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Intercalated soft-crystalline mesophase exhibited by an unsymmetrical twist-bend nematogen†

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A number of new states of matter have been reported in recent years for liquid crystal dimers, most notably the twist-bend nematic phase which exhibits spontaneous breaking of symmetry through the emergence of chiral structures in an achiral fluid. In this communication we report on an unsymmetrical liquid crystal dimer that exhibits a transition from the spontaneously chiral twist-bend nematic phase into a novel smectic liquid crystal phase.

Introduction

The observation of a lower temperature mesophase lacking lamellar or positional molecular order (*i.e.* a nematic-like mesophase),¹ later identified as the ‘twist-bend nematic’ phase (N_{TB}),^{2–10} has motivated a great deal of study into the properties of this intriguing state of matter by a wide range of techniques.^{11–18} In a typical nematic phase rod-like molecules are orientated, on average, parallel to one another along a vector termed the director, n (Fig. 1a). In the case where the rod-like molecules are chiral the structure twists forming a left or right-handed helix (Fig. 1c). Although the helicoidal model of the N_{TB} phase, proposed independently by Meyer and Dozov and depicted in Fig. 1b,^{19,20} is supported by experimental data, alternate models have also been proposed.^{21–24} The observation of direct isotropic liquid to N_{TB} phase transitions, first reported for a mixed dimer/chiral-dopant system²⁵ and then later in pure materials,²⁶ providing a challenge for future theoretical treatment.

That the N_{TB} phase has been observed in bent-core systems,⁸ ether linked dimers,^{27,28} trimers,^{29–32} oligomers³³ and even polymers³⁴ hints at this mesophase being far more universal than was perhaps first thought. A comprehensive structure property relationship remains elusive despite the ever growing number of compounds reported in the literature to exhibit this state of matter.^{35–44} The observation of spontaneous breaking of mirror symmetry in the twist-bend nematic phase leads to the emergence of helical nano-structures in an achiral fluid;^{10,45,46} questions concerning the mechanism of this phenomenon are of fundamental importance to a range of scientific disciplines,^{47–51} and are likely to motivate further study into the N_{TB} phase (and analogous states of matter such as splay-bend modulated phases⁵² or possible smectic

twist-bend mesophases) for some time to come. Possible applications of dimers and oligomesogens that exhibit twist-bend phases include tuneable selective reflection, presenting another motivation for study of these fascinating materials.^{53,54}

In this work we report an unsymmetrical methylene linked bimesogen containing one polar rigid aromatic unit and one ‘apolar’ unit. In addition to exhibiting nematic and twist-bend nematic mesophases this material also exhibits what we believe to be a previously unobserved smectic mesophase.

Experimental

Compound 1 was synthesised, as shown in Scheme 1, *via* the EDAC/DMAP mediated Steglich esterification between (4-(9-(4-hydroxyphenyl)nonyl)phenyl 4-cyanobenzoate), prepared as described previously,²⁹ and 4-pentyloxybenzoic acid.

Small angle X-ray scattering was performed on a Bruker D8 Discover using copper $K\alpha$ radiation ($\lambda = 0.15418$ nm) equipped with a temperature controlled, bored graphite rod furnace. Patterns were collected on a VANTEC 500 area detector (2048 × 2048 pixels) set at a distance of 121 mm from the

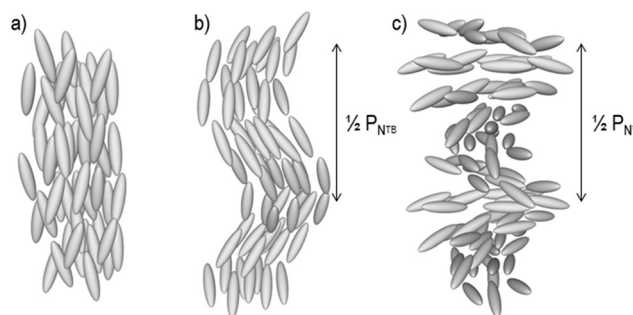
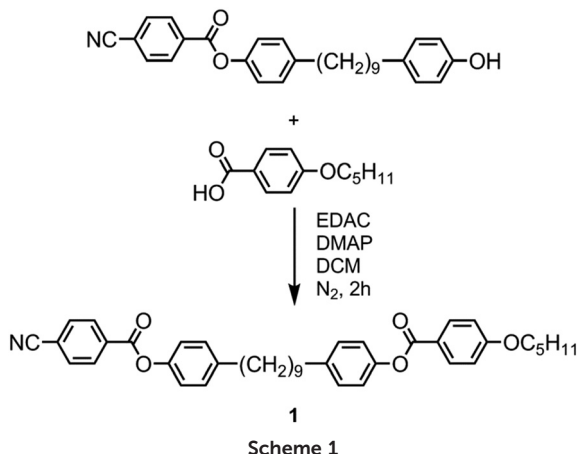


Fig. 1 Local structures and director arrangement in (a) the uniaxial nematic phase, (b) the oblique helicoidal model of the N_{TB} phase and (c) the chiral nematic phase.

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sample, allowing simultaneous observation of wide angle and small angle scattering data. Computational chemistry was performed at the B3LYP/6-31G(d) level of DFT in Gaussian G09 revision e01,⁵⁵ with Gaussian output files rendered using Qutemol.⁵⁶ Full experimental details, including chemical characterisation and descriptions of instrumentation used, are available in the ESI† to this article.

Results

The transition temperatures along with the associated enthalpies and entropies of transition for compound **1** are given in Table 1. Transition temperatures, along with associated enthalpies and entropies were determined by differential scanning calorimetry at a heat/cool rate of 10 °C min⁻¹ and are the mean of 10 cycles; standard deviations are given in parenthesis. The associated enthalpies and entropies of transition are not especially characteristic and are of a comparable magnitude to those reported previously for methylene linked phenylbenzoate dimers.^{38,39,41,43} Both the onset temperature and associated enthalpy of the SmX–N_{TB} transition were found to be invariant when subjected to different heat/cool rates in the range of 1–20 °C min⁻¹, indicating that the transition is not dependent on kinetic processes; contrast this to the N_{TB}–N transition which was previously shown to show a strong dependence on the heat/cool rate.⁹ The magnitude of the enthalpy (Table 1) associated

with this transition to the SmX phase suggests that the phase is highly ordered. Whereas crystalline phases show thermal hysteresis (*i.e.* supercooling), liquid-crystalline or soft-crystalline states of matter do not, and cannot typically be supercooled more than a few tens of mK. In order to demonstrate that the SmX phase is a *bona fide* liquid-crystalline (or possibly soft-crystalline) phase a DSC study was performed whereby the sample was first heated into the isotropic liquid, then cooled into the SmX phase and reheated back into the N_{TB} phase. The lack of thermal hysteresis (Fig. 2) confirms that the transition into the SmX phase is not simply a recrystallization event, but rather a transition to a mesophase.

