Trigonal columnar self-assembly of bent phasmid mesogens†

Huifang Cheng,‡a Ya-xin Li,‡b Xiang-bing Zeng, b Hongfei Gao, a Xiaohong Cheng (✉) a and Goran Ungar (✉)bc

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 noncentrosymmetric 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.1 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.2 Phasmds are a subclass of a wider class of rod-like mesogens with more than one chain at each end, known as polycatenar mesogens. Columnar phases, particularly the most commonly observed hexagonal phase, are normally assembled from disk-like or fan-shaped molecules.3–7 Alternatively a variety of “honeycomb” columnar phases are seen in rod-like amphiphiles with flexible side-chains.8,9 One may ask why phasmidic columnar phases have a 3-arm star cross-section. The aromatic rod-like core in the compounds described here have a bend of 109° in the centre due to the sp3-hybridized methylene group – see Scheme 1. The compounds are labelled IC3/n, with n = 10, 12, 14 the number of carbon atoms in each of the six terminal alky1 chains. They were synthesized by a Cu(i)-catalyzed click reaction.10 All three compounds display a liquid crystal phase, with the texture recorded by polarized optical microscopy (POM) featuring clear developable domains (“spherulites”),11 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
reaction between the bisacetylene 8 and the appropriate substituted aromatic azides 5\*:\[n\] (Scheme 1). Reduction of commercially available 4,4\*; dihydroxybenzophenone 6 with LiAlH\_4/AlCl\_3 yielded 4,4\*; dihydroxydiphenylmethane 7, which was etherified with propargylbromide to yield bisacetylene 8. 4-Azidophenol 4 was synthesized from commercially available 4-aminophenol 3 by formation of the diazonium salt and subsequent substitution with sodium azide.

4 was esterified with the appropriate 3,4,5-trialkoxybenzoic acids 2\*:\[n\] to 4-azidophenyl-3,4,5-trialkoxybenzoates 5\*:\[n\]. Finally click reaction between bisacetylene 8 and aromatic azides 5\*:\[n\] produced the target compounds 1\*:\[n\]. All of the target compounds were purified by column chromatography. For more details, see ESI†.

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 1\*:\[12\]. Equivalent patterns for compounds 1\*:\[10\] and 1\*:\[14\] are shown in ESI†. Fig. S4–S6. The measured and calculated d-spacings for all three compounds are listed in Tables S1–S3 in ESI†. The d\*; 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†).\[21\] In compounds 1\*:\[12\] and 1\*:\[14\] 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.

### Table 1 The phase transition temperatures of compounds 1\*:\[n\]

<table>
<thead>
<tr>
<th>Compd</th>
<th>n</th>
<th>T°C [ΔH/k mol (^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*:[10]</td>
<td>10</td>
<td>Cr(_1) 69.6 [17.3] Cr(_1) 107.0 [33.3] Iso 87.4 [1.2] p31m 52.8 [12.0] M 56.5 [12.3] p3 + Cr(_1) 65.4 [2.4] p31m 90.3 [1.2] Iso + Cr(_1) 108.6 [3.3] Iso</td>
</tr>
<tr>
<td>1*:[12]</td>
<td>12</td>
<td>Cr(_1) 86 [21.1] Cr(_1) 110.2 [41.5] Iso 88.6 [0.7] p31m 58.3 [11.5] M 76.2 [11.6] p31m 89 Cr(_1) 110.3 [35.7] Iso</td>
</tr>
<tr>
<td>1*:[14]</td>
<td>14</td>
<td>Cr(_1) 38.7 [30.5] Cr(_1) 73 [23.1] p31m 82.7 [0.8] Iso 76.2 [0.3] p31m 58.5 [14.6] M 62.5 [14.7] p31m + Cr(_1) 68.2 [1.0] p31m 83.9 [0.6] Iso</td>
</tr>
</tbody>
</table>

\* Peak DSC transition temperatures [and enthalpies] on 1st heating (†), followed by cooling (†), followed by 2nd heating (†), all at 5 K min\(^{-1}\). Cr\(_1\) = crystal, p31m = hexagonal columnar phase with three-fold symmetry, Iso = isotropic melt, and M is a complex metastable unidentified LC phase.
The lattice parameters of IC$^3$/10, IC$^3$/12 and IC$^3$/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.$^{11}$

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 Fig. S3b, d, f, ESI$^\dagger$) we confirm that the slow axis, hence the long axis of the aromatic core, is perpendicular to the column axis (see ESI$^\dagger$). For the calculation of the number of molecules refer to Table S4 in ESI. 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.$^{12}$ 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.

Table 2 Comparison of the values of lattice parameter (in nm) of the hexagonal columnar phase in the three compounds at different temperatures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>60 °C</th>
<th>70 °C</th>
<th>80 °C</th>
<th>90 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC$^3$/10</td>
<td>5.03</td>
<td>4.98</td>
<td>4.94</td>
<td>4.89</td>
</tr>
<tr>
<td>IC$^3$/12</td>
<td>5.23</td>
<td>5.18</td>
<td>5.13</td>
<td></td>
</tr>
<tr>
<td>IC$^3$/14</td>
<td>5.41</td>
<td>5.35</td>
<td>5.28</td>
<td></td>
</tr>
</tbody>
</table>

The high density regions (purple) represent the aromatic moieties, and the blur comes from the time dynamics of model B is available from the ESI.

In (b and c) the view is down the columns. Note that according to the GISAXS pattern in Fig. 2b and Fig. 5a, 5a (ESI$^\dagger$) the column orientation in this figure is as in a film on a horizontal substrate viewed along the substrate surface (see Fig. 59 in ESI$^\dagger$).

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$^\dagger$). 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 ESI$^\dagger$.

The columnar structure in Fig. 3 has 3-fold rather than 6-fold symmetry, and the plane group is $p\overline{3}1m$ rather than the usual $p\overline{6}mnm$ symmetry of the Col$_{hex}$ phase. While the $p\overline{6}mnm$ plane group has a centre of inversion, $p\overline{3}1m$ 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 Col$_{hex}$ phase, showing clearly that the latter phase lacks centre of symmetry and is thus a trigonal phase (see also ESI$^\dagger$).

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 IC$^3$/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 C12H29 chains but with longer arms and a pyridine ring as the bend point.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. Longitudinal 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.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 Colsph phases was thought to be the result of rotational averaging.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 symmetry was claimed for the columnar LC phase.26–28

As hinted in the introduction, beside the already mentioned trigonal columnar phase in anchor-shaped compounds,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.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 sublattices. A recent Monte Carlo simulation helps understand such $p6mm$–$p31m$ transitions.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-assemblies that could, with suitable substituents, be used in ferroelectric, pyroelectric or frequency-doubling optical devices.

The authors acknowledge funding for this work from EPSRC (EP-K034308, EP-P002250), NSFC (No. 21664015, 21602195) and YEDF (ZD2015001). YL thanks CSC for stipend and uOs for waiving tuition fee. For help with synchrotron experiments we thank Prof. N. Terrill and Dr O. Shebanova, beamline I22, Diamond Light Source, and Drs O. Bikondoa, S. Brown and P. Thompson of beamline BM28 at ESRF.

Conflicts of interest
There are no conflicts to declare.

References