\textsuperscript{26–28}

As hinted in the introduction, beside the already mentioned
trigonal columnar phase in anchor-shaped compounds,\textsuperscript{29} there
has been another case of triangular honeycomb LC of straight
rod amphiphiles, where two incompatible side-chains were
attached at each side of the aromatic rod.\textsuperscript{16} While at higher
temperatures the two chain types were mixed in the triangular
channels, a second-order Curie-type transition on cooling
brought about a trigonal $p31m$ phase in which the two side-
chain types were separated in triangles on two separate sub-
lattices. A recent Monte Carlo simulation helps understand
such $p6mm$–$p31m$ transitions.\textsuperscript{29}

In summary, we have synthesised a series of bent-core phasmid compounds and found that they form a trigonal
columnar phase, where the aromatic columns adopt a
3-armed star-shaped cross-section. This finding indicates a
potential new path to creating non-centrosymmetric self-
assemblys that could, with suitable substituents, be used in
ferroelectric, pyroelectric or frequency-doubling optical devices.

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Conflicts of interest
There are no conflicts to declare.

References

1. H. T. Nguyen, C. Destrade and J. Malthète in Handbook of Liquid
Crytstals, ed. D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vill,
2. D. Fazio, C. Mongin, B. Donnio, Y. Galerne, D. Guillou and
3. T. Woehrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum,
L. Jitterschmidt, C. J. Haenle, P. Staffeld, A. Baro, F. Giesselmann
7. T. Kato, M. Yoshio, T. Ichikawa, B. Soberats, H. Ohno and M. Funahashi,
9. G. Ungar, C. Tschierske, V. Abetz, R. Holyst, M. A. Bates, F. Liu,
M. Prehm, R. Kieffer, X. B. Zeng, M. Walker, B. Glettner and
10. C. Dressel, F. Liu, M. Prehm, X. B. Zeng, G. Ungar and C. Tschierske,
17. H. C. Kolb, M. G. Finn and K. B. Sharpless, Angew. Chem., Int. Ed.,
20. X. Tan, L. Kong, H. Dai, X. Cheng, F. Liu and C. Tschierske,
21. G. Ungar, F. Liu, X. B. Zeng, B. Glettner, M. Prehm, R. Kieffer and
25. G. Henrich, A. Omenat, I. Asselberghs, S. Forrier, K. Clays,
2012, 22, 7797.
28. E. Westphal, M. Prehm, I. H. Becktold, C. Tschierske and H. Gallardo,