On cooling from the isotropic liquid it is trivial to identify the first mesophase as the nematic, based on its fluidity and characteristic *schlieren* texture. The identification of the mesophase immediately below the nematic as the twist-bend nematic is also straightforward due to its characteristic optical textures (Fig. 3) and the shape of the peak obtained in DSC thermograms (Fig. 2).⁹ As discussed by Zhu *et al.*,¹³ small-angle X-ray scattering can be used to discriminate between the experimentally observed N_{TB} phase and the theoretically predicted splay-bend nematic, N_{SB}, as the electron density modulation in the former does not lead to Bragg scattering whereas it is expected to in the later. We observe no Bragg scattering at *Q* values as low as 0.06 in the phase immediately below the nematic (Fig. SI-6 in the ESI†) and so we can be confident in our assignment of this mesophase as the twist-bend modulated nematic.

As shown in Fig. 3(a) and (b) a number of crossover points, reminiscent of braids in rope, were seen in the aligned rope texture of the N_{TB} phase, with the ‘length’ of the rope defects being parallel to the rubbing direction of the cell. Insertion of a λ waveplate lead to different colours in adjacent stripes (Fig. 3b), indicating that the optical azimuthal angle alternates between stripes.²¹ Additionally clear striations can be seen within the stripes (Fig. 3b), these being are offset from the length of the rope defects by an average of $\pm 30^\circ$ with the direction alternating in adjacent stripes. Further cooling of compound **1** below 56.1 °C leads to a reversible (see DSC trace in Fig. 2) transition from the N_{TB} phase into to the unknown mesophase, denoted SmX presently. When confined in a 5 ± 0.1 μm cell with antiparallel buffed polyimide alignment layers the N_{TB} phase of **1** gives a well

Table 1 Transition temperatures (°C), associated enthalpies of transition (kJ mol⁻¹) and dimensionless associated entropy of transition ($\Delta S/R$) for compound **1**. Note, the SmX–N_{TB} transition is monotropic, *i.e.* it occurs below the melting point of the sample. Enthalpies and entropies were the mean of 10 cycles as determined by DSC at a heat/cool rate of 10 °C min⁻¹, with standard deviations given in parenthesis. Tabulated DSC data is presented in the ESI

	MP	SmX–N _{TB}	N _{TB} –N	N–Iso
<i>T</i> (°C)	81.4 (0.027)	56.1 (0.009)	91.9 (0.007)	110.8 (0.007)
ΔH (kJ mol ⁻¹)	35.83 (0.194)	10.30 (0.004)	0.31 (0.002)	0.61 (0.002)
$\Delta S/R$	12.15 (0.065)	3.76 (0.001)	0.10 (0.001)	0.19 (0.001)



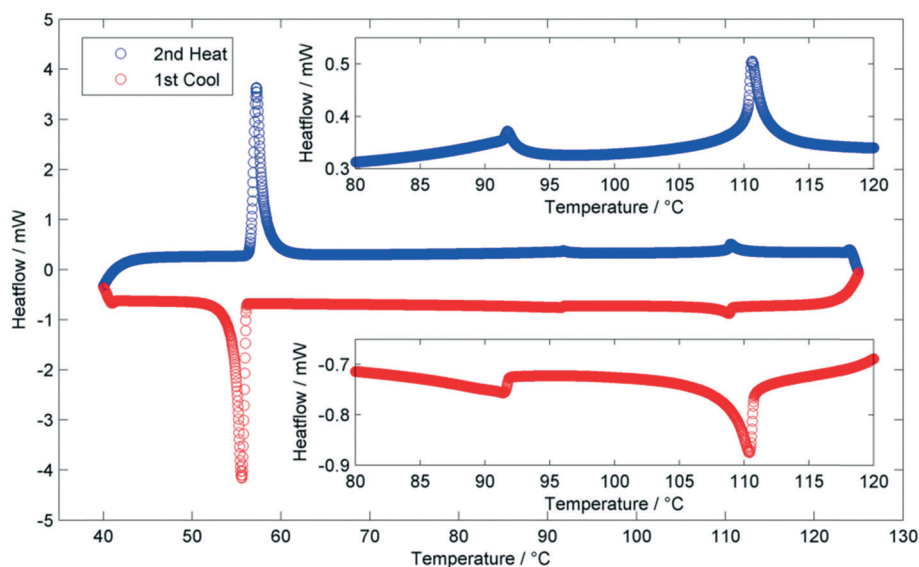


Fig. 2 DSC thermogram of compound **1** obtained at $10\text{ }^{\circ}\text{C min}^{-1}$ on the first cooling cycle (red circles) and second heating cycle (blue circles), with two expansions showing the region between $80\text{--}120\text{ }^{\circ}\text{C}$ which contains the $N_{TB}\text{--}N$ and $N\text{--}Iso$ transitions.

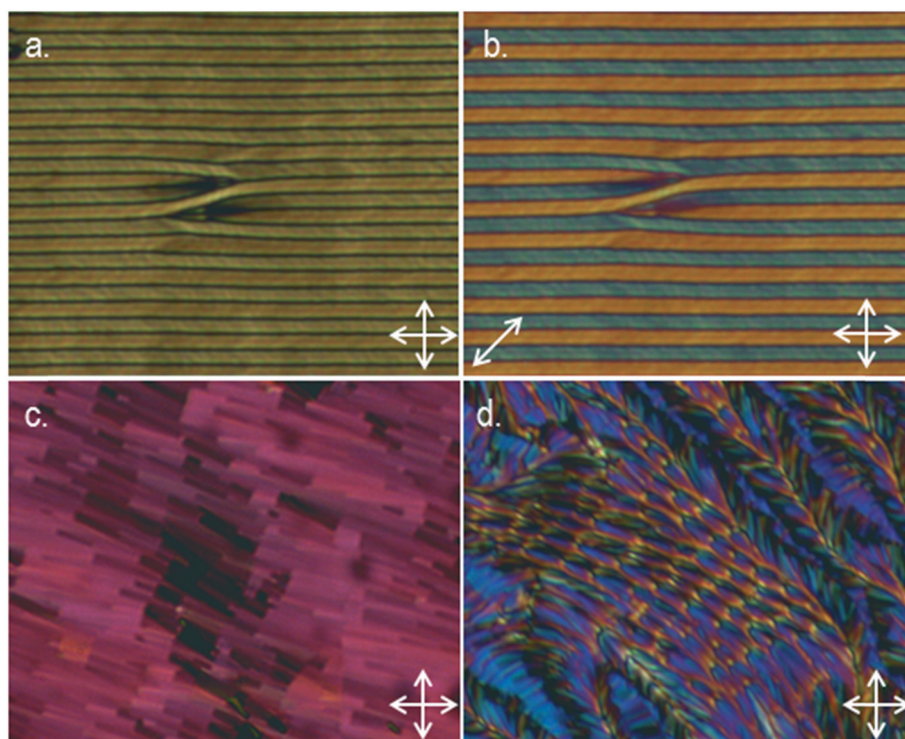


Fig. 3 Photomicrographs ($\times 100$) of the twist bend phase of compound **1**. (a) The well-aligned rope texture of the N_{TB} phase at $86.5\text{ }^{\circ}\text{C}$ confined in a $5 \pm 0.1\text{ }\mu\text{m}$ cell with antiparallel buffed polyimide alignment layers, (b) the same conditions as (a) but with a λ waveplate inserted, (c) the 'blocky' texture of the N_{TB} phase at $89.4\text{ }^{\circ}\text{C}$ in a sample on untreated glass, (d) parabolic defects and the 'blocky' texture on untreated glass at $87.3\text{ }^{\circ}\text{C}$.

aligned rope texture (Fig. 3a and 4a), and at the phase transition the rope texture is partially preserved, either through paramorphosis or this being a characteristic texture of the SmX phase, however the birefringence changes markedly (Fig. 4b and c). If the sample is reheated across the SmX- N_{TB} phase transition then the original rope texture returns (Fig. 4d), however, the interface between adjacent stripes now

appear buckled and the striations set at 30° to the rope length, which persist after cooling into the SmX phase, are more pronounced than they are in the virginal texture (compare Fig. 4a-d).

The behaviour of **1** in a cell was studied under applied electric fields. In the nematic phase at $95\text{ }^{\circ}\text{C}$ a Fréedericksz transition could be observed at low frequency ($<50\text{ Hz}$) with



an applied field of above 1 V_{RMS}. The sample was cooled into the N_{TB} phase to 85 °C where it was possible to observe some form of electrooptic response at an applied voltage of 60 V_{RMS}. With a higher applied voltage (100 V_{RMS}) the sample was reversibly into a reasonably uniform homeotropic state, removal of the field lead to the regrowth of the rope-texture over a period of minutes. When cooled into the SmX mesophase we did not observe any electrooptic response at amplitudes of up to 100 V_{RMS} across a range of frequencies (1 mHz to 100 KHz). Therefore we conclude that the SmX phase does not exhibit any electrooptic behaviour in the voltage regime used in this work.

We next elected to study the nematic, N_{TB} and SmX mesophases of **1** by small angle X-ray scattering using copper K alpha radiation on magnetically aligned samples. The nematic phase was well aligned by the external magnetic field and gave the expected diffuse scattering pattern shown in Fig. 5a. This alignment was partially lost on entering the N_{TB} phase (Fig. 5b). For the nematic phase the orientational order parameter P_2 (Fig. 5c) was calculated as follows: integration of the wide-angle scattering as a function of the angle χ followed by averaging of the two signals gave Fig. 5d, from this the order parameter could be calculated according to Davidson

*et al.*⁵⁷ The alignment of the N_{TB} phase was not sufficient to obtain order parameters, however in the nematic phase the order parameter increases from a value of 0.30 to a maximum of 0.39, these values being comparable to those measured for the nematic phase of methylene linked bimesogens.¹¹

As shown in Fig. 6, in the nematic and twist-bend mesophases only diffuse scattering peaks are seen, with a single wide angle peak and a single small angle peak. These scattering peaks corresponding to the side-to-side and end-to-end separation of molecules respectively, however, as the nematic and N_{TB} phases lack positional ordering the small angle peak occurs at roughly $\frac{1}{2}$ of the molecular length (37.2 Å at the B3LYP/6-31G(d) level of DFT). Upon cooling into the SmX phase the diffraction pattern changes markedly in both the small and wide angle regions. The small-angle scattering peak grows in intensity and becomes significantly more defined, with the average full-width at half-maximum (FWHM) being an order of magnitude larger in the N_{TB} phase than in the SmX phase (0.348 Å⁻¹ and 0.035 Å⁻¹ respectively). The out-of-plane correlation length (ζ , defined as $\zeta = 2\pi/\Delta Q$ increases from an average of 18.1 Å in the N_{TB} phase to 182.1 Å in the SmX mesophase. The SmX phase also exhibits an scattering peak at $Q \approx 0.17$ Å⁻¹ ($d \approx 3.7$ nm) that is both more

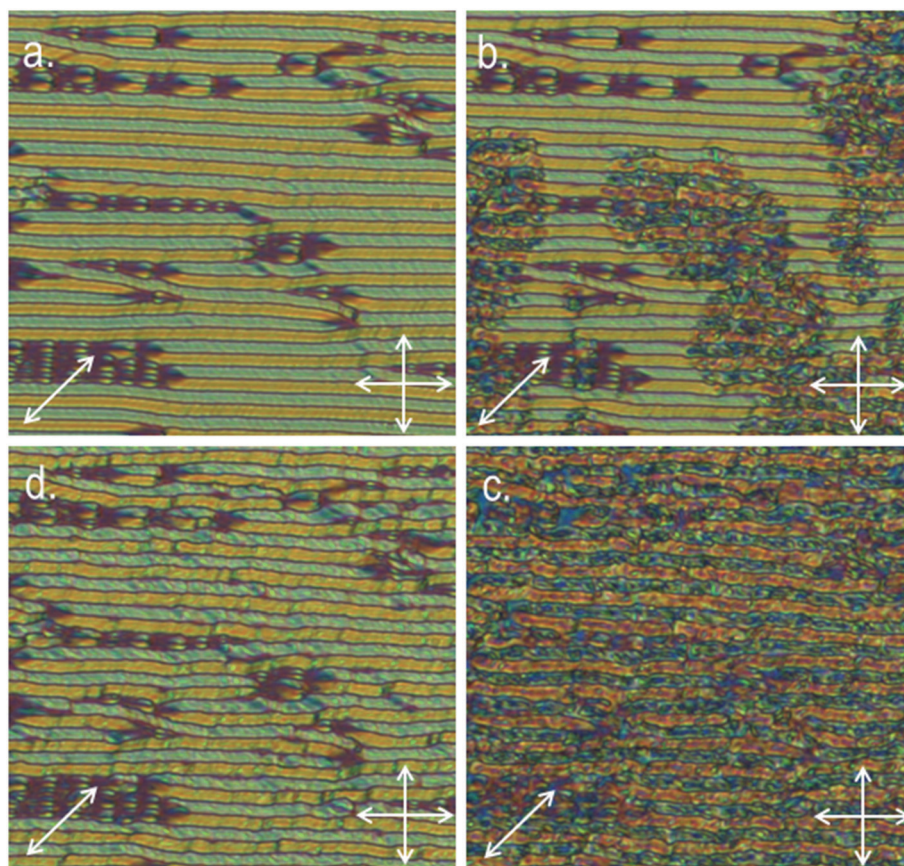


Fig. 4 Photomicrographs, taken with a λ waveplate inserted, of compound **1** ($\times 100$) confined in a 5 ± 0.1 μm cell with antiparallel buffed polyimide alignment layers. The rope texture of **1** at 60.0 °C (a), the onset of the SmX–N_{TB} transition at 56.0 °C (b), the rope texture of the SmX phase at 54.5 °C (c), the rope texture of the N_{TB} phase restored after heating through the SmX–N_{TB} transition, 59.2 °C (d). Photomicrographs correspond to approximately the same area of the sample.



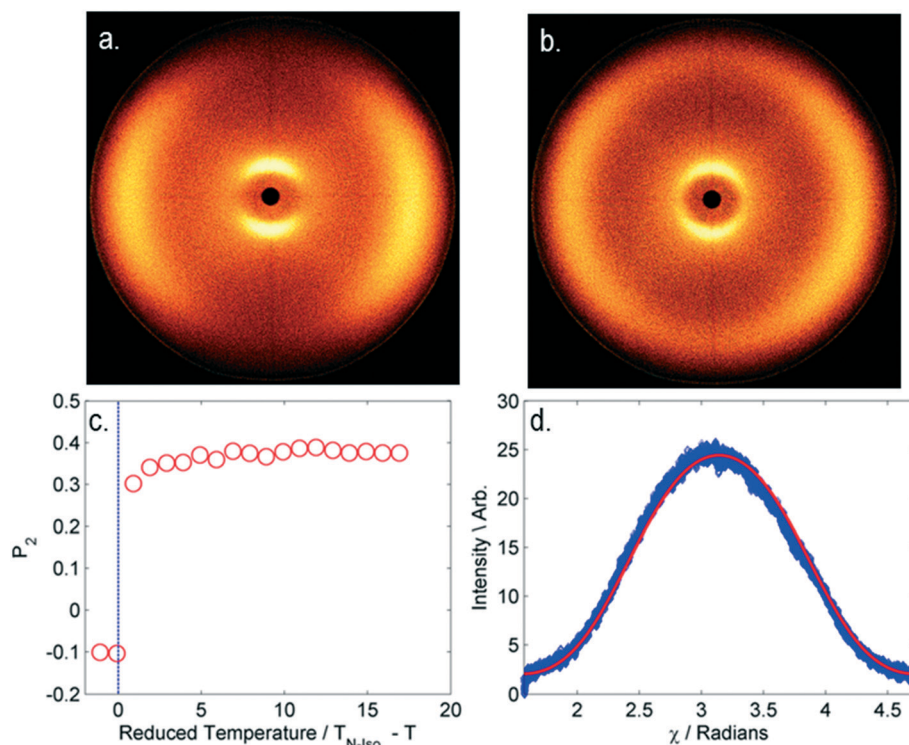


Fig. 5 Two dimensional small-angle X-ray scattering patterns for the nematic phase of **1** at 109 °C (a), the N_{TB} phase of **1** at 89 °C (b), plot of the order parameter P_2 vs. reduced temperature (c), plot of scattered X-ray intensity (blue diamonds) fitted using as described by Davidson *et al.* (red line) as a function of the angle χ for the wide-angle ($2\theta = 15$ – 25) region of compound **1** in the nematic phase at 99 °C (d).

diffuse and less intense than the larger of the two small angle peaks ($Q \approx 0.34 \text{ \AA}^{-1}$, $d \approx 2.0 \text{ nm}$).

The diffuse wide-angle peak present in the twist-bend phase sharpens and splits into two peaks that are not fully resolved at the SmX – N_{TB} transition. The increase in scattered intensity in this region at the SmX – N_{TB} phase transition is further evidence for the large increase in the in-plane correlation length. The wide-angle scattering data, which corresponds to the average lateral separation between molecules, was deconvoluted into two Lorentzian peaks with maxima (Fig. 7) at $Q = 1.3296 \text{ \AA}^{-1}$ ($d \approx 4.73 \text{ \AA}$) and $Q = 1.4114 \text{ \AA}^{-1}$ ($d \approx 4.45 \text{ \AA}$). In the more ordered SmX phase we propose that there are two different average lateral intermolecular distances, one for the polar phenyl 4-cyanobenzoate unit and one for the ‘apolar’ phenyl 4-pentyloxybenzoate group.

From experimental data it is known that the SmX phase is intercalated, with a layer spacing of $\frac{1}{2}$ the molecular length (*i.e.* d/l ratio of 0.5). The in-plane correlation length is relatively large (average of 18 nm) and although we do not observe evidence of hexagonal close packing of molecules this cannot be excluded as the sample is not aligned during SAXS on the SmX phase (Fig. 6b). Assuming the polar phenyl 4-cyanobenzoate units form antiparallel correlated pairs with adjacent polar units, mirroring what is observed in calamitic systems such as 8CB,^{58,59} interdigitated smectic layers will result. The antiparallel correlation between adjacent polar phenyl 4-cyanobenzoates is possibly also the origin of the two distinct spacings seen in the wide angle X-ray scattering ex-

periment (Fig. 7). Additionally this mixed polar/apolar molecular structure will lead to segregation of polar and apolar mesogenic units into adjacent layers. We propose that the scattering peak in the small angle at $Q \approx 0.17 \text{ \AA}^{-1}$ ($d \approx 3.7 \text{ nm}$) is the distance between two ‘like’ (*e.g.* polar–polar and apolar–apolar) layers, which is roughly the molecular length, while the layer spacing at $Q \approx 0.34 \text{ \AA}^{-1}$ ($d \approx 2.0 \text{ nm}$) is the average layer spacing of the two layers and is approximately $\frac{1}{2}$ of the molecular length.

Conclusions

We have prepared and characterised a novel unsymmetrical liquid crystalline dimer which consists of one polar and one non-polar mesogenic unit. In addition to exhibiting the highly topical twist-bend nematic phase this compound also exhibits a smectic mesophase. Transitions from the N_{TB} phase to smectic mesophases still remain rare (we are aware of only a handful of examples) and present rich opportunities for physical study and theoretical treatment of both the local structure, and the processes occurring at the phase transition between, these two mesophases. We note that the lower-temperature phase observed in compound **1** appears unique – based on small angle X-ray scattering data we propose that the local structure is lamellar, with alternating blocks of ‘polar’ and ‘apolar’ mesogenic units. It is believed that this mesophase arises due to the strong intermolecular self-association of nitrile units. With this point in mind it seems



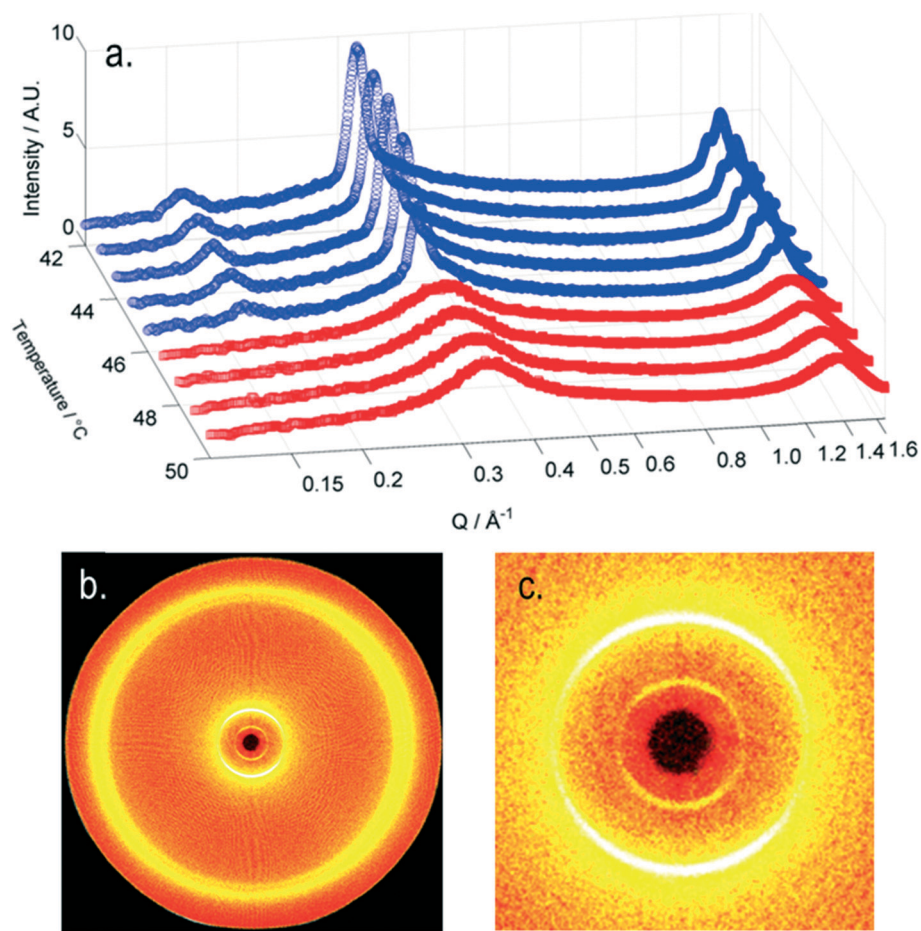


Fig. 6 Small angle X-ray scattering data for compound **1**. (a) Plot of diffraction intensity (arbitrary units) versus Q (\AA^{-1}) as a function of temperature (42–50 $^{\circ}\text{C}$, 1 $^{\circ}\text{C}$ steps), with red circles corresponding to the N_{TB} phase and blue circles to the SmX phase. (b) two dimensional diffraction pattern of the SmX mesophase exhibited by **1** at 47 $^{\circ}\text{C}$ and (c) an expansion of the two-dimensional diffraction pattern showing scattering at small angles ($2\theta = 3$ –10, $Q = 0.1$ –0.6 \AA^{-1}).

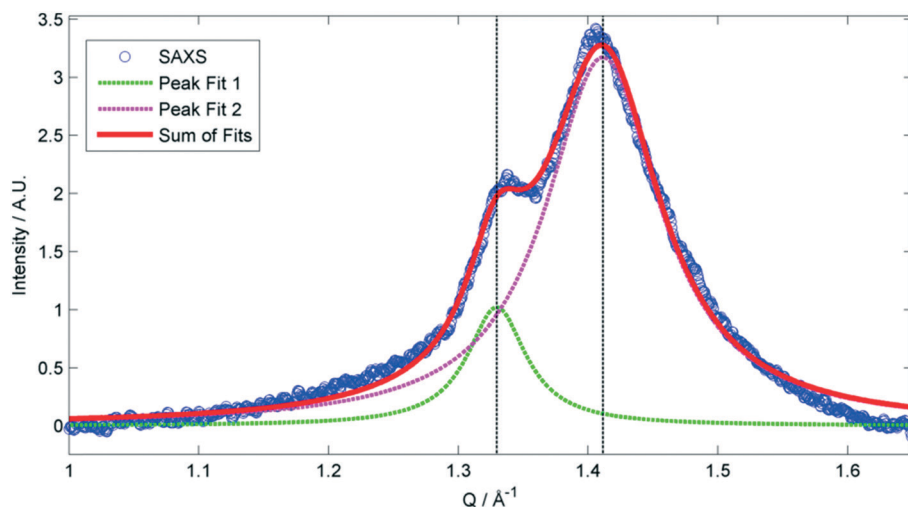


Fig. 7 Plot of scattered X-ray intensity for compound **1** in the SmX mesophase at 50 $^{\circ}\text{C}$ between Q 1.0 and Q 1.65. The overlapping peaks were deconvoluted into two Lorentzian peaks (dashed lines, I_{max} at $Q = 1.3296 \text{\AA}^{-1}$ and $Q = 1.4114 \text{\AA}^{-1}$ respectively) which sum to give the solid red line, giving an R^2 value of >0.99 .



logical that other groups prone to self-association will also support the formation of this mesophase. Studies of the phase by microscopy, calorimetry, SAXS and under applied fields indicate it is soft-crystalline in nature; however the phase does not exhibit thermal hysteresis and thus can be classified as a mesophase rather than a true crystalline state of matter.

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References

- 1 M. Šepelj, A. Lesac, U. Baumeister, S. Diele, H. Loc Nguyen and D. W. Bruce, Intercalated liquid-crystalline phases formed by symmetric dimers with an α,ω -diiminoalkylene spacer, *J. Mater. Chem.*, 2006, **17**, 1154–1165.
- 2 V. P. Panov, M. Nagaraj, J. K. Vij, Y. P. Panarin, A. Kohlmeier, M. G. Tamba, R. A. Lewis and G. H. Mehl, Spontaneous Periodic Deformations in Nonchiral Planar-Aligned Bimesogens with a Nematic-Nematic Transition and a Negative Elastic Constant, *Phys. Rev. Lett.*, 2010, **105**, 167701.
- 3 M. Cestari, S. Diez-Berart, D. A. Dunmur, A. Ferrarini, M. R. de la Fuente, D. J. B. Jackson, D. O. Lopez, G. R. Luckhurst, M. A. Perez-Jubindo, R. M. Richardson, J. Salud, B. A. Timimi and H. Zimmermann, Phase Behaviour and Properties of the Liquid-Crystal Dimer 1''-7''-bis(4-cyanobiphenyl4'-yl) heptane: A Twist-Bend Nematic Liquid Crystal, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2011, **84**, 031704.
- 4 C. S. P. Tripathi, P. Losada-Pérez, C. Glorieux, A. Kohlmeier, M. G. Tamba, G. H. Mehl and J. Leys, Nematic-Nematic Phase Transition in the Liquid Crystal Dimer CB9CB and its Mixtures with 5CB: A High-Resolution Adiabatic Scanning Calorimetric Study, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2011, **84**, 041707.
- 5 V. P. Panov, R. Balachandran, M. Nagaraj, J. K. Vij, M. G. Tamba, A. Kohlmeier and G. H. Mehl, Microsecond Linear Optical Response in the Unusual Nematic Phase of Achiral Bimesogens, *Appl. Phys. Lett.*, 2011, **99**, 261903.
- 6 V. Borshch, Y.-K. Kim, J. Xiang, M. Gao, A. Jákli, V. P. Panov, J. K. Vij, C. T. Imrie, M. G. Tamba, G. H. Mehl and O. D. Lavrentovich, Nematic Twist-Bend Phase with Nanoscale Modulation of Molecular Orientation, *Nat. Commun.*, 2013, **4**, 2635.
- 7 D. Chen, J. H. Porda, J. B. Hooper, A. Klitnic, Y. Shen, M. R. Tuchband, E. Korblova, D. Bedrov, D. M. Walba, M. A. Glaser, J. E. MacLennan and N. A. Clark, A Twist-Bend Chiral Helix of 8 nm Pitch in a Nematic Liquid Crystal of Achiral Molecular Dimers, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 15931–15936.
- 8 D. Chen, M. Nakata, R. Shao, M. R. Tuchband, M. Shuai, U. Baumeister, W. Weissflog, D. M. Walba, M. A. Glaser, J. E. MacLennan and N. A. Clark, Twist-Bend Heliconical Chiral Nematic Liquid Crystal Phase of an Achiral Rigid Bent-Core Mesogen, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2014, **89**, 022506.
- 9 R. J. Mandle, E. J. Davis, C. T. Archbold, S. J. Cowling and J. W. Goodby, Microscopy Studies of the Nematic N_{TB} phase of 1,11-Di-(1''-cyanobiphenyl-4-yl)undecane, *J. Mater. Chem. C*, 2014, **2**, 556–566.
- 10 C. Meyer, G. R. Luckhurst and I. Dozov, The temperature dependence of the heliconical tilt angle in the twist-bend nematic phase of the odd dimer CB7CB, *J. Mater. Chem. C*, 2015, **3**, 318–328.
- 11 Z. Zhang, V. P. Panov, M. Nagaraj, R. J. Mandle, J. W. Goodby, G. R. Luckhurst, J. C. Jones and H. F. Gleeson, Raman scattering studies of order parameters in liquid crystalline dimers exhibiting the nematic and twist-bend nematic phases, *J. Mater. Chem. C*, 2015, **3**, 10007–10016.
- 12 J. P. Jokissari, G. R. Luckhurst, B. A. Timimi, J. Zhu and H. Zimmerman, Twist-bend nematic phase of the liquid crystal dimer CB7CB: orientational order and conical angle determined by ^{129}Xe and ^2H NMR spectroscopy, *Liq. Cryst.*, 2015, **42**, 708–721.
- 13 C. Zhu, M. R. Tuchband, A. Young, M. Shuai, A. Scarrough, D. M. Walba, J. E. MacLennan, C. Wang, A. Hexemer and N. A. Clark, Resonant Carbon K-Edge Soft X-Ray Scattering from Lattice-Free Heliconical Molecular Ordering: Soft Dilative Elasticity of the Twist-Bend Liquid Crystal Phase, *Phys. Rev. Lett.*, 2016, **116**, 147803.
- 14 J. W. Emsley, M. Lelli, H. Joy, M.-G. Tamba and G. H. Mehl, Similarities and differences between molecular order in the nematic and twist-bend nematic phases of a symmetric liquid crystal dimer, *Phys. Chem. Chem. Phys.*, 2016, **18**, 9419–9430.
- 15 S. A. Pardaev, S. M. Shamid, M. G. Tamba, C. Welch, G. H. Mehl, J. T. Gleeson, D. W. Allender, J. V. Selinger, B. Ellman, A. Jakli and S. Sprunt, Second harmonic light scattering induced by defects in the twist-bend nematic phase of liquid crystal dimers, *Soft Matter*, 2016, **12**, 4472–4482.
- 16 B. Robles-Hernandez, N. Sebastian, M. Rosario de la Fuente, D. O. Lopez, S. Diez-Berart, J. Salud, M. B. Ros, D. A. Dunmur, G. R. Luckhurst and B. A. Timimi, Twist, tilt, and orientational order at the nematic to twist-bend nematic phase transition of 1'',9''-bis(4-cyanobiphenyl-4'-yl) nonane: A dielectric, ^2H NMR, and calorimetric study, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2015, **92**, 062505.
- 17 C. T. Archbold, J. L. Andrews, R. J. Mandle, S. J. Cowling and J. W. Goodby, Effect of the Linking Unit on the Twist-Bend Nematic Phase in Liquid Crystal Dimers: A Comparative Study of Two Homologous Series of Methylene and Ether Linked Dimers, *Liq. Cryst.*, 2016, DOI: 10.1080/02678292.2016.1240247, in press.
- 18 J. W. Emsley, M. Lelli, A. Lesage and G. R. Luckhurst, A Comparison of the Conformational Distributions of the Achiral Symmetric Liquid Crystal Dimer CB7CB in the



- Achiral Nematic and Chiral Twist-Bend Nematic Phases, *J. Phys. Chem. B*, 2013, **117**, 6547–6557.
- 19 R. B. Meyer, Structural Problems in Liquid Crystal Physics, in *Les Houches Summer School in Theoretical Physics*, 1973. *Molecular Fluids*, ed. R. Balian and G. Weil, Gordon and Breach, New York, 1976, pp. 273–373.
 - 20 I. Dozov, On the Spontaneous Symmetry Breaking in the Mesophases of Achiral Banana-Shaped Molecules, *Europhys. Lett.*, 2001, **56**, 247–253.
 - 21 E. Gorecka, M. Salmonczyk, A. Zep, D. Pocięcha, C. Welch, Z. Ahmed and G. H. Mehl, Do the Short Helices Exist in the Nematic TB Phase, *Liq. Cryst.*, 2015, **42**, 1–7.
 - 22 A. Hoffmann, A. G. Vanakaras, A. Kohlmeier, G. H. Mehl and D. J. Photinos, On The Structure of the N_X Phase of Symmetric Dimers: Inferences from NMR, *Soft Matter*, 2015, **11**, 850–855, DOI: 10.1039/c4sm02480j.
 - 23 A. G. Vanakaras and D. J. Photinos, A molecular theory of nematic-nematic phase transitions in mesogenic dimers, *Soft Matter*, 2016, **12**, 2208–2220, DOI: 10.1039/C5SM02505B.
 - 24 T. Ivšić, M. Vinković, U. Baumeister, A. Mikleušević and A. Lesac, Towards understanding the N_{TB} phase: a combined experimental, computational and spectroscopic study, *RSC Adv.*, 2016, **6**, 5000–5007, DOI: 10.1039/C5RA26078G.
 - 25 C. T. Archbold, E. J. Davis, R. J. Mandle, S. J. Cowling and J. W. Goodby, Chiral dopants and the twist-bend nematic phase – induction of novel mesomorphic behaviour in an apolar bimesogen, *Soft Mater.*, 2015, **11**, 7547–7557.
 - 26 A. A. Dawood, M. C. Grossel, G. R. Luckhurst, R. M. Richardson, B. A. Timimi, N. J. Wells and U. Z. Yousif, On the twist-bend nematic phase formed directly from the isotropic phase, *Liq. Cryst.*, 2016, **43**, 2–12.
 - 27 R. J. Mandle, E. J. Davis, S. A. Lobato, C. C. A. Vol, S. J. Cowling and J. W. Goodby, Characterisation of an Unsymmetrical, Ether-linked, Fluorinated Bimesogen Exhibiting a New Polymorphism Containing the N_{TB} or ‘Twist-Bend’ Phase, *Phys. Chem. Chem. Phys.*, 2014, **16**, 6907–6915.
 - 28 R. J. Mandle, C. C. A. Voll, D. J. Lewis and J. W. Goodby, Etheric Bimesogens and the Twist-Bend Nematic Phase, *Liq. Cryst.*, 2015, **43**, 13–21, DOI: 10.1080/02678292.2015.1091095.
 - 29 S. M. Jansze, A. Martínez-Felipe, J. D. M. Storey, A. T. M. Marcelis and C. T. Imrie, A Twist-Bend Nematic Phase Driven by Hydrogen Bonding, *Angew. Chem., Int. Ed.*, 2015, **54**, 643–646.
 - 30 D. A. Paterson, A. Martínez-Felipe, S. M. Jansze, A. T. M. Marcelis, J. M. D. Storey and C. T. Imrie, New insights into the liquid crystal behaviour of hydrogen-bonded mixtures provided by temperature-dependent FTIR spectroscopy, *Liq. Cryst.*, 2015, **42**, 928–939.
 - 31 A. Martínez-Felipe and C. T. Imrie, The role of hydrogen bonding in the phase behaviour of supramolecular liquid crystal dimers, *J. Mol. Struct.*, 2015, **1100**, 429–437.
 - 32 Y. Wang, G. Singh, D. M. Agra-Kooijman, M. Gao, H. K. Bisoyi, C. Xue, M. R. Fisch, S. Kumar and Q. Li, Room temperature heliconical twist-bend nematic liquid crystal, *CrystEngComm*, 2015, **1**, 2778–2782.
 - 33 R. J. Mandle and J. W. Goodby, A Liquid Crystalline Oligomer Exhibiting Nematic and Twist-Bend Nematic Mesophases, *ChemPhysChem*, 2016, **7**, 967–970, DOI: 10.1002/cphc.201600038.
 - 34 G. Ungar, V. Percec and M. Zuber, Liquid crystalline polyethers based on conformational isomerism. 20. Nematic-nematic transition in polyethers and copolyethers based on 1-(4-hydroxyphenyl)2-(2-R-4-hydroxyphenyl)ethane with R = fluoro, chloro and methyl and flexible spacers containing an odd number of methylene units, *Macromolecules*, 1992, **25**, 75–80.
 - 35 R. J. Mandle, The dependency of twist-bend nematic liquid-crystals on molecular structure: a progression from dimers to trimers, oligomers and polymers, *Soft Matter*, 2016, **12**, 7883–7901.
 - 36 E. Gorecka, N. Vaupotič, A. Zep, D. Pocięcha, J. Yoshioka, J. Yamamoto and H. Takazoe, A Twist-Bend Nematic (N_{TB}) Phase of Chiral Materials, *Angew. Chem., Int. Ed.*, 2015, **54**, 10155–10159.
 - 37 D. A. Paterson, J. Xiang, G. Singh, R. Walker, D. M. Agra-Kooijman, A. Martínez-Felipe, M. Gao, J. M. D. Storey, S. Kumar, O. D. Larentovich and C. T. Imrie, *J. Am. Chem. Soc.*, 2016, **138**, 5283–5289.
 - 38 R. J. Mandle, E. J. Davis, C. C. A. Voll, C. T. Archbold, J. W. Goodby and S. J. Cowling, The Relationship between Molecular Structure and the Incidence of the N_{TB} Phase, *Liq. Cryst.*, 2015, **42**, 688–703, DOI: 10.1080/02678292.2014.974698.
 - 39 R. J. Mandle, E. J. Davis, C. T. Archbold, C. C. A. Voll, J. L. Andrews, S. J. Cowling and J. W. Goodby, Apolar Bimesogens and the Incidence of the Twist-Bend Nematic Phase, *Chem. – Eur. J.*, 2015, **21**, 8158–8167.
 - 40 Z. Ahmed, C. Welch and G. H. Mehl, The design and investigation of the self-assembly of dimers with two nematic phases, *RSC Adv.*, 2015, **5**, 93513–93521.
 - 41 R. J. Mandle and J. W. Goodby, Progression from Nano to Macro Science in Soft Matter Systems: Dimers to Trimers and Oligomers in Twist-Bend Liquid Crystals, *RSC Adv.*, 2016, **6**, 34885–34893.
 - 42 R. J. Mandle and J. W. Goodby, A Twist-bend Nematic to an Intercalated, Anticlinic, Biaxial Phase Transition in Liquid Bimesogens, *Soft Matter*, 2016, **12**, 1436–1443.
 - 43 R. J. Mandle and J. W. Goodby, Dependence of Mesomorphic Behaviour of Methylene-Linked Dimers and the Stability of the N_{TB}/N_X Phase upon Choice of Mesogenic Units and Terminal Chain Length, *Chem. – Eur. J.*, 2016, **22**, 9366–9374.
 - 44 A. Zep, S. Aya, K. Aihara, K. Ema, D. Pocięcha, K. Madrak, P. Bernatowicz, H. Takezoe and E. Gorecka, Multiple nematic phases observed in chiral mesogenic dimers, *J. Mater. Chem. C*, 2013, **1**, 46–49.
 - 45 J. W. Emsley, P. Lesot, G. R. Luckhurst, A. Meddour and D. Merlet, Chiral solutes can seed the formation of enantiomorphic domains in a twist-bend nematic liquid crystal, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2013, **87**, 040501.



- 46 J. W. Emsley, M. Lelli, A. Lesage and G. R. Luckhurst, A Comparison of the Conformational Distributions of the Achiral Symmetric Liquid Crystal Dimer CB7CB in the Achiral Nematic and Chiral Twist-Bend Nematic Phases, *J. Phys. Chem. B*, 2013, 117, 6547–6557.
- 47 V. Avetisov and V. Goldanskii, Mirror symmetry breaking at the molecular level, *Proc. Natl. Acad. Sci. U. S. A.*, 1996, 93, 11435–11442.
- 48 S. J. Sowerby, W. H. Heckl and G. B. Petersen, Chiral Symmetry Breaking During the Self-Assembly of Monolayers from Achiral Purine Molecules, *J. Mol. Evol.*, 1996, 43, 419–424.
- 49 C. Viedma, Chiral Symmetry Breaking and Complete Chiral Purity by Thermodynamic-Kinetic Feedback Near Equilibrium: Implications for the Origin of Biochirality, *Astrobiology*, 2007, 7, 312–319.
- 50 G. Tschierske and G. Ungar, Mirror Symmetry Breaking by Chirality Synchronisation in Liquids and Liquid Crystals of Achiral Molecules, *ChemPhysChem*, 2016, 17, 9–26.
- 51 M. Alaasar, M. Prehm, Y. Cao, F. Liu and C. Tschierske, Spontaneous Mirror Symmetry Breaking in Isotropic Liquid Phases of Photoisomerizable Achiral Molecules, *Angew. Chem., Int. Ed.*, 2015, 55, 312–316.
- 52 I. Lelidis and G. Barbero, Nematic phases with spontaneous splay-bend deformation: standard elastic description, *Liq. Cryst.*, 2016, 43, 208–215.
- 53 J. Xiang, Y. Li, Q. Li, D. A. Paterson, J. M. D. Storey, C. T. Imrie and O. D. Lavrentovich, Electrically Tunable Selective Reflection of Light from Ultraviolet to Visible and Infrared by Heliconical Cholesterics, *Adv. Mater.*, 2015, 27, 3014–3018.
- 54 Y. Wang, Z. Zheng, H. K. Bisovi, K. G. Gutierrez-Cuevas, L. Wang, R. S. Zola and Q. Li, Thermally reversible full color selective reflection in a self-organized helical superstructure enabled by a bent-core oligomesogen exhibiting a twist-bend nematic phase, *Mater. Horiz.*, 2016, 3, 442–446.
- 55 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision E.01*, Gaussian, Inc., Wallingford CT, 2009.
- 56 M. Tarini, P. Cignoni and C. Montani, Ambient Occlusion and Edge Cueing for Enhancing Real Time Molecular Visualization, *IEEE Trans. Vis. Comput. Graph.*, 2006, 12, 1237–1244.
- 57 P. Davidson, D. Petermann and A. Levelut, The Measurement of the Nematic Order Parameter by X-ray Scattering Reconsidered, *J. Phys. II*, 1995, 5, 113–131.
- 58 G. W. Gray and J. E. Lydon, New Type of Smectic Mesophase?, *Nature*, 1974, 252, 221–222.
- 59 M. Walker and M. R. Wilson, Simulation insights into the role of antiparallel molecular association in the formation of smectic A phases, *Soft Matter*, 2016, DOI: 10.1039/C6SM01920J, in press.

